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SYNTHESIS OF SUBSTITUTED π-CYCLOPENTADIENYL COMPLEXES OF RUTHENIUM, RHODIUM AND IRIDIUM BY A NOVEL REACTION OF INTRAMOLECULAR CONDENSATION OF π-ALLYL LIGAND AND ALKYNE. X-RAY STRUCTURE OF $[\eta\text{-}C_6H_6Ru(\eta\text{-}C_5H_3Ph_2\text{-}1,2)]BF_4$

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Summary

The five-membered carbon ring-forming reaction between π-allyl-π-arene complexes of Ru and π-allyl-π-cyclopentadienyl complexes of Rh and Ir with a series of aryl- and alkyl-substituted alkynes was used to prepare $[\eta\text{-}C_6H_6Ru(\eta\text{-}C_5H_{5\text{-}m\text{-}n}R^1_mR^2_n)]^+$ and $[\eta\text{-}C_5R_5M(\eta\text{-}C_5H_{5\text{-}m\text{-}n}R^1_mR^2_n)]^+$ cations ($R^{1,2}$ = alkyl, aryl; $m = 1, 2$; $n = 1, 2$; M = Rh, Ir; R = H, Me), which were obtained as their BF_4^- or PF_6^- salts in good yields.

The scope of the reaction and the mechanism are discussed. $[\eta\text{-}C_6H_6Ru(\eta\text{-}C_5H_3Ph_2\text{-}1,2)]BF_4$ was characterized by X-ray crystallography.

Introduction

General methods for preparing π-cyclopentadienyls of transition metals include treatment of the transition element compound with alkali metal cyclopentadienide or cyclopentadiene. The use of fulvenes and cyclopentadienones for the formation of π-cyclopentadienyl complexes is of less importance [1]. In all these cases π-cyclopentadienyl complexes are formed from the ready five-membered ring systems.

Moreover, there are several examples of the formation of π-cyclopentadienyl complexes where the five-membered cyclic ligand is constructed in the metal's coordination sphere from fragments, e.g. by the net coupling of two alkyne molecules and a σ-methyl [2] or an alkylidyne [3] ligand, from an alkyne molecule and a σ-bonded substituted vinyl ligand [4], or by cyclic homocondensation of alkyne molecules [5].

No examples of the formation of a π-cyclopentadienyl ligand by combination of two-carbon and three-carbon fragments appear to be known; the closest analogy is the reaction of chlorotrifluoroethylene with π-allyltricarbonylcobalt which affords a cyclopentenyl product [6].

In our study of the reactivity of cationic π-allyl-π-cyclopentadienyl and π-allyl-π-arene complexes of rhodium, iridium and ruthenium, the first example of a π-cyclopentadienyl-forming reaction by (3C + 2C) intramolecular condensation of a π-allyl ligand and an alkyne molecule has been found. Some aspects of this work have been reported in a preliminary form [7–9].

We now wish to report that this reaction is quite general in scope and gives good yields of substituted π-cyclopentadienyl complexes of platinum metals and to describe the molecular structure of one of these complexes.

Results and discussion

Synthesis and structure of [η-C_6H_6Ru(η-$C_5H_3Ph_2$-1,2)]BF_4 *(I)*

Treatment of η-C_3H_5-η-C_6H_6RuCl with silver tetrafluoroborate *, followed by the addition of a 10% excess of tolane in acetone in an inert atmosphere at room temperature, after work-up ** gave a stable, pale yellow, crystalline solid. Since the spectral data for the product could not establish the definite structure, a single crystal X-ray diffraction study was carried out. I was thus characterized as an ionic compound consisting of an [η-C_6H_6Ru(η-$C_5H_3Ph_2$-1,2)]$^+$ complex cation and a tetrahedral BF_4^- anion (mean B–F distance 1.31(2) Å, mean FBF angle 109(2)°). The latter is disordered in the crystal between two orientations differing by a

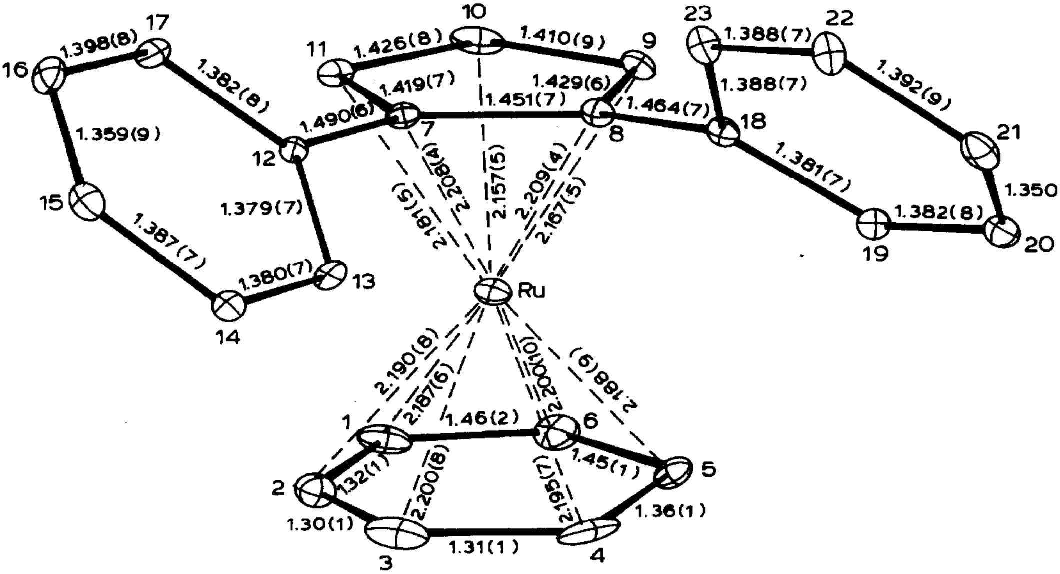

Fig. 1. Molecular structure of [η-C_6H_6Ru(η-$C_5H_3Ph_2$-1,2)]BF_4 (I).

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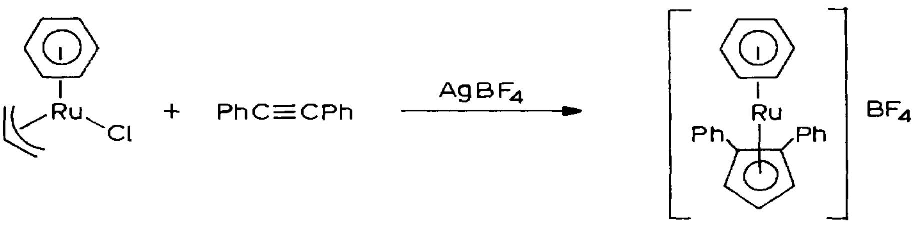
* Treatment of allylic metal chlorides with $AgBF_4$ affords ionic, 16-electron coordinately unsaturated species, in this case [η-C_3H_5Ru(η-C_6H_6)]$^+$.

** Recrystallization of the crude reaction product from acetic acid besides the main product I also yields an insoluble, orange, crystalline solid of stoichiometry $C_{17}H_{18}Ru_2BF_4$. The structure of this by-product is under investigation.

rotation of ca. 60° around the B–F(1) bond, with occupancies of 0.75 (atoms F(2), F(3) and F(4)) and 0.25 (atoms F(2′), F(3′) and F(4′)).

The sandwich cation (see Fig. 1 and bond angles in Table 1) has a non-crystallographic mirror symmetry (except for the phenyl substituents). Both cyclic π-ligands are planar. They are almost parallel to each other (interplanar angle 4.3°). The coordination of the Cp ring with the Ru atom is slightly non-symmetric due to the bulky phenyl substituents; the Ru–C(7) and Ru–C(8) distances (mean 2.209(4) Å) are somewhat longer than the other Ru–C(Cp) distances (mean 2.17(1) Å). To reduce steric hindrance, both phenyl rings are rotated in the same direction (around the C(Cp)–C(Ph) bonds) and their *ipso*-atoms, C(12) and C(18), are bent out of the Cp mean plane by 0.06 and 0.13 Å, respectively, away from the Ru atom. Thus the phenyl ring planes form dihedral angles of 43.9° and 49.6° with the Cp plane. The Ru–C(π-C_6H_6) distances average 2.193(5) Å. The π-benzene ring exhibits strong thermal libration (see thermal parameters in Table 2). Therefore the C–C distances in it vary greatly and are generally shorter (mean 1.37(3) Å) than the usual values in π-arene complexes. The bond distances in cation I are similar to those found in other sandwich π-complexes of ruthenium, viz. ruthenocene [10], η^6-$C_6Me_6Ru(\eta^4$-$C_6Me_6)$ [11] and η-$C_5H_5Ru^+$ (η^6-$C_6H_5\bar{B}Ph_3$) [12]. In the latter structure, the Ru–C(Cp) and Ru–C(Ph) distances average 2.170(6) and 2.195(12) Å, respectively, and the C–C distances in Cp and η^6-$C_6H_5BPh_3$ ligand average 1.397 and 1.408 Å, respectively.

So we have observed a coupling reaction of a π-C_3H_5 ligand with an alkyne molecule to afford a cationic, disubstituted π-cyclopentadienyl derivative of ruthenium:



This result led us to examine the possibility of using this reaction to prepare di-,

(Continued on p. 355)

TABLE 1

BOND ANGLES ω (degrees) OF I

Angle	ω	Angle	ω	Angle	ω
C(2)C(1)C(6)	118.8(9)	C(9)C(8)C(18)	125.3(4)	C(15)C(16)C(17)	120.5(5)
C(1)C(2)C(3)	123.5(8)	C(8)C(9)C(10)	109.3(4)	C(12)C(17)C(16)	120.1(5)
C(2)C(3)C(4)	121.6(8)	C(9)C(10)C(11)	107.9(5)	C(8)C(18)C(19)	121.5(4)
C(3)C(4)C(5)	123.0(8)	C(7)C(11)C(10)	108.3(4)	C(8)C(18)C(23)	120.0(4)
C(4)C(5)C(6)	117.7(8)	C(7)C(12)C(13)	123.1(4)	C(19)C(18)C(23)	118.3(4)
C(1)C(6)C(5)	115.4(9)	C(7)C(12)C(17)	118.4(4)	C(18)C(19)C(20)	120.1(5)
C(8)C(7)C(11)	108.0(4)	C(13)C(12)C(17)	118.5(4)	C(19)C(20)C(21)	121.4(6)
C(8)C(7)C(12)	127.3(4)	C(12)C(13)C(14)	121.5(5)	C(20)C(21)C(22)	120.1(6)
C(11)C(7)C(12)	124.6(4)	C(13)C(14)C(15)	119.4(5)	C(21)C(22)C(23)	118.5(6)
C(7)C(8)C(9)	106.5(4)	C(14)C(15)C(16)	119.9(5)	C(18)C(23)C(22)	121.5(5)
C(7)C(8)C(18)	127.9(4)				

TABLE 2

ATOMIC COORDINATES ($\times 10^4$, for Ru $\times 10^5$) AND ANISOTROPIC THERMAL PARAMETERS $T = \exp[-1/4(B_{11}a^{*2}h^2 + \ldots + 2B_{23}b^*c^*kl)]$ OF I

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru	17847(4)	14245(4)	37582(2)	2.45(2)	5.12(2)	3.29(2)	0.16(1)	−0.15(1)	0.02(1)
C(1)	1552(7)	1443(12)	2612(3)	4.0(3)	17.4(8)	3.3(2)	−0.1(4)	0.1(2)	1.9(4)
C(2)	753(9)	536(8)	2863(4)	7.3(5)	8.9(5)	5.3(3)	1.2(4)	−2.6(3)	−1.8(3)
C(3)	−163(7)	730(8)	3346(4)	4.9(3)	10.0(5)	7.2(4)	−1.6(4)	−2.5(3)	0.2(4)
C(4)	−372(7)	1859(10)	3612(4)	3.3(3)	11.8(6)	6.5(4)	3.0(4)	−0.6(3)	−0.2(4)
C(5)	363(10)	2902(7)	3422(5)	8.6(5)	5.1(3)	9.8(5)	2.4(3)	−4.7(4)	−0.2(3)
C(6)	1395(11)	2739(12)	2881(6)	8.5(6)	12.4(7)	10.9(6)	−6.2(6)	−6.7(5)	8.8(6)
C(7)	3813(4)	717(5)	4054(2)	2.8(2)	4.3(2)	3.5(2)	0.0(2)	−0.6(2)	0.7(2)
C(8)	3643(4)	2000(5)	4323(2)	2.7(2)	4.7(2)	2.8(2)	0.0(2)	−0.2(1)	0.2(2)
C(9)	2512(5)	1962(6)	4794(2)	3.9(2)	6.5(3)	2.8(2)	0.0(2)	0.1(2)	−0.3(2)
C(10)	1993(5)	712(6)	4819(3)	3.4(2)	8.0(3)	3.8(2)	−1.4(2)	−0.1(2)	1.5(2)
C(11)	2799(5)	−62(5)	4363(3)	3.8(2)	5.2(3)	4.4(2)	−0.7(2)	−0.4(2)	1.1(2)
C(12)	4892(4)	249(4)	3569(2)	2.7(2)	3.1(2)	4.2(2)	0.0(1)	−0.6(2)	0.0(2)
C(13)	5296(5)	902(5)	2975(3)	3.7(2)	3.7(2)	4.7(2)	0.3(2)	0.3(2)	0.3(2)
C(14)	6305(5)	443(5)	2540(3)	3.8(2)	5.2(3)	4.9(2)	−0.2(2)	0.1(2)	−0.3(2)
C(15)	6946(5)	−691(6)	2709(3)	3.3(2)	6.2(3)	5.8(3)	0.3(2)	−0.2(2)	−1.7(3)
C(16)	6576(6)	−1338(5)	3299(4)	5.0(3)	4.6(3)	7.1(3)	1.6(2)	−0.6(3)	−0.5(3)
C(17)	5526(5)	−889(5)	3727(3)	4.1(2)	3.9(2)	5.4(3)	0.4(2)	−0.7(2)	0.6(2)
C(18)	4526(5)	3101(4)	4210(2)	3.5(2)	4.2(2)	3.0(2)	0.1(2)	0.0(2)	−0.4(2)
C(19)	4002(6)	4295(5)	4074(3)	5.2(3)	4.8(3)	4.2(2)	0.7(2)	−0.9(2)	−0.3(2)
C(20)	4859(8)	5330(5)	4013(3)	8.7(4)	4.2(3)	4.5(3)	−0.5(3)	−1.0(3)	−0.2(2)
C(21)	6212(8)	5209(6)	4093(3)	7.7(5)	5.5(3)	4.4(3)	−2.3(3)	1.2(3)	−1.1(2)
C(22)	6774(6)	4026(7)	4246(4)	4.0(4)	6.8(3)	7.6(4)	−1.5(3)	1.8(2)	−2.3(3)
C(23)	5917(5)	2981(5)	4296(3)	3.7(2)	4.5(2)	6.1(3)	−0.1(2)	0.4(2)	−1.4(2)
B	532(6)	6971(6)	4036(4)	4.0(3)	4.5(3)	5.9(3)	0.0(2)	0.4(2)	−0.7(3)
F(1)	798(30)	7565(36)	4635(17)	10(1)	12(1)	9.1(6)	−4.3(7)	3.2(6)	−3.7(7)
F(2)	162(14)	7744(7)	3515(5)	26.8(9)	6.6(4)	15.8(7)	2.5(6)	−10.7(7)	1.1(14)
F(3)	1492(11)	6297(14)	3779(5)	10.7(6)	23(1)	11.4(6)	10.0(7)	3.1(4)	−1.2(6)
F(4)	−477(13)	6151(12)	4159(5)	16.2(7)	17.7(8)	13.0(6)	−11.2(6)	6.3(6)	−6.0(6)
F(2′)	1468(18)	7377(18)	3577(18)	9(1)	7.5(8)	6.0(6)	−1.1(8)	5.9(7)	−2.7(6)
F(3′)	613(14)	2632(17)	6116(7)	2.4(5)	8.1(9)	5.9(6)	2.6(5)	0.6(4)	0.0(6)
F(4′)	610(28)	5733(14)	4029(12)	7(1)	1.6(6)	12(1)	1.2(7)	0.8(9)	−0.6(7)

TABLE 3

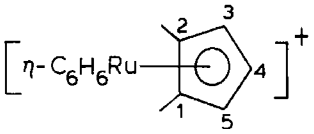
ANALYTICAL DATA FOR THE PRODUCTS ISOLATED

Compound	Yield [a] (%)	M.p. (°C)	Molecular formula	Analyses (Found (calcd.) (%)) C	Analyses (Found (calcd.) (%)) H
$[\eta\text{-}C_6H_6Ru(\eta\text{-}C_5H_3Ph_2\text{-}1,2)]BF_4$ (I)	58.2	235–237	$C_{23}H_{19}RuBF_4$	56.65 (57.17)	3.80 (3.93)
$[\eta\text{-}C_6H_6Ru(\eta\text{-}C_5H_2Ph_3\text{-}1,2,4)]PF_6$ (II)	76.2	240–241	$C_{29}H_{23}RuPF_6$	56.38 (56.41)	4.12 (3.72)
$[\eta\text{-}C_6H_6Ru(\eta\text{-}C_5H_2\text{-}1,2\text{-}Ph_2\text{-}3\text{-}C_6H_4F\text{-}p)]PF_6$ (III)	85.4	266–267	$C_{29}H_{22}RuPF_7$	54.60 (54.81)	3.93 (3.46)
$[\eta\text{-}C_6H_6Ru(\eta\text{-}C_5H_2\text{-}1,2\text{-}Ph_2\text{-}3\text{-}Me)]PF_6$ (IV)	92.3	199–201	$C_{24}H_{21}RuPF_6$	52.07 (51.90)	4.04 (3.78)
$[\eta\text{-}C_3H_5\text{-}\eta\text{-}C_6H_6RuPPh_3)]BF_4\cdot H_2O$ (V)	61.2	229–230	$C_{27}H_{26}RuPBF_4\cdot H_2O$	55.49 (55.21)	4.68 (4.76)
$[\eta\text{-}C_6H_6Ru(\eta\text{-}C_5H_3\text{-}1\text{-}Ph\text{-}2\text{-}Me)]PF_6$ (VI)	33.2 [b]	139–140	$C_{18}H_{17}RuPF_6$	44.66 (45.10)	3.53 (3.54)
$[\eta\text{-}C_6H_6Ru(\eta\text{-}C_5H_3\text{-}1\text{-}Et\text{-}2\text{-}Pr)]PF_6$ (VII)	55.6 [b]	123–125	$C_{16}H_{21}RuPF_6$	41.54 (41.84)	4.60 (4.57)
$[\eta\text{-}C_6H_6Ru(\eta\text{-}C_5H_3\text{-}1\text{-}Ph\text{-}2\text{-}Et)]PF_6$ (VIII)	31.2 [b]	130–131	$C_{19}H_{19}RuPF_6$	46.12 (46.26)	3.71 (3.85)
$[\eta\text{-}C_5H_5Rh(\eta\text{-}C_5H_3Ph_2\text{-}1,2)]BF_4$ (IX)	39.5	215–218	$C_{22}H_{18}RhBF_4$	55.68 (55.97)	3.97 (3.81)
$[\eta\text{-}C_5Me_5Rh(\eta\text{-}C_5H\text{-}1,2\text{-}Ph_2\text{-}3,5\text{-}Me_2)]BF_4$ (X)	67.4	236–237	$C_{29}H_{32}RhBF_4$	60.22 (61.07)	5.45 (5.65)
$[\eta\text{-}C_5Me_5Rh(\eta\text{-}C_5H_2\text{-}1\text{-}Ph\text{-}2,4\text{-}Me_2)]PF_6$ (XI)	55 [c]	212–215	$C_{23}H_{28}RhPF_6$	49.90 (50.03)	5.16 (5.07)
$[\eta\text{-}C_5H_5Ir(\eta\text{-}C_5H_3Ph_2\text{-}1,2)]PF_6\cdot H_2O$ (XII)	60	245–246	$C_{22}H_{18}IrPF_6\cdot H_2O$	41.98 (41.45)	2.81 (2.82)

[a] Yields are of tetrafluoroborate complexes recrystallized from acetic acid, unless otherwise stated. [b] Yields are of analytically pure hexafluorophosphate salts. Yields of crude tetrafluoroborate salts were much higher. [c] Yield is for the tetrafluoroborate analogue purified by recrystallization from a CH_2Cl_2/ether mixture.

TABLE 4

^{1}H NMR SPECTRAL DATA FOR CATIONIC π-BENZENE-π-CYCLOPENTADIENYL COMPLEXES OF RUTHENIUM ^{a}



Complex	Substituted cyclopentadienyl ring			η-C_6H_6 ^{b}	Phenyl protons ^{c}	Other
	H(3)	H(5)	H(4)			
I	5.76 (d,2H)	$J_{34} = J_{45} = 2.5$	5.52 (t,1H)	6.13	7.30–7.50	–
II ^{d}	6.39(s,2H)		–	5.98	7.30–7.80	–
III	–	5.84(s,2H)		6.15	7.45–6.93	–
IV ^{d}	–	5.70(d,1H) ^{e}	5.58(d,1H) ^{e} $J_{45} = 2.5$	6.14	7.60–7.10	2.03 (d, 3H, CH_3)
VI	5.42(dd,1H) ^{e}	5.56(dd,1H) ^{e} $J_{35} = 1,3$	5.28(t,1H) $J_{34} = J_{45} = 2.8$	6.03	7.60–7.26	2.16 (s, 3H, CH_3)
VII ^{f}	5.33(d,2H)		5.21(t,1H)	6.06	–	2.28(t,2H, $\mathit{CH_2}$–CH_2CH_3), 1.47(m,2H, CH_2–$\mathit{CH_2}$–CH_3), 0.95(t,3H, CH_2CH_2–$\mathit{CH_3}$), $J(CH_2–CH_3) = 7.1$, $J(CH_2–CH_2) = 6.8$; 2.35(quartet,2H, $\mathit{CH_2}$–CH_3), 1.13(t,3H, CH_2–$\mathit{CH_3}$), $J(CH_2–CH_3) = 7.6$
VIII	5.48(dd,1H) ^{e} $J_{35} = 1.35$ $J_{34} = 2.69$	5.59(dd,1H) ^{e}	5.39(t,1H) $J_{45} = 2.42$	6.07	7.31–7.43	2.51 (quartet,2H,–$\mathit{CH_2}$–CH_3), 1.11 (t,3H, CH_2–$\mathit{CH_3}$); $J(CH_2–CH_3) = 7.5$
XI ^{g}	–	–	6.24(s,1H)	6.30	7.82–7.28	2.10(s, 3H, CH_3)

[a] Chemical shifts are in ppm in δ-scale; coupling constants are in Hz. The solvent was CD_3CN unless otherwise stated. [b] Resonances are singlets of 6H intensity. [c] All are multiplets. [d] For tetrafluoroborate analogues. [e] The assignment of these protons may be reversed. [f] In $CDCl_3$. [g] XI is $[\eta\text{-}C_6H_6Ru(\eta\text{-}C_5H\text{-}1,2\text{-}Ph_2\text{-}3,5\text{-}Me_2)]BF_4$. The reaction was carried out in acetone-d_6 in a NMR tube.

TABLE 5

^{1}H NMR SPECTRAL DATA FOR RHODIUM COMPLEXES [a]

Compound	Solvent	δ(H)	δ(Me)	δ(Ph)	δ(C_5Me_5)
X	DMSO	5.7 (1H)	1.96 (6H)	7.40–6.90 (10H)	1.84 (15H)
XI	$CDCl_3$	5.40 and 5.64 (each 1H)	2.01 and 2.14 (each 3H)	7.63–7.30	1.83 (15H)

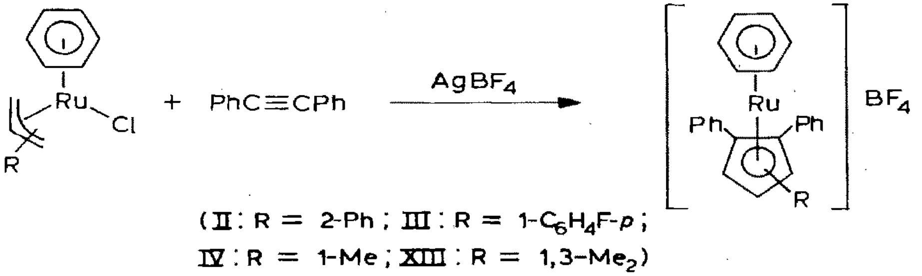
[a] δ in ppm. Resonances are all singlets with the exception of the phenyl multiplets.

tri- and tetra-substituted π-cyclopentadienyl complexes with strictly fixed positions of substituents in the π-cyclopentadienyl ligands. Such five-membered rings might be constructed by introducing appropriate substituents into the π-allyl ligand and by varying the substituents in the alkyne fragment.

The structures * of the products obtained were assigned on the basis of spectroscopic data, particularly ^{1}H NMR spectral data (Tables 4 and 5).

Reactions of mono- and di-substituted allylic complexes of ruthenium with tolane

We found that introduction of alkyl or aryl substituents to different positions of the π-allyl ligand leads to the formation of tri- and tetra-substituted π-cyclopentadienyl complexes of ruthenium (II–IV and XIII):



(II: R = 2-Ph; III: R = 1-C_6H_4F-*p*;
IV: R = 1-Me; XIII: R = 1,3-Me_2)

Under standard conditions (inert atmosphere, acetone, room temperature), the reactions proceed smoothly during a period of 6–8 h and the yields range from 76 to 92%. The products, which are easily purified by recrystallization from acetic acid, are pale yellow, air-stable, crystalline solids. They are soluble in acetone, acetonitrile, dichloromethane but not in methanol, ether or hydrocarbon solvents. Satisfactory carbon and hydrogen elemental analyses were obtained only for hexafluorophosphate salts.

Reactions of $[\eta\text{-}C_3H_5Ru(\eta\text{-}C_6H_6)]BF_4$ with alkynes

The course of the reaction depends markedly on the nature of the acetylenes. The allylic ruthenium complex was treated with a series of alkyl ** and aryl-substituted

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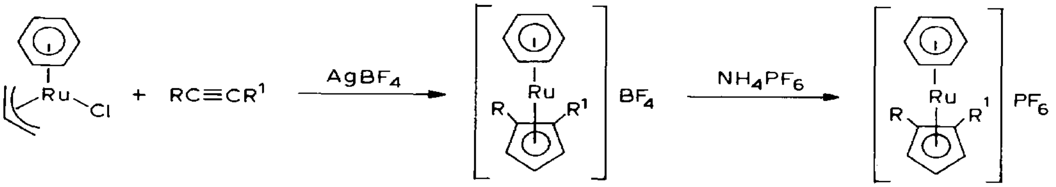
* The complexes reported give satisfactory elemental analyses (Table 3).

** Examination of the reactions of π-allyl complexes of ruthenium, rhodium and osmium with but-2-yne to afford the corresponding cationic 2-5-η-2,3,4,5-tetramethylcyclohexadiene-1-yl-σ-methyl complexes will be published elsewhere.

alkynes to give the expected disubstituted cyclopentadienyl products VI–VIII:



(VI: R = Ph, R^1 = Me ;
VII: R = Et, R^1 = Pr ;
VIII: R = Ph, R^1 = Et)

In all cases the ionic complexes were isolated as their hexafluorophosphate salts. These are white, powdery, stable compounds, obtained in yields up to 59%.

All attempts to prepare cyclic products under our usual conditions by treating the allylic ruthenium chloride complex with ethyne and alkynes bearing electron-withdrawing substituents (acetylenedicarboxylic acid and its dimethyl ether) were unsuccessful. Phenylacetylene also fails to form a π-cyclopentadienyl product when treated with η-C_3H_5-η-C_6H_6RuCl in the presence of $AgBF_4$.

Preparation of polysubstituted dicyclopentadienyl complexes of rhodium

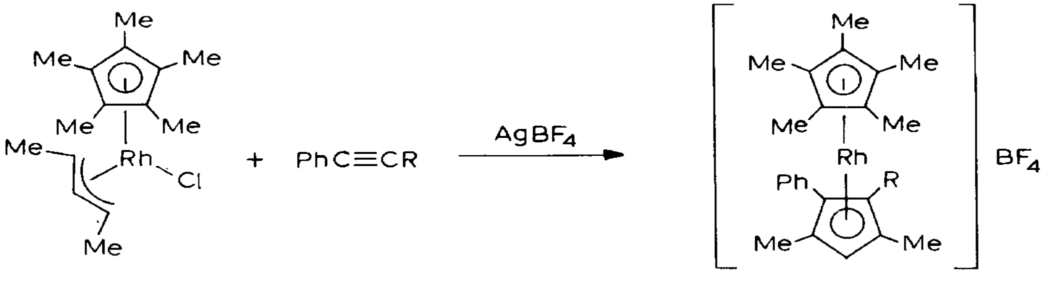
The present reaction was successfully used for the preparation of polysubstituted rhodicenium salts.

Treatment of a solution of η-C_3H_5-η-C_5H_5RhCl in acetone with an excess of $AgBF_4$ resulted in the rapid formation of a precipitate of AgCl and a red solution of [η-C_3H_5Rh(η-C_5H_5)]BF_4. The chloride abstraction reaction was complete in ~ 1 h at room temperature, as monitored by TLC (Silufol, acetone/benzene 1.5/1). On addition of tolane the reaction mixture darkened to a brown-black colour. After 4 h of stirring, tolane was absent in the reaction mixture (Silufol, hexane). After standard work-up a brown oily substance was obtained. This was washed with ethyl acetate and crystallized from acetic acid to give an air-stable, yellow-orange, crystalline solid.

The IR spectrum of the product exhibits a broad, strong band at 1050 cm^{-1} characteristic of BF_4^- anion. The ^{1}H NMR spectrum of the compound (in CD_3CN) contains four sets of signals. The multiplet at δ 7.4 ppm corresponds to the phenyl protons; the resonance at δ 5.9 (d, 5H, $J(^{103}Rh-^1H)$ 0.5 Hz) may be assigned to the protons of the π-C_5H_5 ligand. The substituted cyclopentadienyl ring protons display two resonances in an A_2B pattern complicated by coupling to the ^{103}Rh: $\delta(H_A)$ 6.2 (dd,2H) and $\delta(H_B)$ 6.0 (td,1H), $J(H_AH_B)$ 1.3 Hz; $J(^{103}Rh-H_A) = J(^{103}Rh-H_B)$ 0.5 Hz.

On the basis of the ^{1}H NMR data the product was assigned structure IX. This conclusion was confirmed by the data of the ^{13}C NMR spectrum, which closely resembles that of I [7]. The ^{13}C NMR spectrum (in CD_3CN) exhibits a set of signals corresponding to phenyl carbon atoms in the region of 128.6–130.3 ppm, a resonance due to the π-C_5H_5 ring at δ 88.7 ppm and signals at 84.8, 87.1 and 108.6 ppm, which may be assigned to the C(4), C(3,5) and C(1,2) atoms of the substituted π-cyclopentadienyl ligand, respectively. The coupling constants of carbon atoms with the ^{103}Rh nucleus are in the range of 6.6–8.2 Hz.

By a similar route from η-C_5Me_5-η-1,3-$Me_2C_3H_3RhCl$, the polysubstituted dicyclopentadienylrhodium complexes X and XI were prepared in good yields:



(X: R = Ph,
XI: R = H)

In contrast to the reaction of [η-$C_3H_5Ru(\eta$-$C_6H_6)]BF_4$ with phenylacetylene mentioned above, the η-1,3-dimethylallyl complex of rhodium reacted with this monosubstituted alkyne to give the appropriate rhodicenium cation XI. Purification of the crude reaction product by recrystallization from a CH_2Cl_2/ether mixture much to our surprise gave, besides XI, a small amount of the dinuclear cationic complex $[(\eta\text{-}C_5Me_5)_2Rh_2(\mu\text{-}Cl)_3]BF_4 \cdot 3H_2O$ (red-orange crystals, m.p. 304°C, crystallization from methanol), the molecular structure of which was determined by X-ray crystallography.

Interaction of π-allyl complexes of iridium and osmium with tolane

The π-allyl-π-cyclopentadienyl derivative of iridium reacts with tolane in a similar way to its rhodium analogue.

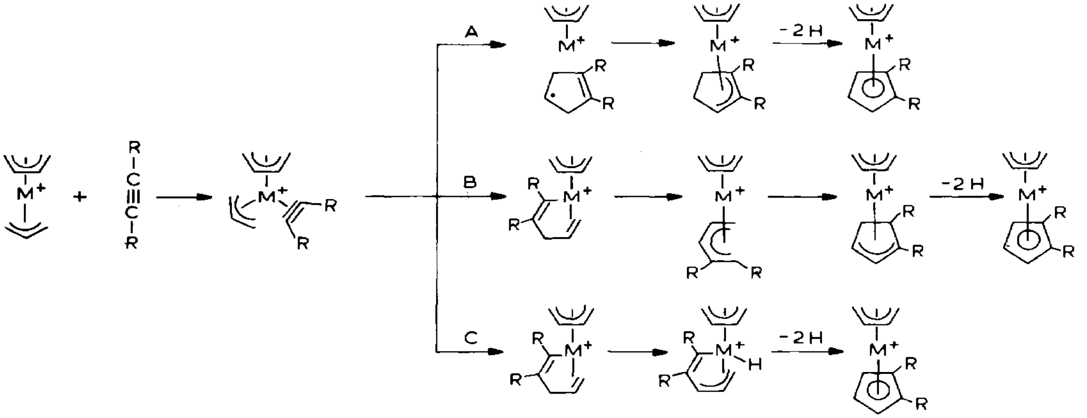
The addition of a two-fold excess of $AgBF_4$ to a stirred solution of η-C_3H_5-η-C_5H_5IrCl in acetone caused slow precipitation of AgCl and formation of $[\eta\text{-}C_3H_5Ir(\eta\text{-}C_5H_5)]BF_4$. After ~ 2 h the formation of the organometallic cation was found (TLC) to be complete and the reaction mixture was treated with tolane. Then the reaction mixture was stirred for 8 h. Standard work-up gave an oily substance which was purified by several precipitations from methanol using ether to give a yellow powder of crude tetrafluorophosphate salt. In order to obtain an analytically pure sample, it was dissolved in boiling water, filtered, and then the filtrate was treated with a small excess of an aqueous solution of NH_4PF_6 to give a white precipitate of $[\eta\text{-}C_5H_5Ir(\eta\text{-}C_5H_3Ph_2\text{-}1,2)]PF_6$ (XII). The ^1H NMR spectrum of XII (in CD_3CN) is essentially the same as that of IX. The set of signals at δ 7.2 ppm corresponds to phenyl protons, the single resonance at δ 5.88 ppm represents the protons of the π-C_5H_5 ligand, and the doublet at δ 6.15 ppm and the triplet at δ 5.94 ppm (J(H–H) 2.5 Hz) are attributed to two types of protons of the substituted cyclopentadienyl ring. The relative intensities of the signals are 10/5/2/1.

The present reaction provides a synthetic approach for the preparation of polysubstituted iridicenium salts.

By contrast to the allylic complexes of ruthenium, rhodium and iridium, no reaction was observed between η-C_3H_5-η-C_6H_6OsCl and tolane under our standard conditions. A mixture of $[\eta\text{-}C_3H_5Os(\eta\text{-}C_6H_6)]BF_4$ and tolane in acetone remained unreacted after 5 days. The ^1H NMR spectrum of the reaction mixture was essentially unchanged; no new peaks were observed and no evidence of the condensation reaction was obtained. The failure of the osmium compound to react is, by itself, surprising.

Mechanism

Scheme 1 shows the probable reaction paths for the formation of a cyclopentadienyl ligand from a π-allyl ligand and an alkyne molecule.



SCHEME 1

Since the initial π-allyl cation is a 16-electron coordinately unsaturated species, the reaction has been suggested to proceed by coordination of the alkyne with the transition metal atom via a π-bond. In order to confirm this suggestion, we examined the electronic spectra of $[\eta\text{-}C_3H_5Ru(\eta\text{-}C_6H_6)]BF_4$ in solvents of different coordinative ability (benzene, ethanol, acetone, dimethyl formamide, CH_3CN and DMSO) in the range from 210 to 500 nm.

The spectrum of an ethanolic solution of the initial organometallic cation (Fig. 2) in the region of *d–d* transitions [13] shows a maximum at 384 nm. As can be seen in Fig. 3, the position of this long-wave band does not essentially change in the spectra of solutions of the cationic complex in benzene, acetone and dimethyl formamide (384–390 nm, $\epsilon \approx 500\text{–}600$).

In DMSO and CH_3CN solutions, the absorption maximum in this region is absent and shoulders at 320–350 nm are observed. Addition of PPh_3 to a solution of π-allyl-π-benzenerutheniumtetrafluoroborate complex in ethanol or acetone causes the same changes in the spectrum (Fig. 2). The resultant spectral pattern is identical to the electronic spectrum of an authentic sample of $[\eta\text{-}C_3H_5\text{-}\eta\text{-}C_6H_6RuPPh_3]BF_4$ (V), in which triphenylphosphine ligand is coordinated to the metal atom. The analogies in the spectral changes indicate that in DMSO and CH_3CN solutions coordination of these solvents to the metal atom also takes place.

These results led us to suggest that (besides acetone) ethanol, benzene and dimethyl formamide would be suitable for the condensation reaction to take place. That the reaction proceeds in DMSO and CH_3CN seems to be unlikely since these solvents form complexes to the metal atom, thus making coordination of the alkyne

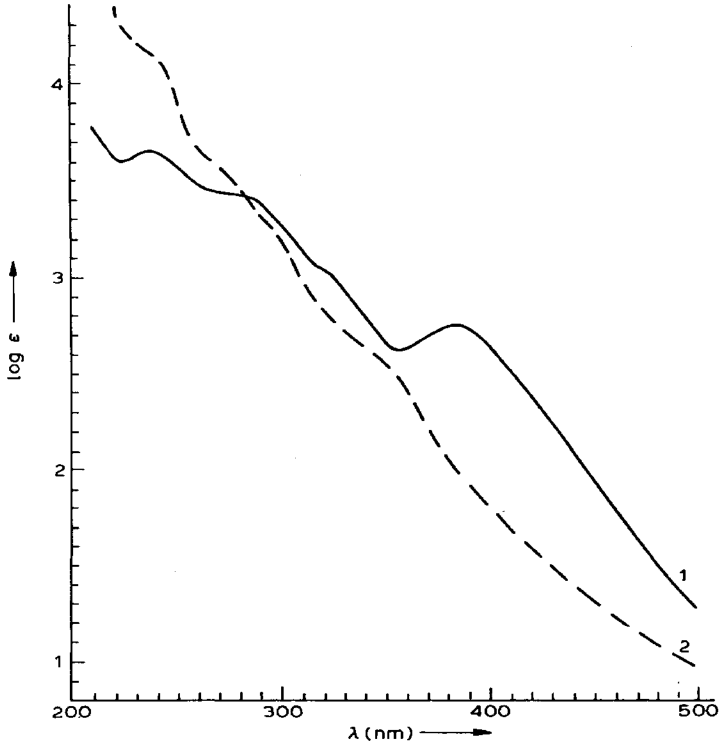


Fig. 2. Electronic spectra of compounds in ethanol: (1) $[\eta\text{-}C_3H_5Ru(\eta\text{-}C_6H_6)]BF_4$ (———) and (2) $[\eta\text{-}C_3H_5\text{-}\eta\text{-}C_6H_6RuPPh_3]BF_4$ (— — —).

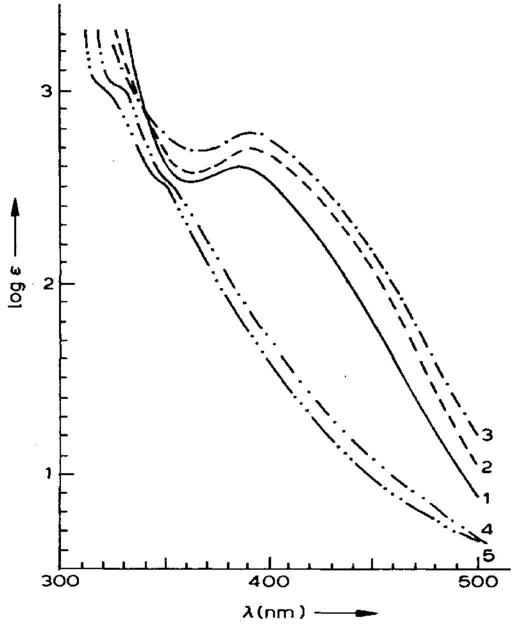


Fig. 3. Electronic spectra of $[\eta\text{-}C_3H_5Ru(\eta\text{-}C_6H_6)]BF_4$: (1) in benzene (———); (2) in acetone (— — —); (3) in dimethyl formamide (–·–·–); (4) in DMSO(–··–); (5) in CD_3CN (–···–).

to the metal atom and the subsequent cyclization process impossible.

^1H NMR monitoring * of the interaction between [η-C_3H_5Ru(η-C_6H_6)]BF_4 and tolane confirms this prediction: I is obtained when the reaction is conducted in ethanol, dimethyl formamide and, as was previously shown, in acetone. In DMSO and CH_3CN the reaction does not occur.

These results clearly point out that the stage of coordination of alkyne to the metal atom plays an essential role in the course of the reaction.

From this point of view, one can readily explain the failure of cyclopentadienyl complexes to form in reactions with acetylenedicarboxylic acid and its dimethyl ether. Due to their weak σ-donor capacity, these alkynes cannot coordinate to the metal atom of the organometallic cation.

Further way of formation of the π-cyclopentadienyl ligand may include the following possible paths (see Scheme 1). Path A: a concerted cycloaddition reaction leads to formation of the π-cyclopentenyl complex, which, after losing two hydrogen atoms, yields the resultant product.

According to path B, the formation of the π-cyclopentadienyl product is thought to proceed in a stepwise manner. Insertion of a coordinated alkyne molecule into a metal–allyl bond yields the postulated δ-pentadienyl species, which may rearrange to the π-pentadienyl system. The latter undergoes a ring-closure reaction affording a five-membered cyclic product.

According to path C, the formation of the π-cyclopentadienyl ligand from the σ-pentadienyl species includes metal-hydride intermediates and the stage of cyclization is regarded as intramolecular insertion of a π-allyl fragment into the metal-carbon σ-bond.

Of the three pathways, we feel path C to be the most plausible since it reflects the essential role of the transition metal in the course of the reaction. In addition, we consider paths A and B to be unlikely possibilities since they include stable intermediates [14] which could be isolated or detected by spectral methods and we obtained no evidence of their formation.

In order to detect possible intermediates of the reaction, we investigated the interaction of [η-C_3H_5Ru(η-C_6H_6)]BF_4 with tolane in the temperature range from −20 to +25°C by means of ^1H NMR spectroscopy. The reaction was carried out in acetone-d_6 in an NMR probe. In the range mentioned, the spectrum of the reaction mixture was acquired at each temperature during 0.5 h ** at 5° steps.

The spectrum of the initial π-allyl cation consists of a single resonance of the π-benzene ring protons at δ 5.98 ppm, doublets at δ 4.78 and δ 1.70 ppm corresponding, respectively, to *syn*- and *anti*-protons of the allylic ligand, and a multiplet at δ 4.6 ppm assigned to the central allylic proton. The intensity ratio of the bands is 6/2/2/1.

The addition of an equimolar *** amount of tolane to the solution of [η-C_3H_5Ru(η-C_6H_6)]BF_4 at −20°C does not lead to changes in the spectrum pattern,

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* The reactions were carried out in deuterated solvents. Since the solubility of [η-C_3H_5Ru(η-C_6H_6)]BF_4 in benzene is too low, ^1H NMR monitoring of the progress of the reaction in this solvent is not possible.

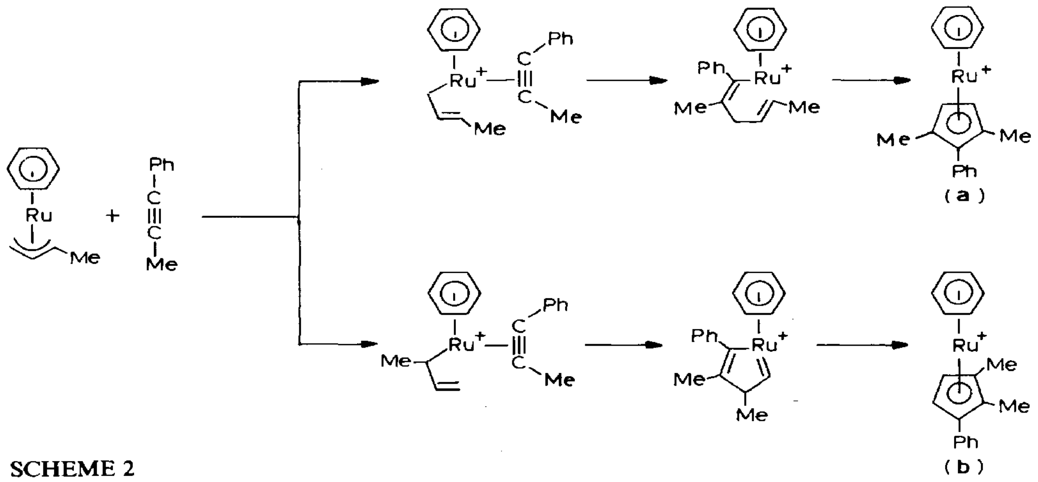
** During acquisition, the spectral pattern was controlled every 5 min.

*** The addition of an excess of tolane to the NMR tube at 25°C causes the reaction to start immediately.

and the spectrum characteristic of the cationic π-allyl-π-benzene complex of ruthenium was observed just up to +25°C. The signals indicative of the formation of the resultant product I appear in the spectrum of the reaction mixture only 0.5 h after the temperature of 25°C was fixed. Moreover, the spectrum also contained resonances corresponding to the initial allylic cation. Any other signals providing evidence for the formation of stable intermediates were not detected.

Now let us consider pathway C in more detail (Scheme 1). The coordination of the alkyne to the transition metal is followed by insertion of an alkyne molecule into the metal–allyl bond. It is conceivable that prior to the intramolecular alkyne insertion, rearrangement of the π-allyl ligand into a σ-allylic transient species occurs as a result of the increasing electron density at the metal atom [15] caused by coordination of the donor alkyne molecule.

Support for the stage of insertion can be obtained from the following experiment. The interaction of the π-crotyl complex of ruthenium with PhC≡CMe, which may result in the formation of two products (a and b, Scheme 2), was examined.



SCHEME 2

Insertion into the allyl–metal bond is known (see, for example, [16]) to be preferential at the unsubstituted end of the unsymmetrical allylic system. With this in mind and on the condition * that insertion of alkyne into the allyl–metal σ-bond occurs as (Me)C=C(Ph)Ru< (a) would be expected to be the predominant product of this reaction. ^{1}H NMR monitoring of the reaction mixture showed the appearance of **a** and **b** in a ratio of 3/2. We consider that this result provides evidence for the suggested stage of insertion. It is notable that if the reaction followed a concerted pathway (path A), equal amounts of both products would be observed.

The stage of formation of metal hydride intermediates and that of intramolecular insertion are the most hypothetical.

In the course of the reaction, two hydrogen atoms are lost from the terminal carbon atoms of the allylic ligand. These hydrogen atoms can be eliminated as gaseous H_2 or they can transfer to the molecule of alkyne or solvent. Examination of

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* The type of insertion postulated is supported by the difference in reactivity of [η-C_3H_5Ru(η-C_6H_6)]BF_4 with PhC≡CPh, PhC≡CMe and, on the other hand, with MeC≡CMe.

the reaction of [η-$C_3H_5Ru(\eta$-$C_6H_6)]BF_4$ with tolane in acetone with the aid of gas chromatography revealed the presence of gaseous H_2 and stilbene in the liquid phase of the reaction mixture. Isopropyl alcohol was not detected. The fact that stilbene (the product of the hydrogen-transfer to the tolane molecule) is formed and the numerous literature reports [17] concerning the ability of platinum metals to transfer H_2 in various hydrogenation processes support the stage of formation of metal hydride intermediates.

The suggested Scheme 1, which is based mainly on literature data, enables us to explain the formation of the final product. However, further work is required to demonstrate the validity of either of these mechanisms.

Conclusion

The coupling reaction of a π-allyl ligand with an alkyne molecule to give a cyclopentadienyl ring is a new type of reaction for π-allyl complexes of the transition elements. It essentially provides a new method of synthesizing a π-cyclopentadienyl ligand.

The reaction proceeds under mild conditions with good yields. It represents a very useful, general synthetic approach to cationic π-arene-π-cyclopentadienyl complexes of Ru and dicyclopentadienyl complexes of Rh and Ir with polysubstituted cyclopentadienyl ligands where the positions of different substituents are strictly fixed. Such complexes would otherwise be inaccessible because the preparation of highly substituted cyclopentadienylmetal complexes has been severely restricted by the difficulty in preparing the corresponding cyclopentadienyl systems.

Experimental

All reactions were carried out under an argon atmosphere. Spectro-quality solvents were used. The starting allylic complexes of ruthenium, rhodium, iridium and osmium [18], and η-1,3-$Me_2C_3H_3$-η-C_5Me_5RhCl [19] were synthesized according to published procedures. $AgBF_4$ was prepared by the method of Meerwein et al. [20]. Bruker WP-200-SY and Bruker WM-250 spectrometers were used for measurement of ^1H NMR spectra. Electronic spectra were recorded on a Specord M40 spectrophotometer.

Preparation of complexes

The following procedure is representative of the syntheses of I–VIII.

To an acetone solution of the corresponding π-allyl-π-arene complex of ruthenium (0.75–3.9 mmol) was added ~ 40–50% excess of silver tetrafluoroborate powder. The resulting suspension was stirred for 1 h. TLC monitoring of the reaction (Silufol, acetone/benzene 1.5/1) showed the disappearance of the starting chloride complex and then the reaction was treated with a 10% excess of the appropriate alkyne (or PPh_3 in the case of formation of V), which caused the colour to change to brown. The reaction mixture was stirred for 6–8 h. Then the reaction mixture was filtered and the solvent was removed in vacuo to leave an oily solid. This was washed with methanol and the solid residue was recrystallized from acetic acid to give pale yellow crystals. These, in the case of II–IV, were converted into the hexafluorophosphate salts.

Compounds VI–VIII were prepared by treating the oily solids dissolved in boiling water directly with an excess of NH_4PF_6.

Analogous to the preceding experiment, the following compounds were prepared: IX (from 0.81 mmol of η-C_3H_5-η-C_5H_5RhCl and 20 mmol of tolane), X (from 1.57 mmol of η-C_5Me_5-η-1,3-$Me_2C_3H_3RhCl$ and 1.74 mmol of tolane), XI (from 1.86 mmol of η-C_5Me_5-η-1,3-$Me_2C_3H_3RhCl$ and 2.05 mmol of phenylacetylene).

The same route was used for the synthesis of XII from 1.2 mmol of η-C_3H_5-η-C_5H_5IrCl and 1.3 mmol of tolane.

Yields and melting points are listed in Table 3. ^{1}H NMR data for V (CD_3CN, δ ppm): 7.72–7.48 (m, 15H, Ph), 5.77 (s, 6H, η-C_6H_6), 4.56 (m, 1H, central allylic proton), 3.57 (d, 2H,H_{syn} of allyl), 1.39 (dd, 2H, H_{anti} of allyl); $J(^1H_{centr.}-^1H_{syn})$ 7 Hz, $J(^{31}P-^1H_{syn}) \leqslant 1$ Hz, $J(^1H_{centr.}-^1H_{anti})$ 11 Hz, $J(^{31}P-^1H_{anti})$ 15 Hz. Electronic spectral data for I (in ethanol): $\lambda_{max} = 237$ nm ($\log \epsilon = 4.5$), 333 nm ($\log \epsilon = 2.7$).

X-ray crystallography. X-Ray single crystal analysis of I was performed with a four-circle Syntex $P2_1$ autodiffractometer (room temperature, graphite monochromated Mo-K_α radiation, $\theta/2\theta$ scan technique, $\theta \leqslant 25°$, 3400 observed reflections with $I \geqslant 2\sigma$). The structure was solved by the heavy atom method and refined by full matrix least-squares to $R = 0.045$ and $R_w = 0.055$, including hydrogen atoms as fixed contributions in the calculated positions with B_{iso} 5.5 Å^2. Atomic coordinates and thermal parameters are listed in Table 2.

Crystal data: monoclinic, at 20°C a 9.867(3), b 10.508(2), c 18.968(5) Å, β 89.96(2)°, V 1967(1) Å^3, $d_{meas.}$ 1.63, $d_{calc.} = 1.64$ g cm^{-3}, $Z = 4$, space group $P2_1/n$.

Acknowledgements

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