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COORDINATIVE UNSATURATION IN π-ALLYLIC BIS(TRIPHENYLPHOSPHINE)RHODIUM(I) COMPLEXES

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Summary

The vacant coordination site in Rh(π-allyl)(PPh_3)$_2$ complexes (π-allyl = C_3H_5, 1-methylallyl, 2-methylallyl) can be occupied by a carbonyl, trifluorophosphine, or dimethylaminodifluorophosphine ligand. Rh(π-C_3H_5)(PPh_3)$_2$-(PF_3) reacts with chloroform to afford *trans*-RhCl(PPh_3)$_2$(PF_3). Hexafluoro-2-butyne inserts into the rhodium—allyl bond of Rh(π-2-methylallyl)(PPh_3)$_2$. Rh(π-C_3H_5)(PPh_3)$_2$ acts as a catalyst for the hydrogenation of 1-octene and cyclohexene.

Results and discussion

Recently [1, 2] we described syntheses of several π-allylic tris(trifluorophosphine)rhodium(I) complexes Rh(π-all)(PF_3)$_3$. The presence of three phosphine ligands in these complexes suggested that the vacant coordination site in the related π-allylic bis(triphenylphosphine)rhodium(I) complexes Rh(π-all)(PPh_3)$_2$ [3] might be readily occupied by suitable fluorophosphine ligands.

This indeed proved to be the case and mixed fluorophosphine-(triphenylphosphine) π-allylic rhodium(I) complexes, Rh(π-all)(PPh_3)$_2$(L), have been synthesised in high yield under mild conditions (eqn. 1 see Table 1). All the

$$\text{Rh}(\pi\text{-all})(\text{PPh}_3)_2 + \text{L} \rightarrow \text{Rh}(\pi\text{-all})(\text{PPh}_3)_2\text{L} \qquad (1)$$

(π-all = C_3H_5, 2-methylallyl, L = PF_3, PF_2NMe_2;
π-all = 1-methylallyl, L = PF_3)

Rh(π-all) (PPh_3)$_2$(L) complexes show enhanced stability in air compared with the starting Rh(π-all)(PPh_3)$_2$ compounds.

Treatment of a solution of Rh(π-2-methylallyl)(PPh_3)$_2$ with carbon monoxide at room temperature immediately leads to the appearance of a carbonyl stretching band at 1940 cm^{-1} in the IR spectrum but a pure π-allylbis-(triphe-

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nylphosphine)carbonyl product could not be isolated*. The analogous compounds Rh(π-all)$(PPh_3)_2$(CO) (π-all = C_3H_5, 1-methylallyl) [ν(CO) 1938 cm^{-1}] have been reported previously by Wilkinson et al. [4], from the reaction between $RhH(PPh_3)_3(CO)$ and allene or butadiene, but no π-allylic compounds were isolated using isoprene or tetramethylallene.

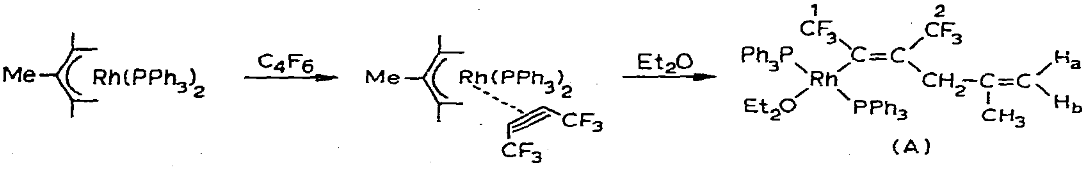
Since Rh(π-all)$(PPh_3)_2$ complexes [made from $RhCl(PPh_3)_3$ and π-allMgBr in ether] often contain a coordinated ether molecule which is rather difficult to remove [3], it would appear that steric difficulties prevent the larger triphenylphosphine occupying the third coordination site in these compounds. The π-allyl bis(triphenylphosphine)rhodium(I) complexes thus contain two electrons less than the number required for the metal to attain the effective number of the next inert gas. There is disagreement about the formulation of the air sensitive Rh(π-C_3H_5)$(CO)_x$ which is variously reported to be a dicarbonyl [5, 6] or a tricarbonyl complex [7]. In analogous π-allylic cobalt(I) complexes a series of Co(π-all)$(CO)_3$ [8—13], Co(π-all)$(PF_3)_3$ [14, 15] and Co(π-all)$(CO)_2(PPh_3)$ [10, 16, 17] compounds are all known, whereas the simple π-allylic triphenylphosphine complexes only contain two phosphine ligands [18—20].

The proton and fluorine NMR spectra of the complexes Rh(π-all)$(PPh_3)_2$L all show the expected features for coordinated π-allylic and fluorophosphine ligands. When a small pressure of PF_3 is introduced above a solution of Rh(π-1-methylallyl)$(PPh_3)_2(PF_3)$ the doublet pattern in the ^{19}F NMR spectrum arising from spin coupling with the rhodium nucleus (^{103}Rh, $I = ½$ 100% natural abundance) collapses to a single line indicated that an intermolecular phosphine exchange process is occurring. We have previously reported similar ligand exchange processes in other rhodium(I)—trifluorophosphine complexes e.g., *trans*-$RhCl(PPh_3)_2(PF_3)$ [21], Rh(π-all)$(PF_3)_3$ [1], and $[RhCl(PF_3)_2]_2$ [22].

When Rh(π-C_3H_5)$(PPh_3)_2(PF_3)$ is dissolved in chloroform there is an immediate reaction and *trans*-$RhCl(PPh_3)_2(PF_3)$ is formed in almost quantitative yield (eqn. 2). Analysis of the volatile products showed the presence of ethylene, propylene and several unidentified chlorinated hydrocarbons, suggesting that the reaction is complex and may involve a free radical process.

$$\text{Rh}(\pi\text{-}C_3H_5)(PPh_3)_2(PF_3) \xrightarrow{CHCl_3} trans\text{-}RhCl(PPh_3)_2(PF_3) \qquad (2)$$

Hexafluoro-2-butyne reacts with Rh(π-2-methylallyl)$(PPh_3)_2$ in benzene at room temperature and extraction of the product with ether affords red crystals of a complex of empirical formula Rh(π-C_4H_7)$(C_4F_6)(PPh_3)_2 \cdot Et_2O$ (A). In view of the availability of a vacant coordination site in the starting π-allylic rhodium complex a likely mechanism would seem to be that given in



(3)

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* We thank H. Hosseini for carrying out this experiment.

eqn. 3. Similar insertion of $CF_3C{\equiv}CCF_3$ into a palladium—allyl bond has been reported recently [23].

The ^1H NMR spectrum clearly shows the presence of the coordinated ether molecule and resonances assignable to the 2-methylallyl fragment [$\tau(H_a)$, $\tau(H_b)$; asymmetric triplet centred at 7.16, $\tau(CH_2)$ 7.38, $\tau(CH_3)$ 9.0]. The ^{19}F NMR spectrum shows two resonances for the non equivalent CF_3 groups [$\phi(CF_{3(1)})$ 52.4 ppm, $\phi(CF_{3(2)})$ 60.3 ppm]. The resonance at highest field occurs as a basic 1/3/3/1 quartet [$J(FF')$ 12 Hz] establishing the *cis*-geometry of the two CF_3 groups about the double bond [24]. The low field resonance is very broad.

Catalytic hydrogenation studies

The existence of a vacant coordination site in $Rh(\pi\text{-all})(PPh_3)_2$ suggested that this type of complex might act as a catalyst for the homogeneous hydrogenation of olefins like the structurally related $RhCl(PPh_3)_3$ [25].

$Rh(\pi\text{-}C_3H_5)(PPh_3)_2$ was found to be an efficient catalyst for the hydrogenation of 1-octene to octane at room temperature and 1 atm. pressure of hydrogen (e.g., 0.108 mol of 1-octene in toluene solution was 96% converted to octane after 10.5 h at 21° in the presence of 0.089 mmol catalyst). No significant isomerisation of the olefin was noted. The catalytic hydrogenation of cyclohexene was somewhat slower. Some darkening of the yellow solution always occurred during the hydrogenation reactions and the exact nature of the active catalyst is uncertain. Since hydrogen uptake occurs in the absence of the olefin, it seems likely that a rhodium hydride is the active catalytic species though the involvement of metallic rhodium cannot be ruled out. In related studies we have shown that $Rh(\pi\text{-}C_3H_5)(PF_3)_3$ reacts readily with hydrogen gas at room temperature to afford $RhH(PF_3)_4$ [26].

Experimental

Reactions were carried out and complexes handled in vacuo or under an atmosphere of dry nitrogen gas. Solvents were dried and freshly distilled before use. $Rh(\pi\text{-}C_3H_5)(PPh_3)_2$ was made from $Rh(\pi\text{-}C_3H_5)_3$ by the method of Powell

TABLE 1

PHYSICAL DATA FOR π-ALLYLICBIS(TRIPHENYLPHOSPHINE)FLUOROPHOSPHINERHODIUM(I) COMPLEXES

Complex	M.p. (°C)	Yield (%)	Analysis found (calcd)(%)		
			C	H	N
$Rh(\pi\text{-}C_3H_5)(PPh_3)_2(PF_3)$	140—150 (slight dec.)	50	61.7 (61.9)	4.6 (4.6)	
$Rh(2\text{-}Me\text{-}\pi\text{-}C_3H_4)(PPh_3)_2(PF_3)$	116—120	93	61.9 (62.3)	4.9 (4.8)	
$Rh(1\text{-}Me\text{-}\pi\text{-}C_3H_4)(PPh_3)_2(PF_3)$	145—155 (slight dec.)	65	62.1 (62.3)	4.9 (4.8)	
$Rh(\pi\text{-}C_3H_5)(PPh_3)_2(PF_2NMe_2)$	120—125	98	63.6 (63.0)	5.7 (6.3)	2.0 (1.8)
$Rh(2\text{-}Me\text{-}\pi\text{-}C_3H_4)(PPh_3)_2(PF_2NMe_2)$	92— 95	83	63.2 (63.4)	5.5 (5.5)	1.9 (1.8)

and Shaw [7], Rh(π-1-methylallyl)(PPh_3)$_2$ from RhH(PPh_3)$_4$ and butadiene [3], and Rh(π-2-methylallyl)(PPh_3)$_2$ from RhCl(PPh_3)$_3$ and 2-methylallyl magnesium bromide [3].

Table 1 reports the physical data for the rhodium complexes prepared.

Reaction between Rh(π-C_3H_5)(PPh_3)$_2$ and trifluorophosphine

A mixture of Rh(π-C_3H_5)(PPh_3)$_2$ (0.372 g, 0.55 mmol), PF_3 (0.0507 g, 0.58 mmol) and toluene (1 ml) was sealed in a sintered ampoule and left at room temperature. After 14h the yellow crystals deposited were filtered and the volatile products removed. The yellow air stable crystalline product was identified as π-allyl(trifluorophosphine)bis(triphenylphosphine)rhodium(I) (0.210 g, 0.28 mmol), m.p., (in vacuo) 140—150° (slight dec.).

NMR spectra: $^1H(\tau)$ H_{anti} 8.20, H_{syn} 7.09, H_c 5.3, $J(H_{syn})(H_c)$ 5.9, $J(H_{anti})(H_c)$ 9.8, $J(PH_c)$ 4.6 Hz. ^{19}F ϕ_F 8.3 ppm (rel. CCl_3F); $^1J(PF)$ 1381, $^2J(RhF)$ 21.5 Hz. (H_c = meso hydrogen).

IR spectrum: 3066m, 3008w, 2970vw, 1482vs, 1436vs, 1311m, 1276w (sh), 1181w, 1158w, 1127w, 1090m, 1070w, 1026w, 997w, 852w(br), 828vs, 808s, 798s, 750m, 742s, 722w, 697vs, 543w, 532w, 510vs cm^{-1} (nujol and hexachlorobutadiene mulls).

A small quantity of an unidentified viscous red oil remained after removal of the volatile products.

Reaction between Rh(1-methyl-π-C_3H_4)(PPh_3)$_2$ and trifluorophosphine

In a similar way, Rh(π-C_4H_7)(PPh_3)$_2$ (0.770 g, 1.13 mmol), PF_3 (0.093 g, 1.06 mmol) and toluene (2 ml) gave after 14h orange crystals of Rh(1-methyl-π-C_3H_4)(PPh_3)$_2$(PF_3) (0.371 g, 0.73 mmol).

NMR spectra: ^{19}F ϕ_F 10.5 ppm (rel. CCl_3F); $^1J(PF)$ 1373, $^2J(RhF)$ 19.0 Hz.

IR spectrum: 3040w, 1580w, 1564w, 1480m, 1434m, 1305w, 1222w, 1180w, 1160w(br), 1087m, 1070w, 1029m, 997w, 966w(br), 877w(br), 855w, 825vs, 806vs, 784s, 696vs, 533m, 512vs, 486w, 444w cm^{-1} (nujol and hexachlorobutadiene mulls).

Reaction between Rh(π-2-methylallyl)(PPh_3)$_2$ and trifluorophosphine

A mixture of Rh(π-2-methylallyl)(PPh_3)$_2$ (0.962 g), trifluorophosphine (0.124 g) and toluene (15 ml) was left to stand at room temperature for 4 h. The solution was concentrated to 5 ml and the resulting yellow crystals were filtered off, washed with hexane and dried. Addition of hexane to the filtrate gave on standing more yellow crystals of the complex Rh(π-2-methylallyl)(PPh_3)$_2$(PF_3) (1.079 g).

NMR spectra: ^1H (τ) CH_3 8.13 [$J(RhH)$ 2 Hz]; H_{anti} 7.86, H_{syn} 6.76.

IR spectrum: 3060m, 3000w, 2910vw, 1482m, 1436s, 1310vw, 1265vw, 1182w, 1158w, 1120vw, 1092m, 1080(sh), 1074(sh), 1028m, 1000w, 970vw, 858vw, 850(sh), 824w, 820s, 800s, 792s, 750m, 742s, 698s, 540m, 510s, 480m cm^{-1} (nujol and hexachlorobutadiene mulls).

Reaction between Rh(π-C_3H_5)(PPh_3)$_2$ and dimethylaminodifluorophosphine

Rh(π-C_3H_5)(PPh_3)$_2$ (0.586 g, 0.87 mmol) and PF_2NMe_2 (0.100 g, 0.88 mmol) were sealed in a sintered ampoule with 15 ml toluene. After 14h at room temperature the yellow crystals of $Rh(\pi\text{-}C_3H_5)(PPh_3)_2(PF_2NMe_2)$ which had formed were filtered off (0.439 g, 0.56 mmol).

NMR spectra: $^{19}F\ \phi_F$ 43.8 ppm (rel. CCl_3F); $^1J(PF)$ 1124 Hz.

IR spectrum: 3068m, 3000w, 2930w, 2886w, 1576m, 1480s, 1434s, 1297m, 1222w, 1190s, 1166w, 1118vw, 1094m, 1089s, 1080m, 1069m, 1026m, 1011m, 993m, 987s, 977s, 972m(sh), 943w, 914w, 894w, 845w, 799w, 766s, 756s, 744s, 706vs, 695vs, 683m(sh), 617w, 564m, 533s, 526s, 504s, 496s, 449m, 430m, 407m cm^{-1} (nujol and hexachlorobutadiene mulls).

Reaction between $Rh(\pi\text{-}2\text{-}methylallyl)(PPh_3)_2$ and dimethylaminodifluorophosphine

PF_2NMe_2 (0.134 g) was sealed with $Rh(\pi\text{-}2\text{-methylallyl})(PPh_3)_2$ (0.822 g) in 10 ml toluene and the mixture shaken at room temperature for 5 h. After removal of the volatile products hexane was added and the resulting oil scratched until the complex $Rh(\pi\text{-}2\text{-methylallyl})(PPh_3)_2(PF_2NMe_2)$ was obtained as a yellow powder (0.884 g).

NMR spectra: ^1H (τ) CH_3 8.07 [$J(RhH)$ 2 Hz], H_{anti} 7.60, H_{syn} 6.60, Me_2NPF_2 7.39.

IR spectrum: 3060w, 1480s, 1434s, 1310vw, 1292w, 1264vw, 1190m, 1155vw, 1120vw, 1090ms, 1030m, 1000vw, 978s, 910vw, 845m, 794vw, 776ms, 760w, 750s, 740s, 700vs, 685s(sh), 538ms, 518vs, 494m cm^{-1} (nujol and hexachlorobutadiene mulls).

Reaction between $Rh(\pi\text{-}C_3H_5)(PPh_3)_2(PF_3)$ and chloroform

A solution of $Rh(\pi\text{-}C_3H_5)(PPh_3)_2(PF_3)$ (0.191 g, 0.25 mmol) in chloroform (0.556 g) was allowed to stand at room temperature for 3 days. The yellow crystals which were deposited (0.181 g, 0.24 mmol) were identified as *trans*-$RhCl(PPh_3)_2(PF_3)$ [13], yield 96%. (Found: C, 57.2; H, 4.1. $C_{36}H_{30}ClF_3P_3Rh$ calcd.: C, 57.58; H, 4.08%). The volatile products were shown to be mainly a mixture of C_2H_4, $CH_3CH{=}CH_2$, a trace of PF_3 and unidentified chlorinated hydrocarbons.

Reaction between $Rh(\pi\text{-}C_4H_7)(PPh_3)_2$ and $CF_3C{\equiv}CCF_3$

A mixture of π-2-methylallylbis(triphenylphosphine)rhodium(I) (0.839 g) and hexafluorobutyne (0.600 g) in 40 ml benzene was shaken in a sealed ampoule for 5 days at room temperature. After removal of the volatile products the residue was extracted with 100 ml of ether, the solution concentrated and placed in the fridge to yield red crystals (0.440 g) of $Rh(C_4H_7C_4F_6)(PPh_3)_2Et_2O$.

(Found: C, 62.6; H, 5.46. $RhP_2F_6OC_{48}H_{47}$ calcd.: C, 62.8; H, 5.13%.)

Catalytic studies

Rigorously anaerobic conditions were used since $Rh(\pi\text{-}C_3H_5)(PPh_3)_2$ was found to catalyse the oxidation of PPh_3 to $OPPh_3$. The reaction vessel was fitted with an efficient magnetic stirrer and condenser system to minimise loss of volatile components in the hydrogen flow. The complex, olefin and solvent were stirred and allowed to equilibrate before hydrogen was bubbled into the solution via a sintered tube and the rate regulated by a needle valve. Samples were withdrawn via a serum cap using a microsyringe and analysed by GLC using nitrogen as carrier gas and a column 9′ × ½″ containing 4% carbowax + 2% KOH on 100—120 mesh Chromosorb G at 50°. The results are listed below:

(a). Hydrogenation of 1-octene. Using 0.055 g $Rh(\pi\text{-}C_3H_5)(PPh_3)_2$; 12.15 g 1-octene and 18 ml toluene:

Time (hours), % octane: 0.50, 16.5; 1.00, 23.2; 1.75, 27.5; 2.50, 34.6; 3.50, 36.8; 4.50, 53.0; 5.50, 60.7; 6.50, 71.4; 7.50, 76.0; 8.50, 89.6; 9.50, 89.9; 10.50, 96.0.

(b) Hydrogenation of cyclohexene. Using 0.036 g $Rh(\pi\text{-}C_3H_5)(PPh_3)_2$, 17.8 g cyclohexene and 18 ml toluene:

Time (hours), % cyclohexene; 1.25, trace; 2.0, 0.85; 3.0, 1.99; 4.0, 3.5; 5.0, 7.0; 6.0, 15.5; 7.0, 17.9; 7.75, 20.9; 9.5, 26.3.

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