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CATIONIC η^3-ALLYL COMPLEXES OF RHODIUM

PAUL POWELL * and LESLIE J. RUSSELL

The Bourne Laboratory, Department of Chemistry, Royal Holloway College, University of London, Egham Hill, Egham, Surrey, TW 20 OEX (Great Britain)

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Summary

The complexes $[Rh(\eta^3\text{-}C_3H_4R)(\eta^5\text{-}C_5R'_5)L]^+BF_4^-$ (R = 1-Me, R' = H, Me; R = 2-Me, R' = H) (L = C_5H_5N, Ph_3P, Ph_3As) have been prepared from $Rh(\eta^3\text{-}C_3H_4R)(\eta^5\text{-}C_5R'_5)Cl$ and $AgBF_4$ in acetone, followed by reaction with the stoicheiometric quantity of L. The ^1H and ^{13}C NMR spectra of the salts are reported and discussed.

Introduction

η^3-Allyl-η^5-cyclopentadienylchlororhodium complexes $RhCl(\eta^3\text{-}C_3H_4R)(\eta^5\text{-}C_5R'_5)$ (I) (R' = H or Me) were first prepared several years ago and are well characterised [1—3]. The related salts $[Rh(\eta^3\text{-}C_3H_4R)(\eta^5\text{-}C_5R'_5)L]^+ X^-$ however, have been mentioned only cursorily in the literature. Powell and Shaw [1] obtained allylcyclopentadienylpyridinerhodium tetraphenylborate by addition of $NaBPh_4$ to a solution of (I) (R = R' = H) and pyridine in aqueous methanol. Hart-Davis and Graham [4] found that the ionic complexes $[Rh(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)PPh_3]^+ X^-$ are formed in 2—5% yield as by-products in the reactions of $Rh(\eta^5\text{-}C_5H_5)(CO)PPh_3$ with allyl halides. In a reference to unpublished work these authors state that the complexes may be better prepared by treating $Rh(C_2H_4)(C_5H_5)PPh_3$ with allyl halides. Some analogous cobalt complexes have been reported [5,6].

Results and discussion

When complexes of type I are treated with alkali metal or silver salts MX in methanol, the chlorine atom is readily exchanged for other groups X (e.g. X = Br, I, NO_3) [7]. We have found that I reacts with silver tetrafluoroborate in acetone to give silver chloride and an orange solution, which probably contains the acetone complex $[Rh(\eta^3\text{-}C_3H_4R)(\eta^5C_5R'_5)L]^+BF_4^-$ (L = $(CH_3)_2CO$). Tetrafluoroborate salts (II—X) can be isolated in 70—75% yield by addition of this solution to a solution of the appropriate ligand L (L = pyridine, Ph_3P, Ph_3As), concentration, and precipitation with diethyl ether. The salts are yellow crystalline materials, soluble in polar organic solvents, and stable to air and moisture. The conductivities of their solutions in methanol are consistent with their formulation as 1 : 1 electrolytes [8] (Table 1).

The ^1H NMR spectra of the ionic complexes II—X are summarised in Table 2. The spectra are consistent with the proposed structures. The equivalence of H^1 and H^3 in the spectra of the 2-methylallyl complexes (VIII, IX and X) indicates that the allyl group is bonded symmetrically to the metal. Other authors have observed small (ca. 0.9 Hz) couplings from ^{103}Rh to the protons of the cyclopentadienyl group in similar complexes [1,9]. We did not observe these couplings, although the cyclopentadienyl resonances are somewhat broadened. The shifts of the protons of the allyl groups are virtually identical in analogous Ph_3P and Ph_3As complexes, whereas when pyridine is the ligand, all the allyl resonances are shifted to low field.

The ^{13}C NMR spectra (broad band proton decoupled) are quoted in Table 3. Conversion of the neutral chlorocomplexes Ia—Ic into the cationic species II—X has little effect on the chemical shifts of the allyl or cyclopentadienyl carbon atoms. Previous work has indicated that the ^{13}C chemical shifts of organic ligands coordinated to transition elements is rather insensitive to the formal charge on the complex [10,11]. The shifts observed in the spectra of our compounds fall in the region typical for η^3-allyl complexes, with the resonance from the central carbon atom C_2 lying to low field of those from C_1 and C_3 [12—15].

For each set of compounds the resonances for all three allylic carbon atoms in the pyridine complexes II, V and VIII lie to low field of those in the corre-

(continued on p. 419)

TABLE 1

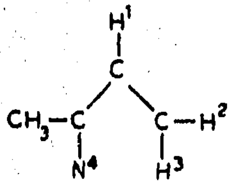
ANALYTICAL DATA FOR THE RHODIUM COMPLEXES $[Rh(C_5R_5)(C_3H_4R)L]^+BF_4^-$

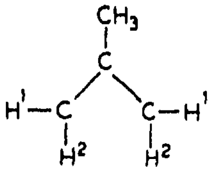
Complex	No.	M.p. (°C)	Found (calcd.) (%)		Λ[a]
			C	H	
$[Rh(1\text{-methylallyl})(C_5Me_5)(C_5H_5N)]^+BF_4^-$	II	152—4 dec.	49.64 (49.70)	5.86 (5.93)	97
$[Rh(1\text{-methylallyl})(C_5Me_5)(PPh_3)]^+BF_4^-$	III	146—8 dec.	59.63 (59.84)	6.02 (5.81)	
$[Rh(1\text{-methylallyl})(C_5Me_5)(AsPh_3)]^+BF_4^-$	IV	160—2 dec.	55.98 (56.01)	5.54 (5.43)	90
$[Rh(1\text{-methylallyl})(C_5H_5)(C_5H_5N)]^+BF_4^-$	V	146—6 dec.	43.47 (43.23)	4.30 (4.40)	
$[Rh(1\text{-methylallyl})(C_5H_5)(PPh_3)]^+BF_4^-$	VI	140—2 dec.	58.12 (56.68)	4.71 (4.76)	
$[Rh(1\text{-methylallyl})(C_5H_5)(AsPh_3)]^+BF_4^-$	VII	168—70 dec.	52.10 (52.63)	4.40 (4.42)	
$[Rh(2\text{-methylallyl})(C_5H_5)(C_5H_5N)]^+BF_4^-$	VIII	148—50 dec.	43.17 (43.23)	4.48 (4.40)	99
$[Rh(2\text{-methylallyl})(C_5H_5)(PPh_3)]^+BF_4^-$	IX	152—4 dec.	54.33 (56.68)	4.70 (4.76)	90
$[Rh(2\text{-methylallyl})(C_5H_5)(AsPh_3)]^+BF_4^-$	X	150—2 dec.	52.32 (52.63)	4.19 (4.42)	91

[a] Equivalent conductivity (ohm^{-1}) in methanol at 25°C (10^{-3} *M* complex). Calc. for KCl at 10^{-3} *M*. 97 ohm^{-1}.

TABLE 2

^1H NMR CHEMICAL SHIFTS [a] (τ) FOR THE COMPLEXES $[Rh(C_5R_5)(C_3H_4R^1)L]^+BF_4^-$



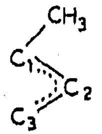


Complex [b]	H^1	H^2	H^3	H^4	Me	C_5Me_5	C_5H_5	Others
II	5.87m, $J(12)$ [c] 7, $J(13)$ 11	6.42d, $J(21)$ 7	7.83d, $J(31)$ 11	7.27m $J(4Me)$ 7, $J(41)$ 11	8.27d, $J(Me4)$ 7	8.43s		Pyridine: 1.52d, 2.17t, 2.53t
III	6.03m, $J(12)$ 7, $J(13)$ 11	7.01d, $J(21)$ 6.5	8.12d, $J(31)$ 12	7.48m	8.42d, $J(Me4)$ 6	8.48s		PPh_3; 2.5(br)
IV	6.04d, $J(12)$ 7, $J(13)$ 11	7.04d, $J(21)$ 7	8.12d, $J(31)$ 11	7.45m		8.45s		$AsPh_3$; 2.6(br)
V	4.65m	5.14d, $J(21)$ 7	7.95d, $J(31)$ 11	6.80m	7.83d, $J(Me4)$ 7		4.35s	Pyridine: 1.08d, 1.84t, 2.34t
VI	4.78m	5.94d, $J(21)$ 7	8.47d, $J(31)$ 11	7.36m	8.16d, $J(Me4)$ 7		4.63s	PPh_3; 2.5(br)
VII	4.78m	5.95d, $J(21)$ 6.5	8.36d, $J(21)$ 11	7.20m, $J(41)$ 10.5, $J(4Me)$ 6.5	8.15d, $J(Me4)$ 6.5		4.53s	$AsPh_3$; 2.5(br)
VIII	5.20	7.92			8.07		4.62s	Pyridine: 1.42d, 2.18t, 2.67t
IX	5.94	8.47			7.93		4.80	PPh_3; 2.5(br)
X	5.83	8.17			7.83		4.57	$AsPh_3$; 2.5(br)

[a] In CD_2Cl_2 at 100 MHz (varian HA 100). In ppm from TMS, τ = 10. [b] For numbering, see Table 1. [c] Coupling constants in Hz, $J(12)$ means $J(H_1H_2)$ etc.

TABLE 3

^{13}C NMR SPECTRA ^{a,b} OF THE COMPLEXES



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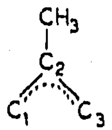
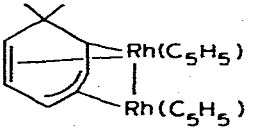


Complex	C_1	C_2	C_3	Methyl	Cp C atoms	Methyls on Cp ring	Ligand
Ia	73.1d, *J* 9	96.6d, *J* 6	58.5d, *J* 10	18.0	98.9d, *J* 6	9.5	
II	77.3d, *J* 9	98.6d, *J* 4	60.5d, *J* 12	17.8	100.6d, *J* 6	9.2	156.8 d, $C_{2,6}$ 140.6 d, C_4 128.3 d, $C_{3,5}$
III	71.3d, *J* 9	92.4 d, *J* 6	52.9 d, *J* 12	17.5	103.9 d, *J* 4	9.6	136.1 d, *J* 10 Hz 132.5 s, C_4 131.8 s, C_1 130.1 d, *J* 10 Hz
IV	70.0 d, *J* 7	92.5 d, *J* 6	51.5 d, *J* 10	17.6	102.9 d, *J* 6	9.8	135.2, $C_{2,6}$ 132.3, C_4 131.9, C_1 130.8, $C_{3,5}$
Ib	81.8 d, *J* 9	88.3 d, *J* 6	54.4 d, *J* 10	22.0	88.3 d, *J* 6	9.5	
VI	76.5 d, *J* 10	84.6 d, *J* 4	48.1 d, *J* 10	22.5	93.9 d, *J* 4	9.2	135.8 d, $C_{2,6}$ *J* 10 Hz 132.9 s, C_4 130.3 d, $C_{3,5}$
VII	75.2 d, *J* 9	84.6 d, *J* 6	46.8 d, *J* 10	22.3	91.9 d, *J* 4	9.6	134.7, $C_{2,6}$ 133.1, C_1 132.5 C_4 130.8, $C_{3,5}$
Ic	59.1 d, *J* 10	107.9 d, *J* 6		25.2	88.6 d, *J* 6	9.8	
VIII	60.1 d, *J* 10	111.8 d, *J* 6		25.5	90.1 d, *J* 4		158.6, $C_{2,6}$ 140.6, C_4 127.6, $C_{3,5}$
IX	51.8 d, *J* 10	108.2 d, *J* 6		26.6	94.4 d, *J* 4		135.8 d, *J* 10 Hz 133.4 133.0 130.2 d, *J* 10 Hz
X	48.7 d, *J* 10	106.7 d, *J* 6		24.0	90.5 d, *J* 6		132.8, $C_{2,6}$ 130.6 129.5 128.6

[a] In CD_3NO_2 at 22.63 MHz. Shifts in ppm relative to TMS as internal reference, 0 ppm. [b] Coupling constants $J(^{103}Rh-^{13}C)$ in Hz.

sponding triphenylphosphine and triphenylarsine compounds. Substitution of C_5H_5 by C_5Me_5 in 1-methylallyl complexes leads to downfield shifts of C_2 and C_3, but upfield shifts of C_1 and the methyl group.

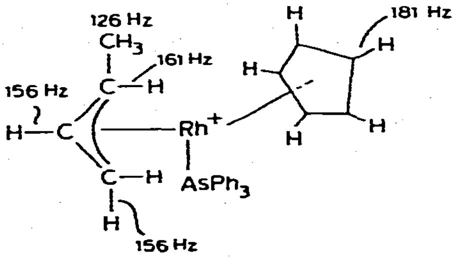
^{103}Rh—^{13}C couplings were observed in all the spectra (Table 3). The ^{103}Rh—C_5R_5 coupling constants are in the range 4—6 Hz, as observed by Lewis and coworkers for compound XI [16]. The coupling constants between ^{103}Rh and the carbon atoms of the η^3-allyl group are 9—12 Hz to C_1 and C_3 and 4—6 Hz to C_2. These values are close to those found in the spectrum of compound XI, where the couplings are 9 and 10 Hz respectively to the two outer, and 7 Hz to the central carbon atom of the η^3-allyl group [16]. These couplings are similar to those observed in the spectra of 1,5-CODRh(C_5H_5) and $(C_2H_4)_2Rh(C_5H_5)$ viz. 14 and 10 Hz respectively to the metal-bonded carbon atoms of the olefinic ligands [17].



(XI)

The resonances of the pyridine ligand are assigned following Bancroft et al. [18] and of the Ph_3P and Ph_3As ligands after Gansow and Kimura [19].

The undecoupled spectrum of compound VII was also run to obtain values for the ^{13}C—^1H coupling constants. These are shown below. They are typical of η^3-allyl and η^5-cyclopentadienyl complexes [12].



Experimental section

All reactions were carried out in an atmosphere of dry oxygen-free nitrogen. The chlorocomplexes Ia, Ib and Ic were prepared by literature methods [1—3].

General method for preparation of the salts II—X

Silver tetrafluoroborate (1 mmol) was added to a solution of the chloro complex (1 mmol) in acetone (20 cm^3) with stirring. After 10 min the precipitated silver chloride was filtered off and a solution of the ligand (1 mmol) in acetone (10 cm^3) added to the filtrate. After 30 min stirring the solution was concentrated by evaporation under reduced pressure and the complex precipitated by addition of diethyl ether (ca. 50 cm^3). The samples were recrystallised by dissolving in acetone, filtering if necessary and precipitating with diethyl ether. Yields were of the order of 70—75%.

^{1}H NMR spectra were measured in CD_2Cl_2 solution at 100 MHz on a Varian HA 100 spectrometer. ^{13}C NMR spectra were obtained at P.C.M.U., Harwell.

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