COMMUNICATION

SYNTHESIS, FORMATION CONSTANTS AND REACTIONS OF CATIONIC RHODIUM(I) COMPLEXES OF NITRILES

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Abstract—Reactions of Rh(ClO₄)(CO)(PPh₃)₂ with nitriles produce new cationic rhodium(I) complexes, [RhL(CO)(PPh₃)₂]ClO₄ [L = CH₃CN (1), CH₃CH₂CH₂CN (2) or C₆H₅CN (3)], whose spectral data suggest that the nitriles are coordinated through the nitrogen atom. Formation constants for the reaction Rh(ClO₄)(CO)(PPh₃)₂+L \Rightarrow [RhL(CO)(PPh₃)₂]ClO₄, have been measured to be 1.01×10^5 M⁻¹ (CH₃CN), 1.07×10^5 M⁻¹ (CH₃CH₂CH₂CN) and 2.59×10^4 M⁻¹ (C₆H₅CN) at 25°C in monochlorobenzene. The differences in the formation constants for the different nitriles seem to be predominantly due to differences in ΔH (not to differences in ΔS). The nitriles in 1–3 are readily replaced with nitrogen base ligands (unsaturated nitriles and pyridine) and PPh₃.

The synthesis, physical properties and chemical reactivities of cationic rhodium(I) complexes of saturated nitriles¹⁻³ and iridium(I) complexes of unsaturated⁴⁻⁶ and saturated⁷ nitriles, [ML(CO) (PPh₃)₂]ClO₄ (M = Rh or Ir, L = unsaturated or saturated nitriles), have been reported recently. This communication reports the synthesis, formation constants with thermodynamic parameters, and reactions of new cationic rhodium(I) complexes of saturated and aromatic nitriles.

[‡] The molar conductance of a standard 1:1 electrolyte, $[(C_3H_7)_4N]PF_6$, in dichloromethane at 25°C was measured to be 110 Ω^{-1} cm² mol⁻¹. Addition of nitriles (L) into the yellow solution of $Rh(ClO_4)(CO)(PPh_3)_2$ in benzene at 25°C under nitrogen resulted within 5 min in yellow-orange microcrystals of $[RhL(CO)(PPh_3)_2]ClO_4$ [eqn (1)] :†

 $Rh(ClO_4)(CO)(PPh_3)_2 + L$

$$\rightarrow$$
 [RhL(CO)(PPh₃)₂]ClO₄, (1)

where $L = CH_3CN$ (1), $CH_3CH_2CH_2CN$ (2) or C_6H_5CN (3). Complexes 1-3 are stable in the solid state in air and in solution under nitrogen at 25°C, and soluble in polar solvents (chloroform, dichloromethane and acetonitrile) and insoluble in non-polar solvents (benzene and hexane). The molar-conductance values (110-120 Ω^{-1} cm² mol⁻¹) of 1-3 (5.0 × 10⁻⁵ M in dichloromethane) suggest that the complexes are 1:1 electrolytes.[‡]

IR spectral data (Table 1) unambiguously show that nitriles in complexes 1-3 are coordinated to rhodium through the nitrogen atom, and not through the π -system of the nitrile group. It is wellknown that v(CN) for a nitrile increases upon coordination through the nitrogen atom,⁸⁻¹⁰ while it decreases significantly upon coordination through the π -system of the nitrile group.¹⁰ A broad and strong absorption band at *ca* 1100 cm⁻¹ (not listed in Table 1) observed for all the complexes is attributable to the anionic tetrahedral ClO₄ (T_d) group.¹¹

^{*}Author to whom correspondence should be addressed. † One drop (*ca* 0.75 mmol) of a nitrile (CH₃CN, CH₃CH₂CH₂CN or C₆H₅CN), 1.20 g (0.26 mmol) of Rh(ClO₄)(CO)(PPh₃)₂ and 10 cm³ of benzene were used. The yellow-orange crystals were collected by filtration, washed with benzene (5 cm³) and hexane (15 cm³), and dried *in vacuo*. The yield was *ca* 85% based on [RhL(CO)(PPh₃)₃]ClO₄ [L = CH₃CN (1), CH₃CH₂ CH₂CN (2) or C₆H₅CN (3)]. Found: C, 59.5; H, 4.8; N, 1.6%. Calc. for RhC₃₉H₃₃NClO₅P₂ (1): C, 58.8; H, 4.2; N, 1.8%. Found: C, 60.7; H, 4.4; N, 1.7%. Calc. for RhC₄₁H₃₇NClO₅P₂ (2): C, 59.8; H, 4.5; N, 1.7%. Found: C, 62.6; H, 3.9; N, 1.7%. Calc. for RhC₄₄H₃₅N-ClO₅P₂ (3): C, 61.6; H, 4.1; N, 1.6%.

Tabl	e 1.	IR (in	Nu	jol), elec	tronic at	osorpti	ion (in monochlorobenzene)
and	${}^{1}\mathbf{H}$	NMR	(in	CDCl ₃)	spectral	data	for	[RhL(CO)(PPh ₃) ₂]ClO ₄
		[L = C]	H₃C	N (1), C	H ₃ CH ₂ C	H ₂ CN	(2)	or C ₆ H ₅ CN (3)]

	IR absorption (c	Electronic absorption (nm)				
Compound	$\nu(CN) [\Delta \nu(CN)]^a$	v(CO) ^b	$\lambda_{\max}(\varepsilon)^c$			
1	2291 (36)	2000	374 (3500)			
2	2291 (40)	2020	375 (3550)			
3	2270 (40)	2026	379 (3460)			
	¹ H NMR chemical shift (ppm) ^d					
CH ₃ CN	1.73 (s, CH_3)					
CH ₃ CH ₂ CH ₂ CN	0.77 (t, CH_3), 1.35 (m, CH_3CH_2), 2.09 (t, CH_2CN) ca 7.5 (m, C_6H_5)					
C ₆ H ₅ CN						
1	1.55 (s, CH ₃)					
2	0.23 (t, CH ₃), 0.75 (m, CH ₃ CH ₂), 1.83 (t, CH ₂ CN)					
3	$ca 7.5 (m, C_6 H_5)$					

^{*a*} Weak. $\Delta v(CN) = v(CN)$ of coordinated nitrile -v(CN) of free nitrile. ^{*b*} Very strong.

^cAt 25[°]C under nitrogen in the presence of excess corresponding L.

^{*d*}At 25°C at 60 MHz. All complexes (1–3) show a multiplet due to the phenyl protons of PPh₃ at *ca* 7.5 ppm. Relative to TMS.

which supports the view that the complexes are 1:1 electrolytes as confirmed by the conductance measurements. It is noticed in Table 1 that v(CO) for the CH₃CN complex (1) is lower than those of other nitrile complexes.

Electronic absorption spectral data (Table 1) also suggest that 1–3 are four-coordinated rhodium(I) complexes and the nitriles in 1–3 are coordinated through the nitrogen atom. It is well-known that the four-coordinated rhodium(I) complexes RhA(CO)(PPh₃)₂ [A = monodentate nitrogen base ligand such as NCO, NO₂, NCS or N(CN)₂]¹² and [RhL(CO)(PPh₃)₂]ClO₄ (L = monodentate nitrile coordinated through the nitrogen atom)³ show an absorption band at 365–383 nm (ε 3400–4300).

The observed chemical shifts of the nitrile protons in 1 and 2 (Table 1) and the ratios (not

given in Table 1) of the phenyl protons of PPh₃ to nitrile protons clearly indicate a RhL(PPh₃)₂ $(L = CH_3CN \text{ or } CH_3CH_2CH_2CN)$ moiety in 1 and 2. It is seen in Table 1 that all protons of nitriles in 1 and 2 showed upfield shifts relative to those of the free nitriles as observed for related rhodium(I) and iridium(I) complexes of nitriles coordinated through the nitrogen atom.^{2,3,6} The spin coupling between ¹⁰³Rh and the protons of coordinated nitriles has not been observed for the complexes prepared in this study.

Formation constants and thermodynamic parameters have been determined for eqn (2):*

$$Rh(ClO_4)(CO)(PPh_3)_2 + L$$

$$\Rightarrow [RhL(CO)(PPh_3)_2]ClO_4 \quad (2)$$

where $L = CH_3CN$, $CH_3CH_2CH_2CN$, C_6H_5CN .

It is noticed in Table 2 that the formation constant of 3 is smaller than those of 1 and 2, which seems to be predominantly due to differences in ΔH (not to differences in ΔS).

Nitriles in 1-3 are readily replaced by nitrogen and phosphorus base ligands according to eqn (3):

$$[RhL(CO)(PPh_3)_2]ClO_4 + L'$$

$$\rightarrow [RhL'(CO)(PPh_3)_2]ClO_4 + L, \quad (3)$$

where $L = CH_3CN$, $CH_3CH_2CH_2CN$ or C_6H_5CN ; and $L' = CH_2$ —CHCN,¹ CH_2 —C(CH₃)CN,³

^{*} Formation constants for eqn (2) were determined in the same manner as described for the formation constants of [RhL(CO)(PPh₃)₂]ClO₄ (L = unsaturated nitriles coordinated through the nitrogen atom).³ The molar conductances of 1-3 in monochlorobenzene are practically zero, indicating that the ionization [RhL(CO)(PPh₃)₂] ClO₄ \rightarrow [RhL(CO)(PPh₃)₂]⁺ + ClO₄⁻ is negligible, while that in dichloromethane is 110-120 Ω^{-1} cm² mol⁻¹, suggesting that the complexes undergo complete ionization. A similar observation was previously reported for the related complexes of unsaturated nitriles³ and Rh(ClO₄)(CO)(PPh₃)₂.¹¹

Table 2. Formation constants and thermodynamic	parameters f	for the reaction			
$Rh(ClO_4)(CO)(PPh_3)_2 + L \rightleftharpoons [RhL(CO)(PPh_3)_2]ClO_4$	$(L = CH_3)$	CN, CH_3CH_2			
CH_2CN or C_6H_5CN) in monochlorobenzene					

L	Formation constant ^a (M ⁻¹)	ΔH^{h} (kcal mol ⁻¹)	ΔS (cal mol ⁻¹ deg ⁻¹)
CH₃CN	1.01×10^{5}	-7.3 ± 0.8	-2 ± 3
CH₃CH₂CH₂CN	1.07×10^{5}	-7.3 ± 0.4	-1 ± 1
C₀H₅CN	2.59×10^{4}	-6.7 ± 0.1	-2 ± 0.3

^a At 25°C.

^b In the region of 25–55°C.

CH₂=CHCH₂CN,³ cis,trans-CH₃CH=CHCN,³ PPh₃¹³ or C₅H₅N.¹³

The reactions of 1–3 with unsaturated aldehydes, however, do not produce [Rh(RCH=CHCHO) (CO)(PPh₃)₂]ClO₄ (R = H or CH₃), which are readily formed by the reactions of Rh(ClO₄) (CO)(PPh₃)₂ with RCH=CHCHO.¹⁴

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