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SOME 2,7-DIMETHYLOCTA-2,6-DIENE-1,8-DIYLRUTHENIUM PHOSPHINE, FLUOROPHOSPHINE AND CARBONYL COMPLEXES

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Summary

Dichloro(2,7-dimethylocta-2,6-diene-1,8-diyl)ruthenium(IV), $[RuCl_2C_{10}H_{16}]_2$, reacts with carbon monoxide or phosphines to afford air stable complexes of the type $RuCl_2C_{10}H_{16}\cdot L$ [L = CO, PF_3, PPh_3, Me_2NPF_2, CF_3PCl_2, and $P(OCH_2)_3CPh$]. The ^1H and ^{19}F NMR spectra of these compounds are presented and discussed. In $RuCl_2C_{10}H_{16}(Me_2NPF_2)$ the two fluorine atoms are magnetically non-equivalent. $RuCl_2C_{10}H_{16}\cdot PF_3$ reacts with excess PF_3, and subsequent addition of PPh_3 affords the ruthenium(II) complex *cis*-$RuCl_2(PF_3)_2(PPh_3)_2$.

Introduction

Several π-allylic complexes of ruthenium have been described in the literature [1—6]. Butadiene [1, 2] and isoprene [3] react with ruthenium trichloride to afford dichloro(dodeca-2,6,10-triene-1,12-diyl)ruthenium(IV), I, and dichloro(2,7-dimethylocta-2,6-diene-1,8-diyl)ruthenium(IV), II, respectively. An X-ray study of II has established that it is dimeric with two chlorine bridges between the ruthenium atoms.

Results and discussion

We find that II readily reacts at room temperature with carbon monoxide and tertiary phosphines to afford air stable complexes of the type $RuCl_2C_{10}H_{16}\cdot L$, III, [L = CO, PF_3, PPh_3, Me_2NPF_2, CF_3PCl_2, $P(OCH_2)_3CPh$] (Table 1). In the case of the triphenylphosphine complex the reaction product obtained from a $CHCl_3$/hexane mixture crystallises with one molecule of chloroform solvate.

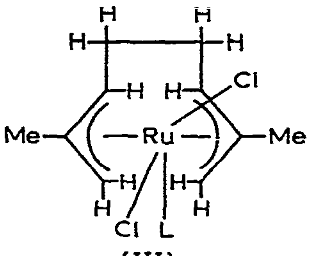
The complexes III (L = PF_3, Me_2NPF_2), are particularly interesting in that they represent the first examples of fluorophosphine complexes of a transition metal in an unusually high oxidation state (in this case formally Ru^{IV}). Normally fluorophosphines and particularly PF_3 tend to stabilise low oxidation

TABLE 1

ANALYTICAL DATA AND OTHER PHYSICAL PROPERTIES FOR SOME DICHLORO(2,7-DIMETHYLOCTA-2,6-DIENE-1,8-DIYL)RUTHENIUM COMPLEXES

Compound	Colour	Yield (%)	M.p. (°C)	Analysis found (calcd.) (%)		
				C	H	Cl
$RuCl_2(C_{10}H_{16})CO^a$	Yellow-orange	54	>130 (dec)	39.5 (39.3)	4.9 (4.8)	
$RuCl_2(C_{10}H_{16})CF_3PCl_2$	Orange-brown	76	92–98	28.2 (27.6)	3.3 (3.4)	
$RuCl_2(C_{10}H_{16})P(OCH_2)_3CPh$	Yellow	71	>210 (dec)	46.4 (46.3)	5.4 (5.25)	
$RuCl_2(C_{10}H_{16})PF_3$	Orange	65	130–131 (dec)	30.3 (30.3)	4.1 (4.1)	18.25 (17.9)
$RuCl_2(C_{10}H_{16})PPh_3 \cdot CHCl_3$	Orange-brown	67	108–110	50.85 (50.5)	4.8 (4.7)	26.4 (25.7)
$RuCl_2(C_{10}H_{16})PF_2NMe_2{}^b$	Yellow	100	90 (dec)	34.2 (34.2)	5.3 (5.3)	15.6 (16.8)

[a] ν (CO) 2062 cm^{-1}. [b] N, analysis 3.3 (3.3) %.



(III)

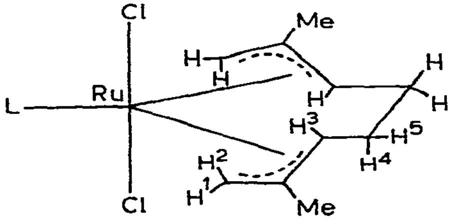
states of transition metals [7—9]. An X-ray study of III (L = PF_3) is currently underway.

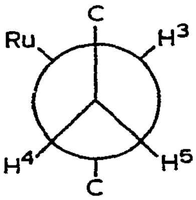
The carbonyl complex III (L = CO) [ν(CO) 2062 cm^{-1}], has been mentioned previously by Porri et al. [3] without experimental or analytical details. We find its ^1H NMR spectrum (vide infra) differs from that previously published [3], but is very similar to those of the analogous phosphine complexes reported here. The carbonyl complex reacts with PF_3 in CH_2Cl_2 at 60° to afford III (L = PF_3), together with other unidentified products.

III (L = PF_3) reacts further with an excess of PF_3 at 60° and treatment of the product with Ph_3P affords pale yellow crystals of the ruthenium(II) complex $RuCl_2(PF_3)_2(PPh_3)_2$ (IV).

Nuclear magnetic resonance spectra

The proton NMR spectra of the complexes which are shown in Fig. 1 all exhibit a resonance of relative intensity 3 for the methyl group and five equally intense resonances attributable to the five types of protons of the 2,7-dimethylocta-2,6-diene-1,8-diyl ligand (Table 2). This implies that there is either a C_2 rotation axis or a plane of symmetry and the non equivalence of protons H^4 and H^5 is presumably a consequence of the presence of the adjacent asymmetric carbon (attached to H^3) viz:





$H^5 \neq H^4$

The complexes III [L = Me_2NPF_2, PPh_3, $P(OCH_2)_3CPh$] show additional lines

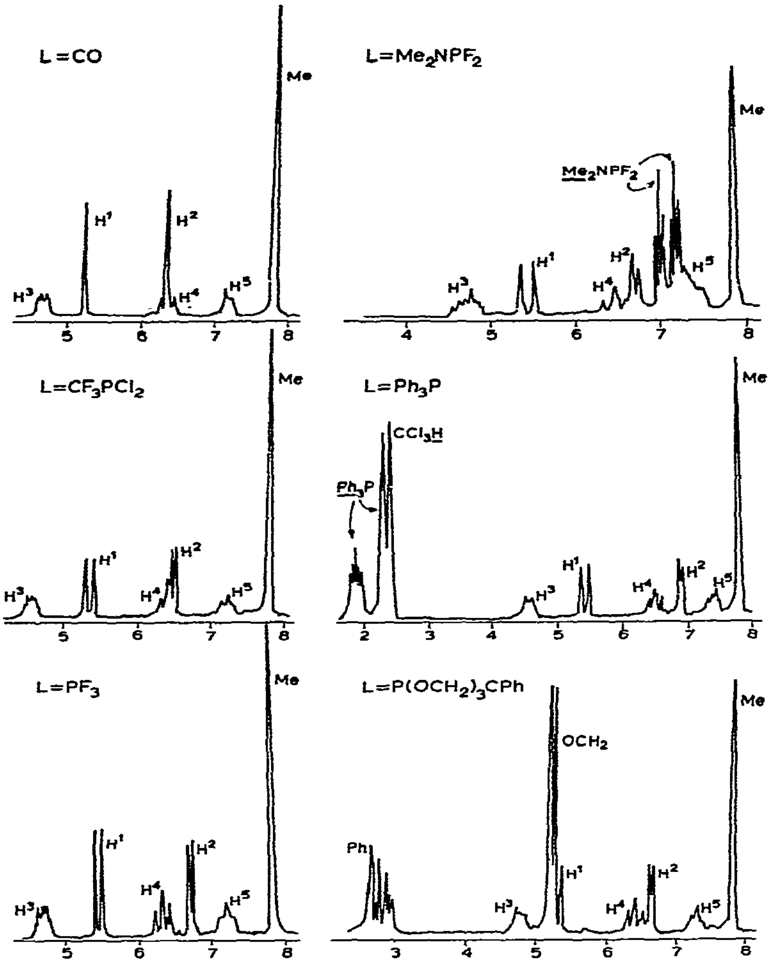


Fig. 1. 100 MHz ^{1}H NMR spectra of $RuCl_2(C_{10}H_{16})L$.

TABLE 2

^{1}H NMR DATA FOR $RuCl_2(C_{10}H_{16})$ L COMPLEXES[a]

L	$\tau(H^1)$	$\tau(H^2)$	$\tau(H^3)$	$\tau(H^4)$	$\tau(H^5)$	$\tau(CH_3)$	$J(PH^1)$ (Hz)	$J(PH^2)$ (Hz)	$J(PCH_3)$ (Hz)
CO	5.20s	6.35s	4.62m	6.35m	7.20m	7.78s			
PF_3[b]	5.34d	6.69d	4.56m	6.27m	7.16m	7.79d	9.8	4.8	1.5
CF_3PCl_2[c]	5.33d	6.48d	4.50m	6.40m	7.20m	7.78d	11.5	5.2	1.5
PPh_3	5.55d	6.92d	4.74m	6.55m	7.37m	7.73s	9.5	3.5	
Me_2NPF_2	5.35d	6.63d	4.64m	6.50m	b.m.	7.77d	9.6	4.8	1.2
$P(OCH_2)_3CPh$	5.28d	6.63d	4.72m	6.40m	7.25m	7.79d	9.0	4.0	<1

[a] s singlet, d doublet, t triplet, m multiplet, b broad. [b] $\phi(F) = +22.0$ ppm (rel. CCl_3F); $^1J(PF) = 1374$ Hz. [c] $\phi(F) = +66.8$ ppm (rel. CCl_3F); $^2J(PF) = 77$ Hz.

in the ^{1}H NMR spectra from protons present in the phosphine ligands. The resonances of the H^1, H^2, and CH$_3$ protons for all the phosphine complexes, but not the carbonyl compound, appear as 1/1 doublets, clearly arising from spin-coupling with the phosphorus nucleus. Unlike the ^{1}H NMR spectrum of $(RuCl_2C_{10}H_{16})_2$ itself which shows a pronounced temperature dependence [10] the spectra of the carbonyl and phosphine complexes are not significantly affected either by temperature changes or by the addition of free phosphine ligand.

Fluorine NMR spectra

The ^{19}F NMR spectrum of III (L = PF_3) shows the expected simple 1/1 doublet pattern [^1J(PF) 1374 Hz], centred at 22.0 ppm to high field of CCl_3F, which is characteristic of a single PF_3 molecule coordinated to a transition metal [7]. The addition of free PF_3 has no effect on the appearance of the NMR spectra, indicating that in contrast to π-allyl rhodium trifluorophosphine complexes no ready intermolecular exchange is occurring [11].

The ^{19}F NMR spectrum of III (L = Me_2NPF_2) on the other hand, exhibits eight lines of equal intensity indicating that the two fluorine atoms of the Me_2NPF_2 ligand are magnetically non equivalent and have different chemical shifts (Table 3).

A similar non equivalence of the fluorine atoms was reported recently by King et al. [12] for a number of PF_2NR_2 substituted cyclopentadienyl metal carbonyl complexes. These authors attributed the non equivalence of the two fluorines to restricted rotation around the transition metal phosphorus bond, although in their complexes non equivalence could arise simply because the phosphine is bonded to the metal atom which is in an asymmetric environment. In such a case the fluorine atoms would remain magnetically inequivalent even if there was rapid rotation about the metal—phosphorus bond.

In the case of the complex III (L = Me_2NPF_2), there is either a C_2 axis or a plane of symmetry in the molecule and the magnetically inequivalent fluorine atoms presumably does reflect lack of free rotation about the phosphorus—ruthenium bond.

A variable temperature ^{19}F NMR study on III (L = Me_2NPF_2) shows that as the temperature is raised the chemical shift difference [$\phi(F^2)-\phi(F^1) = \Delta\phi(F)$] and the fluorine—fluorine coupling constant $^2J_{F_1F_2}$ both steadily decrease in magnitude (Table 3 and Fig. 2).

The ^{19}F NMR spectrum of $RuCl_2(PF_3)_2(PPh_3)_2$, IV, exhibits the typical

TABLE 3

VARIABLE TEMPERATURE ^{19}F NMR DATA FOR $RuCl_2(C_{10}H_{16})(Me_2NPF_2)$ (IN *sym*-$C_2H_2Cl_4$)

Temp. (°C)	$^1J(PF^1)^a$	$^1J(PF^2)^a$	$^2J(F^1F^2)^a$	$\phi(F^1)^b$	$\phi(F^2)^b$	$\Delta\phi(F)^c$
−10	1206	1181	14	42.0	45.6	3.6
25	1211	1194	12	42.8	44.6	1.8
50	1219	1201	11	43.2	44.3	1.1
70	1220	1206	10	43.4	44.2	0.8

^{a} In Hz. ^{b} In ppm rel. $CFCl_3$. ^{c} Chemical shift difference $\phi(F^2)-\phi(F^1)$.

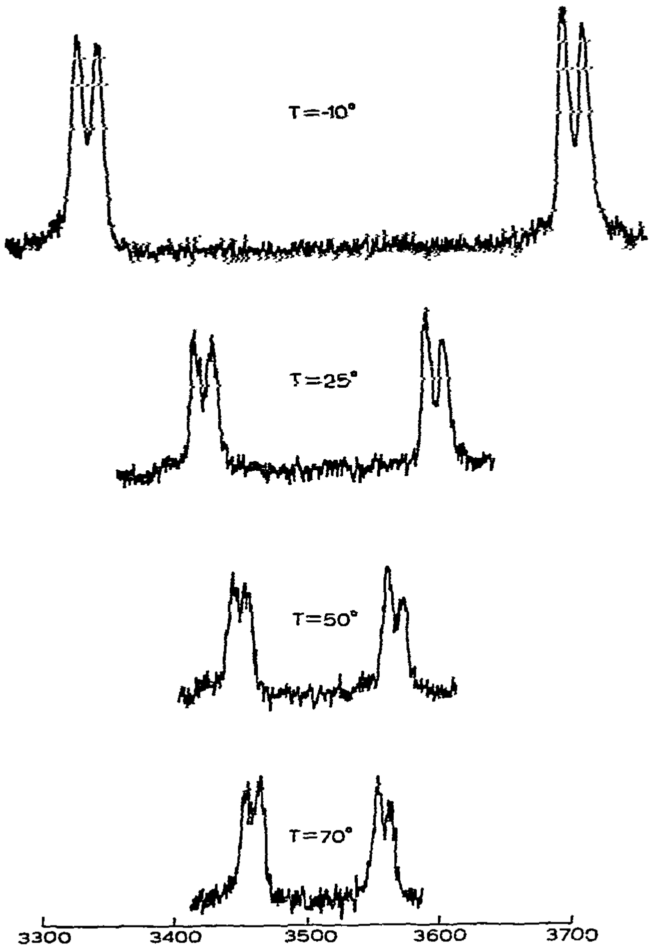
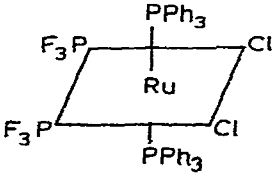
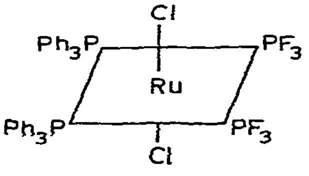


Fig. 2. Low field half 94.1 MHz ^{19}F spectra of RuCl$_2$(C$_{10}$H$_{16}$)Me$_2$NPF$_2$ at various temperatures (Figures are in Hz to high field of CCl$_3$F). An identical pattern is observed at higher field.

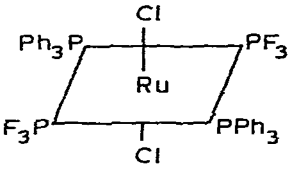
pattern expected for an $[X_3A]_2$ spin system [7] (X = fluorine, A = phosphorus). The magnetic equivalence of the PF$_3$ groups is consistent with the stereochemistry being IVa, IVb, or IVc, but by analogy with RuH$_2$(PF$_3$)$_2$(PPh$_3$)$_2$ which is



(IVa)



(IVb)



(IVc)

known to have a *cis*-dihydrido configuration [14] we assign structure IVa.

Experimental

$(RuCl_2C_{10}H_{16})_2$ was prepared by the published method [3]. It was found to be pinkish-purple, rather than red-brown as previously reported. Me_2NPF_2 was prepared as described elsewhere [7] and CF_3PCl_2 by treating CF_3PI_2 with $HgCl_2$. The preparation of $P(OCH_2)_3CPh$ is described elsewhere [13]. ^1H and ^{19}F NMR spectra were recorded on a Varian HA 100 NMR spectrometer operating at 100 MHz and 94.1 MHz respectively.

Dichloro(2,7-dimethylocta-2,6-diene-1,8-diyl)carbonylruthenium

$(RuCl_2C_{10}H_{16})_2$ (0.530 g) was dissolved in 20 ml methylene chloride and carbon monoxide bubbled through the solution for 90 min. The light-orange solution was evaporated to dryness and the product (0.311 g) crystallised from chloroform/hexane at -20°.

Dichloro(2,7-dimethylocta-2,6-diene-1,8-diyl)trifluorophosphineruthenium

$(RuCl_2C_{10}H_{16})_2$ (0.546 g) and trifluorophosphine (0.287 g) were sealed off together with 10 ml of methylene chloride. After a few minutes at room temperature the deep-purple solution became light-orange yellow. After removal of PF_3 (0.124 g) and solvent, the orange solid residue was crystallised from chloroform/hexane to give the product (0.453 g) as well formed orange crystals.

Reaction of $RuCl_2C_{10}H_{16}\cdot CO$ with trifluorophosphine

$RuCl_2C_{10}H_{16}\cdot CO$ (0.182 g) and trifluorophosphine (0.6889 g) were sealed off with 5 ml CH_2Cl_2 and heated at 60° overnight. After removal of the volatiles the orange oily residue was dissolved in chloroform/hexane added and the sample placed in the freezer. A few orange crystals separated and were identified as $RuCl_2C_{10}H_{16}\cdot PF_3$. The remaining yellow oil showed IR bands in the carbonyl stretching region at 2080m, 2020vs and 1972s(sh) cm^{-1} and very strong P—F stretching frequencies.

Dichloro(2,7-dimethylocta-2,6-diene-1,8-diyl)trifluoromethyldichlorophosphineruthenium

$[RuCl_2C_{10}H_{16}]_2$ (0.152 g) and trifluoromethyldichlorophosphine (0.086 g) were sealed off with methylene chloride (5 ml). An orange solution formed after a few minutes at room temperature and after removal of the volatile products under vacuum the product (0.18 g) remained as an orange oil which solidified on standing in the refrigerator.

Dichloro(2,7-dimethylocta-2,6-diene-1,8-diyl)triphenylphosphineruthenium-(chloroform solvate)

$[RuCl_2C_{10}H_{16}]_2$ (0.305 g) and triphenylphosphine (0.272 g) were dissolved in 10 ml CH_2Cl_2 under dry nitrogen to give a brown solution. After 2 h at room temperature the solvent was removed under vacuum and the brown residue crystallised from chloroform/hexane to yield orange-brown crystals (0.465 g).

Dichloro(2,7-dimethylocta-2,6-diene-1,8-diyl)4-phenyl-2,6,7-trioxa-1-phosphabicyclo(2,2,2)octaneruthenium

$[RuCl_2C_{10}H_{16}]_2$ (0.323 g) and $P(OCH_2)_3CPh$ (0.236 g) in 10 ml CH_2Cl_2

were stirred at room temperature for 1 h. The solution became yellow orange immediately. After removal of solvent under vacuum the residue was recrystallised from $CHCl_3$/hexane to yield the yellow solid complex (0.384 g).

Dichlorobis(trifluorophosphine)bis(triphenylphosphine)ruthenium(II)
$[RuCl_2C_{10}H_{16}]_2$ (0.494 g), trifluorophosphine (0.612 g), and methylene chloride (10 ml) were sealed off together in a glass ampoule, and the mixture warmed from -196° to room temperature. The colour of the solution changed from deep-red to orange indicating formation of $RuCl_2C_{10}H_{16}\cdot PF_3$. The ampoule was then heated at 60° for 18 h and the solution became deep-red. After removal of excess PF_3 and solvent the resulting deep-red oil was refluxed for 2 h with a solution of triphenylphosphine (0.857 g) in methylene chloride (30 ml). The orange solution was filtered, solvent removed and the oily product washed with a large volume of hexane and four 20 ml portions of methanol. The pale-yellow crystalline solid product (0.386 g, 27%), m.p. 191-193° (dec), was recrystallised from methylene chloride/methanol (Found: C, 49.6; H, 3.7; Cl, 8.1. $C_{36}H_{30}Cl_2F_6P_4Ru$ calcd.: C, 49.5; H, 3.4; Cl, 8.0%.)

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