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Reactions of α-phenylethynyl-*trans*-β-styryl complexes with isonitriles: hemi-labile alkyne coordination

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Abstract

Treatment of the complex $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$ (1) with one equivalent of CNR (R = ^tBu, $C_6H_3Me_2$-2,6) gives $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CNR)(CO)(PPh_3)_2]$. Addition of a further equivalent of isonitrile and $[NH_4]PF_6$ leads to the salts $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CNR)_2(CO)(PPh_3)_2]$-$PF_6$ and the mixed species $[Ru\{C(C{\equiv}CPh){=}CHPh\}(CO)(CN^tBu)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]PF_6$. The related $[Ru\{C(C{\equiv}CPh){=}CHPh\}(CN^tBu)(CO)_2(PPh_3)_2]PF_6$ is obtained by successive treatment of $[Ru(CO)_2(PPh_3)_3]$ with diphenylbutadiyne, hexafluorophosphoric acid and isonitrile or of **1** with carbon monoxide, $AgPF_6$, and CN^tBu.

We have recently been interested in the synthesis and reactivity of complexes featuring the unusual α-phenylethynyl-*trans*-β-styryl ligand which results from the hydroruthenation of diphenylbutadiyne. The coordinatively unsaturated complex $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$ which is obtained from the reaction of $[RuClH(CO)(PPh_3)_3]$ with diphenyl butadiyne [1] is related to the σ-aryl complexes $[Ru(C_6H_4R)Cl(CO)(PPh_3)_2]$ (R = H, Me-4) [2] and the σ-vinyl derivatives $[Ru(CR'{=}CHR'')Cl(CO)(PPh_3)_2]$ studied extensively by Santos and co-workers [3]. The recent report on the reactions of the vinylogues with isonitriles which lead to carbonyl/vinyl ligand-coupling [4] prompts us to report our findings with the α-phenylethynyl-trans-β-styryl system.

In a manner analogous to the reactions of $[Ru(CH{=}CHR')Cl(CO)(PPh_3)_2]$ (R' = $SiMe_3$, CMe_3, n-C_8H_{17}, Ph, CO_2Et) with CN^tBu [4], and that previously reported between $[Ru(C_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$ and *p*-tolylisonitrile [5], $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$ reacts with one equivalent of isonitrile CNR (R = ^tBu, $C_6H_3Me_2$-2,6) to give the coordinatively saturated species $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CNR)(CO)(PPh_3)_2]$ (Scheme 1, selected physical data for the new complexes are listed in Table 1). Roper has suggested that the kinetic product of addition to this class of compounds involves coordination of the incoming ligand trans to the σ-organyl ligand [5] and this is borne out by the crystallographically characterised complex $[Os(C_6H_4Me\text{-}4)Cl(CO)(SNNMe_2)$-$(PPh_3)_2]$ obtained from the reaction of $[Os(C_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$ with

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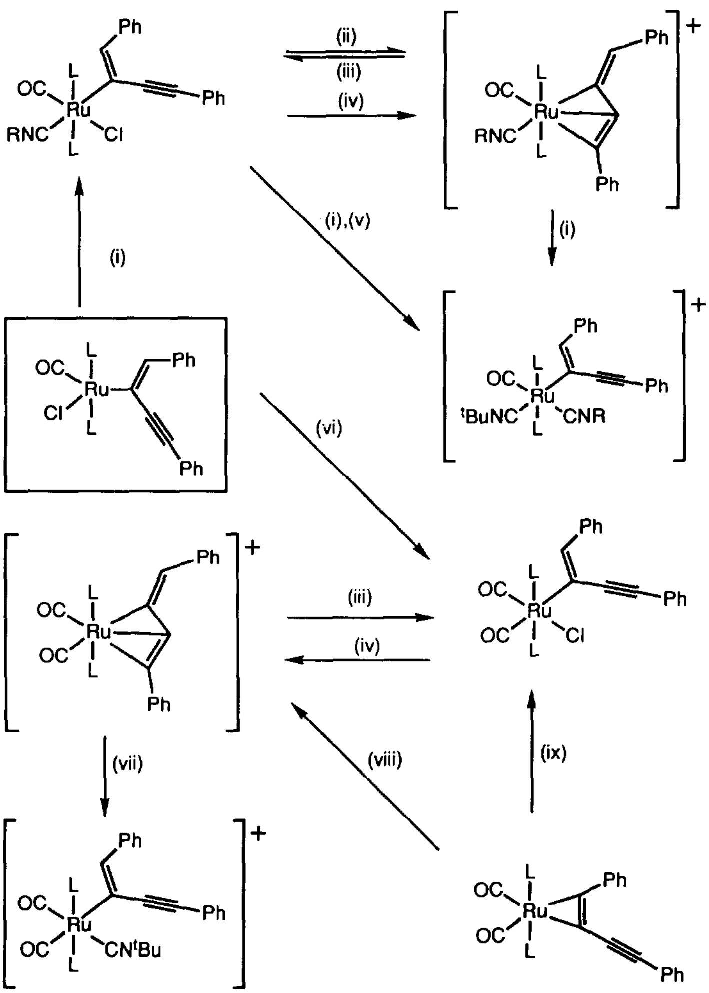

Scheme 1. Synthesis and reactions of α-phenylethynyl vinyl complexes, L = PPh_3. Reagents: (i) CNR; R = ${}^tBu$, $C_6H_3Me_2$ (ii) $-Cl^-$ (iii) $+Cl^-$ (iv) Ag^+, $-AgCl$ (v) NH_4PF_6, EtOH (vi) CO (vii) CN^tBu (viii) HX; X = ClO_4, PF_6 (ix) HCl. Conditions: All reactions except (ix) in CH_2Cl_2, ambient temp., 5–30 min; (ix) tetrahydrofuran, ambient temp., 30 min.

thionitrosodimethylamine [6]. This geometry leaves the isonitrile and σ-organyl ligand unfavourably disposed for migratory insertion ligand processes.

The chloride ligand in the complex $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CN^tBu)(CO)(PPh_3)_2]$ is labile (cf. the complex $[Ru(C_6H_4Me\text{-}4)Cl(CO)(SNNMe_2)(PPh_3)_2]$ [6]). Solutions of $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CN^tBu)(CO)(PPh_3)_2]$ in dichloromethane/ethanol (1 : 1) under ambient conditions react with an excess of isonitrile CNR (R = ${}^tBu$, $C_6H_3Me_2$-2,6) in the presence of $[NH_4]PF_6$ to give the salts $[Ru\{C(C{\equiv}CPh){=}CHPh\}(CNR)(CN^tBu)(CO)(PPh_3)_2]PF_6$. This result appears to contrast with the observation by Santos and co-workers that $[Ru(CH{=}CHR')Cl(CO)(PPh_3)_2]$ reacts with an excess of CN^tBu to give the salts of the complexes $[Ru\{C(O)CH{=}CHR'\}(CN^tBu)_3(PPh_3)_2]^+$, migration of the σ-vinyl group to the carbonyl ligand

Table 1

Spectroscopic data ([Ru] = Ru{C(C≡CPh)=CHPh}(CO)(PPh_3)$_2$)

Complex	IR [a] (cm^{-1})		NMR [b] (δ)	
	ν(CO)	ν(CN)	$^{31}P\{^1H\}$	^1H
[Ru](CN^{t}Bu)Cl	1958	2155	28.1	1.03 [s, 9H, C(CH_3)$_3$]
(cream)	(1966)	(2167)		6.60 [s(br), 1H, =C*H*Ph]
[Ru](CNC_6H_3Me-2,6)Cl	1960	2140	27.5	1.96 [s, 6H, C_6H_3(CH_3)$_2$]
(cream)	(1970)	(2125)		6.53 [s(br), 1H, =C*H*Ph]
[Ru](CO)Cl	1976	–	24.9	6.46 [s(br), 1H, =C*H*Ph]
(cream)	(1968)			
	2042	–		
	(2040)			
[Ru](CN^{t}Bu)$_2$]$^+$	2020	2160	32.8	1.03 [s, 18H, C(CH_3)$_3$]
(pale pink)	(2024)	(2165)		6.12 [s(br), 1H, =C*H*Ph]
		2190		
		(2194)		
[Ru](CN^{t}Bu)(CNC_6H_3Me-2,6)]$^+$	2023	2149	31.5	1.04 [s, 9H, C(CH_3)$_3$],
(purple)	(2016)	(2152)	30.5	1.95, 1.99 [s × 2, 6H, C_6H_3(CH_3)$_2$]
		2173		6.05, 6.34 [s(br) × 2, 1H, =C*H*Ph]
		(2176)		
[[Ru](CO)]$^+$	2052	–	32.8	6.66 [s(br), 1H, =C*H*Ph]
(yellow)	(2052)			
	2004			
	(2001)			
[[Ru](CO)(CN^{t}Bu)]$^+$	2068	2160	27.2	1.06 [s, 9H, C(CH_3)$_3$]
(yellow)	(2065)	(2169)		6.02 [s(br), 1H, =C*H*Ph]
	2026			
	(2022)			

[a] Data were obtained from solutions of the complexes in dichloromethane, values in parentheses obtained from Nujol mulls. [b] From saturated solutions of the complex in $CDCl_3$ at ambient temperature, chemical shifts (δ) in ppm relative to internal Me_4Si (δ 0.00) or external H_3PO_4 (δ 0.00). All complexes gave satisfactory elemental microanalyses (CH, and N).

having occurred [4]. In a related reaction the vinyl group in the complex [Os(CH=CHPh)Cl(CS)(PPh_3)$_2$] readily undergoes migration to the thiocarbonyl ligand upon treatment with *p*-tolyisonitrile [7]. This latter process is, however, driven in part by the favourable bidentate coordination of the thioacyl group to osmium. A plausible intermediate in the addition of the second isonitrile to [Ru{C(C≡CPh)=CHPh}Cl(CN^{t}Bu)(CO)(PPh_3)$_2$] would be the cationic complex [Ru{η^3-C(C≡CPh)=CHPh}(CN^{t}Bu)(CO)(PPh_3)$_2$]$^+$ and indeed the perchlorate salt of such a complex is the product of the reaction of [Ru{C(C≡CPh)=CHPh}Cl(CN^{t}Bu)(CO)(PPh_3)$_2$] with silver perchlorate. Subsequent treatment of this salt with one equivalent of CN^{t}Bu provides [Ru{C(C≡CPh)=CHPh}(CN^{t}Bu)$_2$(CO)(PPh_3)$_2$]ClO_4.

It is not clear why the migratory insertion of the carbonyl ligand should prevail in the case of the complexes [Ru(CH=CHR′)Cl(CO)(PPh_3)$_2$] and not for [Ru{C(C≡CPh)=CHPh}Cl(CNR)(CO)(PPh_3)$_2$], but the presence of an α-substituent on the vinyl group might sterically hinder the swivelling needed to approach the migratory insertion transition state. This interpretation is consistent with Santos' observation that [Ru(CPh=CHPh)Cl(CO)($PPh_3)_2$] with excess CN^{t}Bu leads to a complex formulated as [Ru{C(O)CPh=CHPh}Cl(CN^{t}Bu)$_2$($PPh_3)_2]^+$ [4].

An alternative route to cationic σ-α-phenylethynyl-trans-β-styryl complexes was developed based on the activation of diphenylbutadiyne towards protonation which accompanies coordination to an electron-rich metal centre. Thus [Ru(CO)$_2$($PPh_3)_3$] treated with diphenylbutadiyne leads to the zerovalent complex [Ru(CO)$_2$(η^2-PhC-CCCPh)($PPh_3)_2$] by analogy to the reaction described for tolane [8]. Careful addition of one equivalent of HCl leads to the complex [Ru{C(C≡CPh)=CHPh}Cl-(CO)$_2$($PPh_3)_2$] (excess HCl provides [RuCl$_2$(CO)$_2$($PPh_3)_2$]), however addition of an acid, the conjugate base of which is non-nucleophilic (HBF_4, HPF_6, $HClO_4$) leads to the isolation of salts of the complex [Ru(PhCCCCHPh)(CO)$_2$($PPh_3)_2]^+$. This species would appear to possess a weakly *trihapto* PhCCCCHPh ligand as suggested for [Ru{η^3-C(C≡CPh)=CHPh}(CN^{t}Bu)(CO)($PPh_3)_2]^+$ above (cf.[9.10]). Addition of CN^{t}Bu leads to metallacycle opening and formation of the complex [Ru(η^1-C(C≡CPh)=CHPh)(CO)$_2$(CNR)($PPh_3)_2]^+$. The precursor complex is also available via the abstraction of chloride from [Ru{C(C≡CPh)=CHPh}Cl(CO)$_2$($PPh_3)_2$], this complex being obtained quantitatively by carbonylation of [Ru{C(C≡CPh)=CHPh}-Cl(CO)($PPh_3)_2$], in addition to the hydrochlorination route outlined above.

We are currently investigating further reactions of complexes of both *trihapto* and *monohapto* α-alkynyl-*trans*-β-vinyl ligands.

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