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Preliminary communication

BASIC METALS

XXI*. THE STRONG ELECTROPHILICITY OF COORDINATED C_2H_4 IN DICATIONIC ETHYLENE-RHODIUM(III) AND -RUTHENIUM(II) COMPLEXES

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Summary

The complexes $[C_5H_5Rh(PMe_3)_2C_2H_4]X_2$ ($X = PF_6, BF_4$) and $[C_6H_6Ru(PMe_3)_2C_2H_4](PF_6)_2$ have been prepared by reaction of $[C_5H_5RhC_2H_5(PMe_3)_2]X$ and $[C_6H_6RuC_2H_5(PMe_3)_2]X$ with $[CPh_3]X$. The ethylene ligand in the dications is readily attacked by nucleophiles N, where N = NEt_3, PR_3 (R = Me, i-Pr, Ph), $P(OR)_3$ (R = Me, Ph), SCN^- and probably I^-, to form complexes containing $Rh—C_2H_4N$ and $Ru—C_2H_4N$ bonds.

We recently prepared the monocationic ethylene complexes $[C_6H_6RuR(PMe_3)C_2H_4]^+$ with R = H or CH_3 and showed that the complex with R = CH_3 reacts with trimethylphosphine to give $[C_6H_6RuCH_3(PMe_3)C_2H_4PMe_3]^+$, which was isolated as the PF_6 salt [2]. The formally isoelectronic cation $[C_5H_5RhCH_3(PMe_3)C_2H_4]^+$ behaves similarly, i.e. it reacts with PMe_3 to give $[C_5H_5RhCH_3(PMe_3)C_2H_4PMe_3]^+$ [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 $[C_5H_5Rh(PMe_3)_2C_2H_4]^{2+}$ than in $[C_5H_5RhCH_3(PMe_3)C_2H_4]^+$. This dication was produced in quantitative yield by reaction of $[C_5H_5RhC_2H_5(PMe_3)_2]PF_6$ [5] with $[CPh_3]PF_6$ in nitromethane at room temperature.

$$[C_5H_5RhC_2H_5(PMe_3)_2]PF_6 + [CPh_3]PF_6 \rightarrow \underset{(I)}{[C_5H_5Rh(PMe_3)_2C_2H_4](PF_6)_2} + CPh_3H \qquad (1)$$

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*For Part XX see ref. 1.

The corresponding BF_4 salt $[C_5H_5Rh(PMe_3)_2C_2H_4](BF_4)_2$ (II) was obtained in quantitative yield from $[C_5H_5RhC_2H_5(PMe_3)_2]I$ [5] and $[CPh_3]BF_4$ (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 $[C_5H_5Rh(PMe_3)_2C_2H_4N](BF_4)_2$.

$$\mathrm{II} + \mathrm{N} \rightarrow [C_5H_5Rh(PMe_3)_2C_2H_4N](BF_4)_2 \qquad (2)$$

(III: $N = PMe_3$)
(IV: $N = P\text{-}i\text{-}Pr_3$)
(V: $N = NEt_3$)

In the reaction with PMe_3 a small amount ($\leqslant$ 10%) of $[C_5H_5Rh(PMe_3)_3](BF_4)_2$ [3] is also formed. The Rh—C_2H_4N bonds in the dications of III—V are remarkably stable, e.g. there is no ethylene elimination, accompanied by formation of $[C_5H_5Rh(PMe_3)_3]^{2+}$, on heating complex III at 60°C in nitromethane for 2 h.

The reaction of II with $P(OMe)_3$ 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.

$$\mathrm{II} + P(OMe)_3 \rightarrow \underset{\text{(VI)}}{[C_5H_5Rh(PMe_3)_2C_2H_4P(OMe)_3](BF_4)_2} \qquad (3)$$

$$\mathrm{VI} + NaI \rightarrow \underset{\text{(VII)}}{[C_5H_5Rh(PMe_3)_2C_2H_4P(O)(OMe)_2]BF_4} + MeI + NaBF_4 \qquad (4)$$

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 $[C_5H_5Rh(PMe_3)_2C_2H_4SCN]BF_4$ (VIII), and on warming in nitromethane this slowly looses ethylene to give either $[C_5H_5Rh(PMe_3)_2NCS]^+$ or $[C_5H_5Rh(PMe_3)_2SCN]^+$. The re-

$$\begin{tikzcd}
{[C_6H_6RuC_2H_5(PMe_3)_2]PF_6} \arrow[r, "{[CPh_3]PF_6}", "-CPh_3H"'] & {} \\
\underset{\text{(IX)}}{[C_6H_6Ru(PMe_3)_2C_2H_4](PF_6)_2} \arrow[r, "PR_3"] \arrow[d, "P(OR)_3"] & \underset{\substack{\text{(X: R = Me)} \\ \text{(XI: R = i-Pr)} \\ \text{(XII: R = Ph)}}}{[C_6H_6Ru(PMe_3)_2C_2H_4PR_3](PF_6)_2} \\
\underset{\substack{\text{(XIII: R = Me)} \\ \text{(XIV: R = Ph)}}}{[C_6H_6Ru(PMe_3)_2C_2H_4P(OR)_3](PF_6)_2} \arrow[d, "NaI"', "(R = Me)"] & \\
\underset{\text{(XV)}}{[C_6H_6Ru(PMe_3)_2C_2H_4P(O)(OMe)_2]PF_6} + MeI + NaPF_6 &
\end{tikzcd}$$

SCHEME 1

action of II with NaI in methanol at 55°C after 5 h yields only $[C_5H_5Rh(PMe_3)_2I]^+$ [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 $[C_5H_5Rh(PMe_3)_2I]^+$, a multiplet (I = 5H) at δ 5.67 and a virtual triplet (I = 18H) at 1.67 ppm which we tentatively attribute to the cation $[C_5H_5Rh(PMe_3)_2C_2H_4I]^+$. It seems that at low temperatures nucleophilic addition of the anion to the olefin is the preferred reaction, whereas at higher temperatures the cations $[C_5H_5Rh(PMe_3)_2Y]^+$ (Y = NCS, 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 $[C_6H_6Ru(PMe_3)_2C_2H_4]^{2+}$ has also been prepared (Scheme 1). It is interesting to note that the difference in reactivity between $C_5H_5Rh(PMe_3)_2$ [5] and $C_6H_6Ru(PMe_3)_2$ [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	$\delta(C_nH_n)$	J(PH)	J(RhH)	$\delta(PMe_3)$	J(RhH)	$\delta(C_2H_4)$	δ(N)	J(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 2.90 m	15.0[c]
V	5.70 t	1.0		1.70 d of vt	0.9	3.3; 1.7 m[b]	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(PH) = J(RhH) = 2.0. [b] Partial overlap with the Rh—PMe_3 signal. [c] J(HH) = 7.0. [d] J(HH) = 7.0. [e] Overlap with the C_2H_4 signal of VII; see text. [f] J(PH) = 4.0. [g] Partial overlap with the Ru—PMe_3 signal. [h] Assignment not possible due to overlap with the Ru—PMe_3 and the $CHMe_2$ signals.

TABLE 2

^{31}P NMR SPECTRA OF COMPLEXES III, IV, VII, IX—XV IN CD_3NO_2 (δ in ppm, H_3PO_4 ext., J in Hz; s, singlet; d, doublet; t, triplet)

Complex	$\delta(PMe_3)$	J(RhP)	J(PP)	δ(N)	J(RhP)	J(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 $Ru—C_2H_4N$ bonds.

The ^1H and ^{31}P 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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