

Preliminary communication

BASIC METALS

XXI*. THE STRONG ELECTROPHILICITY OF COORDINATED C₂H₄ IN DICATIONIC ETHYLENE-RHODIUM(III) AND -RUTHENIUM(II) COMPLEXES

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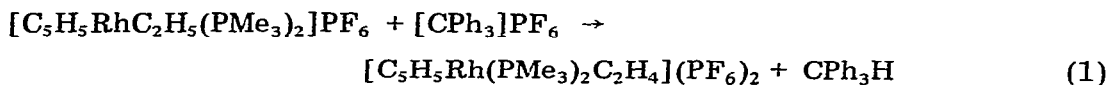
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Summary

The complexes [C₅H₅Rh(PMe₃)₂C₂H₄]X₂ (X = PF₆, BF₄) and [C₆H₆Ru(PMe₃)₂-C₂H₄](PF₆)₂ have been prepared by reaction of [C₅H₅RhC₂H₅(PMe₃)₂]X and [C₆H₆RuC₂H₅(PMe₃)₂]X with [CPh₃]X. The ethylene ligand in the dications is readily attacked by nucleophiles N, where N = NEt₃, PR₃ (R = Me, i-Pr, Ph), P(OR)₃ (R = Me, Ph), SCN⁻ and probably I⁻, to form complexes containing Rh—C₂H₄N and Ru—C₂H₄N bonds.

We recently prepared the monocationic ethylene complexes [C₆H₆RuR(PMe₃)₂-C₂H₄]⁺ with R = H or CH₃ and showed that the complex with R = CH₃ reacts with trimethylphosphine to give [C₆H₆RuCH₃(PMe₃)₂C₂H₄PMe₃]⁺, which was isolated as the PF₆ salt [2]. The formally isoelectronic cation [C₅H₅RhCH₃(PMe₃)₂C₂H₄]⁺ behaves similarly, i.e. it reacts with PMe₃ to give [C₅H₅RhCH₃(PMe₃)₂C₂H₄PMe₃]⁺ [3].

In the light of the general variation of reactivity of metal complexes containing unsaturated hydrocarbon ligands [4] we expected the ethylene to be more electrophilic in the dication [C₅H₅Rh(PMe₃)₂C₂H₄]²⁺ than in [C₅H₅RhCH₃(PMe₃)₂C₂H₄]⁺. This dication was produced in quantitative yield by reaction of [C₅H₅RhC₂H₅(PMe₃)₂]PF₆ [5] with [CPh₃]PF₆ in nitromethane at room temperature.

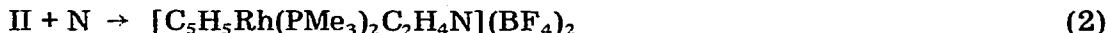


(I)

*For Part XX see ref. 1.

The corresponding BF_4 salt $[\text{C}_5\text{H}_5\text{Rh}(\text{PMe}_3)_2\text{C}_2\text{H}_4](\text{BF}_4)_2$ (II) was obtained in quantitative yield from $[\text{C}_5\text{H}_5\text{RhC}_2\text{H}_5(\text{PMe}_3)_2]\text{I}$ [5] and $[\text{CPh}_3]\text{BF}_4$ (molar ratio 1/2.5) in nitromethane.

Complex II reacts with nucleophiles such as tertiary phosphines or amines (CH_3NO_2 , 25°C , 10 min) to form $[\text{C}_5\text{H}_5\text{Rh}(\text{PMe}_3)_2\text{C}_2\text{H}_4\text{N}](\text{BF}_4)_2$.



(III: N = PMe_3)

(IV: N = $\text{P-}i\text{-Pr}_3$)

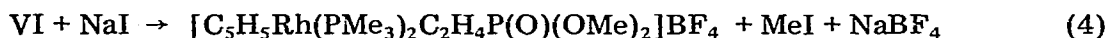
(V: N = NEt_3)

In the reaction with PMe_3 a small amount ($\leq 10\%$) of $[\text{C}_5\text{H}_5\text{Rh}(\text{PMe}_3)_3](\text{BF}_4)_2$ [3] is also formed. The $\text{Rh}-\text{C}_2\text{H}_4\text{N}$ bonds in the dications of III–V are remarkably stable, e.g. there is no ethylene elimination, accompanied by formation of $[\text{C}_5\text{H}_5\text{Rh}(\text{PMe}_3)_3]^{2+}$, on heating complex III at 60°C in nitromethane for 2 h.

The reaction of II with $\text{P}(\text{OMe})_3$ yields a mixture of two products. The ^1H NMR spectrum of the reaction solution shows two signals in the C_5H_5 region at δ 5.62 and 5.67 ppm, which are assigned to the complexes VI and VII. Stirring of the nitromethane solution with NaI (25°C , 15 min) gives VII quantitatively.

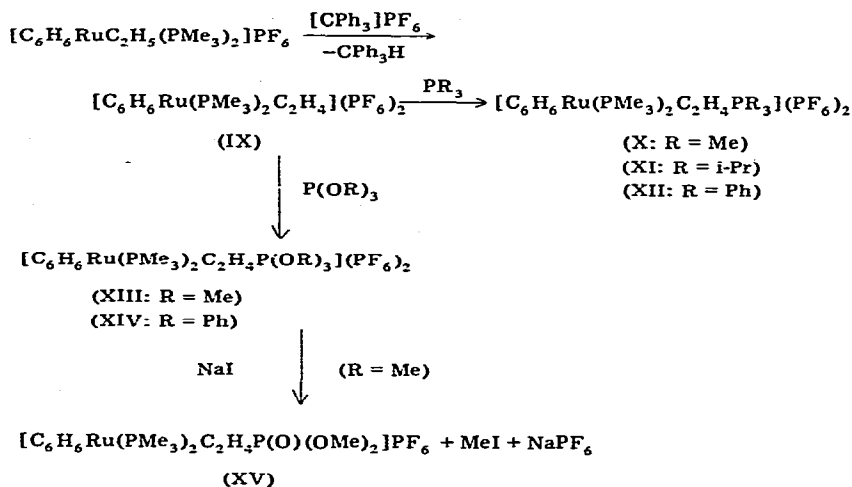


(VI)



(VII)

Complex II also reacts with anionic nucleophiles N, but in this case the products of nucleophilic addition of N to the coordinated ethylene are more labile. With KSCN (CH_3OH , 25°C , 1 h) the product of the reaction is $[\text{C}_5\text{H}_5\text{Rh}(\text{PMe}_3)_2\text{C}_2\text{H}_4\text{SCN}]\text{BF}_4$ (VIII), and on warming in nitromethane this slowly loses ethylene to give either $[\text{C}_5\text{H}_5\text{Rh}(\text{PMe}_3)_2\text{NCS}]^+$ or $[\text{C}_5\text{H}_5\text{Rh}(\text{PMe}_3)_2\text{SCN}]^+$. The re-



(X: R = Me)

(XI: R = $i\text{-Pr}$)

(XII: R = Ph)

action of II with NaI in methanol at 55°C after 5 h yields only $[\text{C}_5\text{H}_5\text{Rh}(\text{PMe}_3)_2\text{I}]^+$ [5], but at room temperature and shorter reaction times the ^1H NMR spectrum of the reaction mixture shows, in addition to the signals of II and $[\text{C}_5\text{H}_5\text{Rh}(\text{PMe}_3)_2\text{I}]^+$, a multiplet ($I = 5\text{H}$) at δ 5.67 and a virtual triplet ($I = 18\text{H}$) at 1.67 ppm which we tentatively attribute to the cation $[\text{C}_5\text{H}_5\text{Rh}(\text{PMe}_3)_2\text{C}_2\text{H}_4\text{I}]^+$. It seems that at low temperatures nucleophilic addition of the anion to the olefin is the preferred reaction, whereas at higher temperatures the cations $[\text{C}_5\text{H}_5\text{Rh}(\text{PMe}_3)_2\text{Y}]^+$ ($\text{Y} = \text{NCS}, \text{I}$) are formed, either by direct replacement of ethylene by the anion or by a β -elimination route.

The PF_6^- salt of the dication $[\text{C}_6\text{H}_6\text{Ru}(\text{PMe}_3)_2\text{C}_2\text{H}_4]^{2+}$ has also been prepared (Scheme 1). It is interesting to note that the difference in reactivity between $\text{C}_5\text{H}_5\text{Rh}(\text{PMe}_3)_2$ [5] and $\text{C}_6\text{H}_6\text{Ru}(\text{PMe}_3)_2$ [6] towards electrophiles is reflected in the chemical behaviour of the corresponding ethylenebis(phosphine) dications.

TABLE 1

^1H NMR SPECTRA OF COMPLEXES II–XV IN CD_3NO_2 (δ in ppm, J in Hz; d, doublet; t, triplet; q, quartet; m, multiplet; vt, virtual triplet)

Complex	$\delta(\text{C}_n\text{H}_n)$	$J(\text{PH})$	$J(\text{RhH})$	$\delta(\text{PMe}_3)$	$J(\text{RhH})$	$\delta(\text{C}_2\text{H}_4)$	$\delta(\text{N})$	$J(\text{PH})$
II	6.33 d of t	1.0	0.4	2.03 d of vt	0.9	4.23 "q" ^a		
III	5.67 m			1.70 d of vt	0.9	2.6; 1.9 m ^b	1.88 d	14.0
IV	5.70 t	1.1		1.70 d of vt	0.9	2.6; 1.9 m ^b	1.47 d of d	15.0 ^c
V	5.70 t	1.0		1.70 d of vt	0.9	3.3; 1.7 m ^b	2.90 m 1.17 t ^d 3.30 q ^d	
VI	5.62 m			1.68 d of vt	0.9	^e	4.22 d	11.0
VII	5.67 m			1.70 d of vt	0.9	1.9 m ^b	3.77 d	10.5
VIII	5.67 d of t	1.1	0.4	1.70 d of vt	0.9	3.7; 1.9 m ^b		
IX ^a	6.88 t	0.6		1.89 vt		3.49 t ^f		
X	6.01 t	0.85		1.59 vt		2.7 m ^g	1.88 d	13.8
XI	6.09 t	0.95		1.66 vt		^h	1.50 m 2.65 m	
XII	6.09 t	0.85		1.39 vt		3.45 m	7.92 m	
XIII	6.01 t	0.85		1.59 vt		2.8 m ^g	4.21 d	10.8
XIV	5.88 t	0.9		1.44 vt		3.2 m	7.52 m	
XV	5.97 t	0.85		1.58 vt		3.3 m	3.75 d	10.6

^a $J(\text{PH}) = J(\text{RhH}) = 2.0$. ^b Partial overlap with the Rh–PMe₃ signal. ^c $J(\text{HH}) = 7.0$. ^d $J(\text{HH}) = 7.0$.

^e Overlap with the C₂H₄ signal of VII; see text. ^f $J(\text{PH}) = 4.0$. ^g Partial overlap with the Ru–PMe₃ signal.

^h Assignment not possible due to overlap with the Ru–PMe₃ and the CHMe₂ signals.

TABLE 2

^{31}P NMR SPECTRA OF COMPLEXES III, IV, VII, IX–XV IN CD_3NO_2 (δ in ppm, H₃PO₄ ext., J in Hz; s, singlet; d, doublet; t, triplet)

Complex	$\delta(\text{PMe}_3)$	$J(\text{RhP})$	$J(\text{PP})$	$\delta(\text{N})$	$J(\text{RhP})$	$J(\text{PP})$
III	5.2 d of d	142.3	2.5	22.7 d of t	9.9	2.5
IV	5.9 d of d	141.5	2.5	39.2 d of t	8.8	2.5
VII	6.2 d of d	145.5	1.2	29.0 d of t	8.1	1.2
IX ^a	10.53 s					
X ^a	4.83 d		3.3	23.45 t		3.3
XI	4.20 d		3.0	38.34 t		3.0
XII	3.94 d		3.3	18.46 t		3.3
XIII	4.21 d		3.0	43.52 t		3.0
XIV	3.76 d		4.5	28.77 t		4.5
XV	4.47 d		3.0	30.73 t		3.0

^a In acetone-*d*₆.

Like the neutral ruthenium complex $C_6H_6Ru(PMe_3)_2$, the dication $[C_6H_6Ru(PMe_3)_2C_2H_4]^{2+}$ is much more selective than the rhodium analogue and reacts with tertiary phosphines and phosphites, but not with tertiary amines, to form products containing Ru—C₂H₄N bonds.

The ¹H and ³¹P NMR data for $[C_nH_nM(PMe_3)_2C_2H_4]X_2$ (II, IX) and the complexes obtained by nucleophilic addition to the ethylene ligand are summarised in Tables 1 and 2.

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