Heteronuclear and heterovalent diphenylphosphido-bridged complexes of rhodium, iridium and ruthenium. Crystal structure of [(C$_5$Me$_5$)ClRh(μ-Cl)(μ-PPh$_2$)Rh(COD)] · $\frac{1}{2}$Et$_2$O (COD = 1,5-cyclooctadiene)

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Abstract

Mononuclear complexes of formulae [LMCl$_2$(HPRR′)], [LMCl(HPR$_2$)$_2$]BF$_4$ and [LM(acac)-(HPR$_2$)]BF$_4$ (M = Rh, Ir; L = C$_5$Me$_5$. M = Ru; L = *p*-Cymene; R = Ph, H; R′ = H; Hacac = acetylacetone, but not in all possible combinations) have been prepared from the corresponding [{LMCl}$_2$(μ-Cl)$_2$] or [LMCl(acac)] and HPRR′. Complexes [LMCl$_2$(HPPh$_2$)] [L = C$_5$Me$_5$; M = Rh (I), Ir (IV), L = *p*-Cymene; M = Ru (VII)] react with [M′(μ-OMe)(diolefin)]$_2$ (M′ = Rh; diolefin = tetrafluorobenzobarrelene (TFB), 1,5-cyclooctadiene (COD). M′ = Ir; diolefin = COD) to yield diphenyl-phosphido-bridged complexes of formula [LMCl$_2$(μ-PPh$_2$)M′(diolefin)]. The structure of [(C$_5$Me$_5$)ClRh-(μ-Cl)(μ-PPh$_2$)Rh(COD)]·$\frac{1}{2}$Et$_2$O has been determined by X-ray diffraction methods. The complex consists of two moieties, (C$_5$Me$_5$)RhCl and Rh(COD), doubly-bridged by a diphenylphosphido group and a chlorine atom. The two rhodium atoms are separated by 3.3657(6) Å.

Introduction

Although a variety of dinuclear diphenylphosphido-bridged rhodium(I) complexes are known [1–4], phosphido-bridged rhodium(III) complexes are very scarce [5,6], and as far as we know no heterovalent Rh(III)–Rh(I) phosphido-bridged complexes have been described previously. Furthermore, no (C$_5$Me$_5$)Ir(III) nor (*p*-Cymene)Ru(II) phosphido complexes have been reported so far. On the other hand, we have prepared a variety of di- or tetranuclear, homo- or heterometallic, homo- or heterovalent compounds by treating complexes containing ligands having acidic N–H protons with acetylacetonate or methoxide complexes [7–11]. In this paper we describe extension of our work to diphenylphosphido-bridged complexes. First, we describe the preparation of various types of mononuclear rhodium(III), iridium(III) or ruthenium(II) complexes containing primary or secondary phosphine

Table 1

Analytical results, molar conductivities, yields, colour and IR ^{a} data for the mononuclear complexes

Complex	Analysis (found (calcd.) (%))		λM (ohm^{-1} cm^2 mol^{-1})	Yield (%)	Colour	ν(P–H) (cm^{-1})	ν(M–Cl) (cm^{-1})
	C	H					
[(C$_5$Me$_5$)RhCl$_2$(HPPh$_2$)] (I)	53.4 (53.3)	5.6 (5.3)	–	92	red	–	260
[(C$_5$Me$_5$)RhCl$_2$(HPCy$_2$)] (II)	50.9 (52.1)	7.6 (7.5)	–	83	red	–	270
[(C$_5$Me$_5$)RhCl$_2$(H$_2$PPh)] (III)	44.8 (45.8)	5.2 (5.3)	–	78	reddish-orange	2395, 2335	275, 260
[(C$_5$Me$_5$)IrCl$_2$(HPPh$_2$)] (IV)	45.1 (45.2)	5.1 (5.4)	–	89	yellow	–	285, 255
[(C$_5$Me$_5$)IrCl$_2$(HPCy$_2$)] (V)	43.5 (44.3)	6.7 (6.4)	–	87	orange	–	300, 270
[(C$_5$Me$_5$)IrCl$_2$(H$_2$PPh)] (VI)	37.5 (37.8)	4.4 (4.4)	–	84	yellow	2390, 2350	290, 265
[(p-Cymene)RuCl$_2$(HPPh$_2$)] (VII)	53.2 (53.7)	5.3 (5.1)	–	95	reddish-orange	–	290
[(p-Cymene)RuCl$_2$(HPCy$_2$)] (VIII)	51.2 (52.4)	7.7 (7.4)	–	89	orange	2340, 2310	290
[(p-Cymene)RuCl$_2$(H$_2$PPh)] (IX)	45.9 (46.2)	5.2 (5.1)	–	91	orange	2380, 2360	290

| Compound	C%	H%			Color		
[(C₅Me₅)RhCl(HPPh₂)₂]BF₄ (X)	55.9 (55.7)	4.6 (5.1)	145	93	yellow	–	280
[(C₅Me₅)RhCl(HPCy₂)₂]BF₄ (XI)	54.2 (53.9)	8.1 (8.1)	140	80	yellow	2330	285
[(C₅Me₅)IrCl(HPPh₂)₂]BF₄ (XII)	49.1 (49.7)	4.7 (4.5)	151	84	yellow	–	300
[(C₅Me₅)IrCl(HPCy₂)₂]BF₄ (XIII)	48.3 (48.2)	7.6 (7.3)	142	74	yellow	2340	280
[(C₅Me₅)Rh(acac)(HPPh₂)]BF₄ (XIV)	53.4 (53.1)	5.4 (5.4)	145	83	yellow	–	–
[(C₅Me₅)Rh(acac)(HPCy₂)]BF₄ (XV)	51.8 (52.2)	7.7 (7.1)	148	71	yellow	2330	–
[(C₅Me₅)Ir(acac)(HPPh₂)]BF₄ (XVI)	46.9 (46.3)	4.9 (4.7)	154	86	yellow	–	–
[(C₅Me₅)Ir(acac)(HPCy₂)]BF₄ (XVII)	46.4 (45.6)	6.9 (6.4)	148	86	yellow	2320	–
[(p-Cymene)Ru(acac)(HPPh₂)]BF₄ (XVIII)	54.2 (53.4)	5.6 (5.3)	147	91	orange-yellow	–	–
[(p-Cymene)Ru(acac)(HPCy₂)]BF₄ (XIX)	52.1 (52.3)	7.6 (7.2)	151	86	orange-yellow	–	–

[a] Nujol mulls.

ligands, and then studies of the reactions of some of these mononuclear species containing P–H protons with the di-μ-methoxo compounds [M$'(\mu$-OMe)(diolefin)] [M$'$ = Rh, diolefin = tetrafluorobenzobarrelene (TFB), 1,5-cyclooctadiene (COD); M = Ir, diolefin = COD] that have enabled us to prepare dinuclear heterovalent or heterometallic diphenylphosphido-bridged complexes.

Results and discussion

Neutral mononuclear complexes

The dinuclear complexes [(LMCl)$_2(\mu$-Cl)$_2$] (L = C$_5$Me$_5$, M = Rh, Ir [12]. L = p-Cymene, M = Ru [13]) react with phosphine ligands (HPRR$'$), in 1/2 molar ratio, to give air-stable solids of formula [LMCl$_2$(HPRR$'$)], as shown in eq. 1.

$$[(LMCl)_2(\mu\text{-}Cl)_2] + 2\ HPRR' \rightarrow 2[LMCl_2(HPRR')] \tag{1}$$
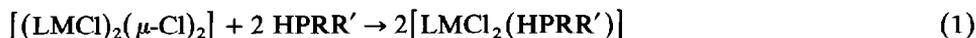
L	M	R = R$'$ = Ph	R = R$'$ = Cy	R = H, R$'$ = Ph
C$_5$Me$_5$	Rh	I	II	III
C$_5$Me$_5$	Ir	IV	V	VI
p-Cymene	Ru	VII	VIII	IX

The preparation of complex I has been previously reported [14]. Carty et al. have prepared complex VII by another route [15]. Table 1 lists the analytical and IR data for the isolated complexes. The IR spectra show ν(Rh–Cl) bands in the 250–300 cm^{-1} range along with characteristic P–H bands of the phosphine ligands.

The characterization of these complexes was completed by ^{1}H and ^{31}P NMR studies and Table 2 lists the spectral data. The relative intensities and multiplicities are in agreement with the proposed formulations. In particular, the protons of the C$_5$Me$_5$ group of complexes I–VI appear as a doublet due to the ^4J(P–H) coupling to the phosphorus nucleus of the coordinated phosphine. These ligands retain the proton (or protons) after coordination. Thus, a resonance is present in all cases in the 4.23 to 7.43 ppm region, with a large coupling constant, assigned to ^1J(P–H) ranging from 352.3 to 413.4 Hz. The ^{31}P{^{1}H} NMR spectra consist of one doublet for the rhodium complexes (I–III) (^1J(Rh–P) values are similar to those found for related complexes [5]) and one singlet for the others (IV–IX). The δ P values show the expected features upon change in the phosphine or the metal [16].

Cationic mononuclear complexes

Addition of one equivalent of tetrafluoroboric acid and the required amount of HPR$_2$ ligands to a suspension of [(C$_5$Me$_5$)MCl(acac)] (M = Rh, Ir; Hacac = acetylacetone [17]) in acetone, affords the corresponding cationic complexes of general formula [(C$_5$Me$_5$)MCl(HPR$_2$)$_2$]BF$_4$ (eq. 2).

$$[(C_5Me_5)MCl(acac)] + HBF_4 + 2\ HPR_2 \rightarrow [(C_5Me_5)MCl(HPR_2)_2]BF_4 + Hacac \tag{2}$$
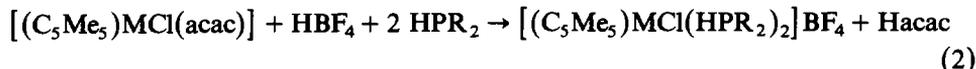
M	R = Ph	R = Cy
Rh	X	XI
Ir	XII	XIII

Table 2

Relevant ^{1}H and ^{31}P{^{1}H}NMR data ^{a,b} for the mononuclear complexes

Complex	^{1}H					^{31}P	
	p-Cymene ^{c}			C$_5$Me$_5$	H–PRR′	δ P	^{1}J(Rh–P)
	Me	^{i}Pr	H$_{AB}$				
I	–	–	–	1.53d ^{4}J(P–H) = 3.9	6.75d ^{1}J(P–H) = 403.5	13.9d	140.7
II	–	–	–	1.64d ^{4}J(P–H) = 3.6	4.23dt ^{1}J(P–H) = 352.3 ^{3}J(H–H) = 5.1	36.8d	138.2
III	–	–	–	1.58d ^{4}J(P–H) = 4.6	5.57d ^{1}J(P–H) = 385.9	–35.2d	142.2
IV	–	–	–	1.55d ^{4}J(P–H) = 2.5	7.43d ^{1}J(P–H) = 411.0	–9.7s	–
V	–	–	–	1.63d ^{4}J(P–H) = 2.4	4.55dt ^{1}J(P–H) = 359.4 ^{3}J(H–H) = 5.6	7.9s	–
VI	–	–	–	1.62d ^{4}J(P–H) = 4.0	5.87d ^{1}J(P–H) = 394.1	–57.1s	–
VII	1.98s	0.96d; 2.50sp ^{3}J(H–H) = 6.9	5.40s	–	6.40d ^{1}J(P–H) = 413.4	21.6s	–
VIII	2.10s	1.22d; 2.70sp ^{3}J(H–H) = 6.9	5.49s	–	4.35dt ^{1}J(P–H) = 370.2 ^{3}J(H–H) = 3.4	40.3s	–
IX	2.10s	1.18d; 2.60sp ^{3}J(H–H) = 6.9	5.21; 5.37 J$_{AB}$ = 5.5	–	5.64d ^{1}J(P–H) = 388.7	–29.3s	–
X	–	–	–	1.45t ^{4}J(P–H) = 3.8	6.38d ^{1}J(P–H) = 411.1	13.3d	129.9
XI	–	–	–	1.74t ^{4}J(P–H) = 3.2	4.26 ^{1}J(P–H) = 360.0	31.2d	129.4
XII	–	–	–	1.49t ^{4}J(P–H) = 2.5	7.03d ^{1}J(P–H) = 424.1	–18.9s	–
XIII	–	–	–	1.80bs	4.51d ^{1}J(P–H) = 369.9	–2.8s	–
XIV	–	–	–	1.52d ^{4}J(P–H) = 4.2	6.60d ^{1}J(P–H) = 378.4	8.5d	150.4
XV	–	–	–	1.56d ^{4}J(P–H) = 3.8	4.35dt ^{1}J(P–H) = 339.7 ^{3}J(H–H) = 13.9	31.0d	150.3
XVI	–	–	–	1.53d ^{4}J(P–H) = 2.7	6.64d ^{1}J(P–H) = 402.1	–8.7s	–
XVII	–	–	–	1.53d ^{4}J(P–H) = 2.5	4.49dt ^{1}J(P–H) = 362.3 ^{3}J(H–H) = 6.8	11.6s	–
XVIII	1.97s	1.18d; 2.46sp ^{3}J(H–H) = 6.2	5.65; 5.70 J$_{AB}$ = 5.4	–	7.23d ^{1}J(P–H) = 386.7	10.8s	–
XIX	2.02s	1.25d; 2.53sp ^{3}J(H–H) = 6.9	5.68; 5.77 J$_{AB}$ = 5.9	–	5.26dt ^{1}J(P–H) = 353.3 ^{3}J(H–H) = 6.1	23.7s	–

^{a} Measured in CDCl$_3$(^{1}H) or CDCl$_3$/CHCl$_3$ (1/1)[^{31}P{^{1}H}] at room temperature; chemical shifts relative to SiMe$_4$ (^{1}H) or 85% H$_3$PO$_4$ [^{31}P{^{1}H}] as external standards; J in Hz. ^{b} Abbreviations: s, singlet; d, doublet; dt, doublet of triplets; sp, septet; bs, broad singlet. ^{c} Labelling of p-cymene protons:
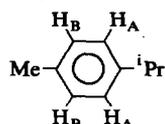
It is noteworthy that the related acetylacetonate ruthenium complex [(p-Cymene)RuCl(acac)] [18] reacts differently with HBF_4 and $HPPh_2$. Thus, the complexes [(p-Cymene)RuCl$_2$(HPPh$_2$)] (VII) and [(p-Cymene)Ru(acac)(HPPh$_2$)]-BF$_4$ (XVIII) (see below) are obtained by protonation of the acac group by tetrafluoroboric acid or by displacement of the chloride by the phosphine, respectively.

Analytical and IR data and molar conductivities of complexes X–XIII are consistent with their proposed formulations (Table 1). Thus, their IR spectra show no acetylacetonate bands of the starting material but contain the typical absorptions of the BF$_4$ anion with Td symmetry. Complexes XI and XIII show a medium band at 2330 and 2340 cm^{-1}, respectively, assigned to a ν(P–H) vibration.

Table 2 lists the ^{1}H and ^{31}P{^{1}H} NMR data for the new cationic complexes. As expected, the protons of the C$_5$Me$_5$ group appear as a triplet because of coupling to the two equivalent phosphorus nuclei. The P–H protons show a large ^1J(P–H) coupling constant and, in the dicyclohexylphosphine complexes XI and XIII, an additional ^3J(H–H) coupling with the protons of the cyclohexyl groups. The ^{31}P{^{1}H} NMR spectra consist of a doublet for the rhodium complexes and a singlet for the iridium ones.

In absence of HBF$_4$, the chloride ion of the acetylacetonate complexes [LMCl(acac)] (L = C$_5$Me$_5$, M = Rh, Ir; L = p-Cymeme, M = Ru) could be removed by addition of stoichiometric amounts of NaBF$_4$ and HPR$_2$, to give the cationic complexes [LM(acac)(HPR$_2$)]BF$_4$ (eq. 3). Analytical data and the IR (Table 1), ^{1}H, and ^{31}P{^{1}H} NMR spectra (Table 2) support the proposed formulations.

$$[LMCl(acac)] + NaBF_4 + HPR_2 \rightarrow [LM(acac)(HPR_2)]BF_4 + NaCl \qquad (3)$$
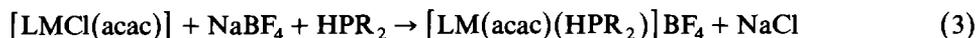
L	M	R = Ph	R = Cy
C$_5$Me$_5$	Rh	XIV	XV
C$_5$Me$_5$	Ir	XVI	XVII
p-Cymene	Ru	XVIII	XIX

As expected, in these cationic mononuclear complexes, as in the other types of mononuclear complexes reported in this paper, the larger the cone angle of the phosphine the higher is the δ P value [16]. The δ P values for the rhodium complexes are higher than those for the related iridium compounds [16], and the highest δ P values are those for the corresponding ruthenium complexes, except for complex XIX.

Dinuclear complexes

The diphenylphosphine ligand of the neutral complexes I, IV and VII can be deprotonated by reaction with the di-μ-methoxo dimeric complexes [M'(OMe)(diolefin)]$_2$ (M' = Rh, diolefin = TFB, COD; M' = Ir, diolefin = COD) [19] to give rise to dinuclear heterovalent Rh(III)–Rh(I) or heterodinuclear Ir–Rh, Ru–Rh and Ru–Ir complexes, in which the resulting diphenylphosphido anion bridges the two metal atoms (eq. 4).

$$[LMCl_2(HPPh_2)] + \tfrac{1}{2}[M'(OMe)(diolefin)]_2 \rightarrow$$

$$[LMCl_2(\mu\text{-}PPh_2)M'(diolefin)] + MeOH \qquad (4)$$
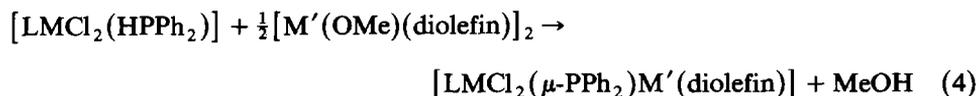
L	M	M'	diolefin
C_5Me_5	Rh	Rh	TFB (XX)
C_5Me_5	Rh	Rh	COD (XXI)
C_5Me_5	Ir	Rh	COD (XXII)
p-Cymene	Ru	Rh	TFB (XXIII)
p-Cymene	Ru	Rh	COD (XXIV)
p-Cymene	Ru	Ir	COD (XXV)

Table 3 collects some physical data for these new dinuclear complexes. The high yields point to the absence of any significant redistribution reactions, and the reaction provides a good method of preparing this type of complexes.

Table 4 lists the ^1H and $^{31}P\{^1H\}$ NMR data for the complexes. The chemical shifts, multiplicities and intensities of the proton resonances are in good agreement with the proposed formulations. The $^{31}P\{^1H\}$ NMR spectra of complexes XX–XXIV provide important information about their dinuclear nature. The existence of two different coupling constants ^1J(Rh–P) for complexes XX and XXI and the coupling constants observed for complexes XXII–XXIV support their dinuclear formulation. As expected the values of the ^1J(Rh(III)–P) coupling constants are lower than the ^1J(Rh(I)–P) ones [20]. The upfield position of the μ-PPh_2 resonances in all cases implies the absence of metal-metal bond. Similar correlations have been noted for μ-PPh_2 complexes by several groups [3–6,21]. Consistently, the molecular structure of complex XXI shows no significant metal–metal interaction (see below).

On the assumption that the PPh_2 group is bridging, two binuclear structures (A and B) can be proposed depending on whether or not the second chlorine atom is bridging. The X-ray structural study of $[(C_5Me_5)ClRh(\mu\text{-}Cl)(\mu\text{-}PPh_2)Rh(COD)]$ · $\frac{1}{2}Et_2O$ (XXI) confirms the doubly-bridged structure A for this complex. Nevertheless, the ^1H NMR data for ruthenium complexes XXIII–XXV exclude the structure A for them in solution. Their ^1H NMR spectra show only one AB system and one doublet assigned to the aromatic and the isopropyl methyl protons of the p-cymene ligand, respectively (Table 4). It would be expected for structure A that both groups of proton resonances would appear twice because the three ligands forming the

Table 3
Analytical results, yields and colour of the dinuclear complexes

Complex	Analysis (found (calcd.) (%))		Yield (%)	Colour
	C	H		
$[(C_5Me_5)RhCl_2(\mu\text{-}PPh_2)Rh(TFB)]$ (XX)	49.7 (49.6)	3.8 (3.8)	79	brown
$[(C_5Me_5)RhCl_2(\mu\text{-}PPh_2)Rh(COD)]$ (XXI)	51.2 (51.1)	5.4 (5.3)	77	brown
$[(C_5Me_5)IrCl_2(\mu\text{-}PPh_2)Rh(COD)]$ (XXII)	44.5 (45.3)	4.6 (4.7)	82	orange
$[(p\text{-}Cymene)RuCl_2(\mu\text{-}PPh_2)Rh(TFB)]$ (XXIII)	49.1 (49.8)	3.5 (3.7)	88	orange
$[(p\text{-}Cymene)RuCl_2(\mu\text{-}PPh_2)Rh(COD)]$ (XXIV)	52.1 (52.3)	5.6 (5.2)	90	orange
$[(p\text{-}Cymene)RuCl_2(\mu\text{-}PPh_2)Ir(COD)]$ (XXV)	45.7 (45.5)	4.9 (4.6)	67	orange-brown

Table 4

Relevant ^{1}H and ^{31}P{^{1}H} NMR data ^{a,b} for the dinuclear complexes

Complex	^{1}H				^{31}P		
	p-Cymene ^{c}			C$_5$Me$_5$	δ P	^{1}J(Rh(III)–P)	^{1}J(Rh(I)–P)
	Me	^{i}Pr	H$_{AB}$				
XX	–	–	–	1.38d ^{4}J(P–H) = 2.6	28.9dd	110.3	139.3
XXI	–	–	–	1.32d ^{4}J(P–H) = 2.4	19.6dd	109.8	124.8
XXII	–	–	–	1.34d ^{4}J(P–H) = 1.0	−28.7d	–	120.5
XXIII	1.81s	0.88d; 2.20sp ^{3}J(H–H) = 6.9	5.18; 5.31 J$_{AB}$ = 5.6	–	14.1d	–	136.8
XXIV	1.83s	0.84d; 2.20sp ^{3}J(H–H) = 6.9	5.07; 5.27 J$_{AB}$ = 5.7	–	4.0d	–	122.9
XXV	1.84s	0.88d; 2.20sp ^{3}J(H–H) = 6.8	5.08; 5.27 J$_{AB}$ = 5.9	–	−25.3d	–	–

^{a} Measured in CDCl$_3$(^{1}H) or CDCl$_3$/CHCl$_3$(1/1)(^{31}P{^{1}H}) at room temperature; chemical shifts relative to SiMe$_4$(^{1}H) or 85% H$_3$PO$_4$(^{31}P{^{1}H}) as external standards; J in Hz. ^{b} Abbreviations: s, singlet; d, doublet; dd, doublet of doublets; sp, septet. ^{c} The labelling of p-cymene protons is the same as in Table 2.

three legs of the piano-stool arrangement around the ruthenium atom are different (terminal chloride, bridging chloride, and diphenylphosphido) [22]. The observed spectra can be accounted for if we assume that the p-cymene ruthenium complexes XXIII–XXV have a triply-bridged structure of the **B** type (Fig. 1) with the M′ atom adopting a square pyramidal geometry and the phosphido group in the apical position. A structure of this type has been established by an X-ray study for the related complex [(p-Cymene)Ru(μ-Cl)$_2$(μ-pz)Rh(TFB)] (pz = pyrazolate), although the apical position of the distorted square pyramidal coordination around the rhodium is occupied by one of the two chlorine atoms [9]. The spectral data for complexes XX and XXII are compatible with both the **A** and **B** type of structure.

Attempts to prepare related complexes using the same method but starting from II, III, V, VIII and IX were unsuccessful. On the other hand, bubbling of carbon monoxide (at room temperature and atmospheric pressure) through dichloro-

A   **B**

$\ominus$ ≡ C$_5$Me$_5$ or p−cymene   ‖ ≡ diolefin
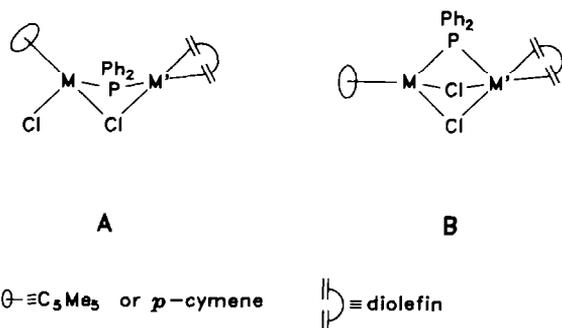
Fig. 1. The doubly-bridged structure **A** and the triply-bridged structure **B**.

methane solutions of complexes XX–XXV cleaves the chloride–phosphido-bridge, and we have detected spectroscopically the presence in the products of [{LMCl}$_2$(μ-Cl)$_2$][12,13] and [{(C$_5$Me$_5$)RhCl}$_2$(μ-PPh$_2$)$_2$] [5], along with other unidentified carbonyl species.

Molecular structure of [(C$_5$Me$_5$)ClRh(μ-Cl)(μ-PPh$_2$)Rh(COD)] · ½Et$_2$O (XXI)

The crystal structure consists of discrete neutral dinuclear complexes separated

Table 5

Final atomic coordinates ($\times 10^4$) for the non-hydrogen atoms for [(C$_5$Me$_5$)ClRh(μ-Cl)(μ-PPh$_2$)Rh(COD)] · ½Et$_2$O (XXI)

Atom	x	y	z
Rh(1) [a]	30880(3)	14344(3)	16149(2)
Rh(2) [a]	14658(4)	19622(4)	31584(2)
Cl(1)	307(1)	442(1)	1585(1)
Cl(2)	3323(1)	572(1)	2772(1)
P	2711(1)	3402(1)	2361(1)
C(1)	3386(5)	1516(6)	508(2)
C(2)	4681(5)	2486(5)	899(2)
C(3)	5429(5)	1692(5)	1313(2)
C(4)	4661(6)	181(5)	1127(3)
C(5)	3434(6)	84(6)	632(3)
C(6)	2308(7)	1880(9)	−18(3)
C(7)	5245(7)	4041(6)	818(3)
C(8)	6863(5)	2270(7)	1797(3)
C(9)	5147(9)	−1000(7)	1447(4)
C(10)	2349(7)	−1270(7)	285(4)
C(11)	1712(5)	4593(5)	1963(2)
C(12)	806(5)	4097(5)	1327(3)
C(13)	−60(6)	4957(6)	1057(3)
C(14)	−20(6)	6303(6)	1394(3)
C(15)	885(6)	6799(6)	2015(3)
C(16)	1740(6)	5958(5)	2301(3)
C(17)	4566(5)	4588(5)	2731(2)
C(18)	5296(6)	4240(5)	3311(3)
C(19)	6759(6)	5051(6)	3579(3)
C(20)	7497(7)	6230(7)	3272(4)
C(21)	6775(6)	6620(6)	2706(3)
C(22)	5317(5)	5816(5)	2431(3)
C(23)	−327(5)	2995(5)	3390(3)
C(24)	1007(6)	3659(5)	3833(2)
C(25)	1292(8)	3433(7)	4596(3)
C(26)	776(8)	1872(7)	4736(3)
C(27)	1022(7)	851(6)	4120(3)
C(28)	−93(7)	183(6)	3599(3)
C(29)	−1728(7)	415(7)	3504(4)
C(30)	−1752(6)	1981(6)	3635(3)
O(1) [b]	5464(15)	10095(13)	4963(8)
C(31) [b]	5590(26)	11107(15)	5555(8)
C(32) [b]	4852(25)	8614(13)	4972(9)
C(33) [b]	5491(29)	12572(15)	5366(12)
C(34) [b]	3970(26)	7852(20)	4283(11)

[a] Atomic coordinates for these atoms are expressed × 10^5. [b] These atoms were included in the crystal structure as an idealized model for the disordered solvent.
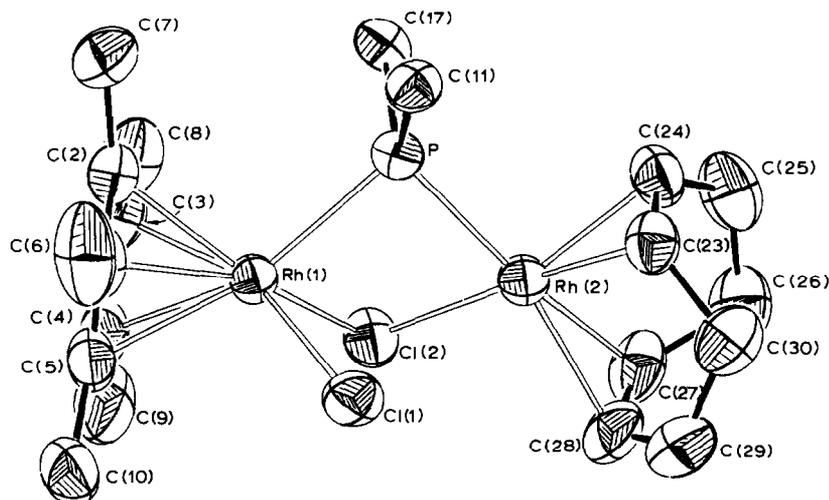
Fig. 2. An ORTEP plot of the structure of [(C₅Me₅)ClRh(μ-Cl)(μ-PPh₂)Rh(COD)] (XXI) showing the atomic numbering scheme. Only the *ipso* carbons of the phenyl groups are shown for clarity.

Table 6

Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses for [(C₅Me₅)ClRh(μ-Cl)(μ-PPh₂)Rh(COD)] · ½Et₂O (XXI)

Rh(1)–P	2.346(1)	Rh(2)–P	2.303(2)
Rh(1)–Cl(2)	2.462(2)	Rh(2)–Cl(2)	2.456(1)
Rh(1)–Cl(1)	2.420(1)	Rh(2)–C(23)	2.113(5)
Rh(1)–C(1)	2.143(4)	Rh(2)–C(24)	2.100(5)
Rh(1)–C(2)	2.154(4)	Rh(2)–C(27)	2.224(6)
Rh(1)–C(3)	2.143(4)	Rh(2)–C(28)	2.195(6)
Rh(1)–C(4)	2.228(6)	P–C(11)	1.826(5)
Rh(1)–C(5)	2.238(6)	P–C(17)	1.830(4)
C(1)–C(2)	1.421(5)	C(1)–C(6)	1.491(8)
C(1)–C(5)	1.440(8)	C(2)–C(7)	1.490(7)
C(2)–C(3)	1.414(7)	C(3)–C(8)	1.498(6)
C(3)–C(4)	1.451(6)	C(4)–C(9)	1.496(10)
C(4)–C(5)	1.396(8)	C(5)–C(10)	1.493(7)
C(23)–C(24)	1.404(6)	C(26)–C(27)	1.506(8)
C(23)–C(30)	1.523(7)	C(27)–C(28)	1.365(8)
C(24)–C(25)	1.516(7)	C(28)–C(29)	1.532(9)
C(25)–C(26)	1.522(9)	C(29)–C(30)	1.512(9)
G–Rh(1)–Cl(1) [a]	125.53(8)	Cl(2)–Rh(2)–P	80.98(4)
G–Rh(1)–Cl(2) [a]	124.15(8)	Cl(2)–Rh(2)–M(1) [a]	167.75(11)
G–Rh(1)–P [a]	135.56(8)	Cl(2)–Rh(2)–M(2) [a]	93.60(12)
Cl(1)–Rh(1)–Cl(2)	88.84(5)	P–Rh(2)–M(1) [a]	97.56(10)
Cl(1)–Rh(1)–P	87.15(4)	P–Rh(2)–M(2) [a]	174.58(12)
Cl(2)–Rh(1)–P	80.02(5)	M(1)–Rh(2)–M(2) [a]	87.77(15)
Rh(1)–Cl(2)–Rh(2)	86.38(5)		
Rh(1)–P–C(11)	116.8(1)	Rh(2)–P–C(11)	119.2(1)
Rh(1)–P–C(17)	111.2(1)	Rh(2)–P–C(17)	112.6(1)

[a] M(1) and M(2) represent the midpoints of the C(23)–C(24) and C(27)–C(28) olefin double bonds and G represents the centroid of the pentamethylcyclopentadienyl ring.

by normal Van der Waals distances. Figure 2 shows a view of the complex with the atom labelling used. Atomic positional parameters and selected bond lengths and angles are presented in Tables 5 and 6, respectively. The complex consists of two rhodium atoms in two different formal oxidation states (Rh(1), oxidation state III, Rh(2), oxidation state I), with pseudo-octahedral and square planar coordinations, respectively, and bridged by a chlorine atom and a diphenylphosphido group. The separation between the two rhodium atoms is 3.3657(6) Å, outside the normal limits for a Rh–Rh bonding interaction [23]. Consistently, the δ P value was not shifted to low field (δ P = 19.6 ppm) [3–6,21]. The rhodium(III) atom is η^5-bonded to a C_5Me_5 ligand and, as a consequence of the asymmetry of coordination around the metal, presents different Rh–C(ring) distances. In this respect the C_5Me_5 ring has C–C distances (Table 6) suggesting some degree of localization into an "ene–enyl" form, as previously observed for some Rh(III)(C_5Me_5) complexes [11,17,24]. The phosphorus atom eclipses the C(2) ring carbon atom, and the Rh(1)–Cl(1) and Rh(1)–Cl(2) bonds project onto the C(1)–C(5) and C(3)–C(4) bonds, respectively. The longer Rh–C(ring) distances (Rh(1)–C(4) and Rh(1)–C(5)) involve the carbon atoms with greater double bond:
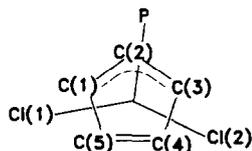
The rhodium(III) atom is also coordinated to a terminal (Cl(1)) and a bridging (Cl(2)) chlorine ligand and to the phosphorus atom of the diphenylphosphido group. The terminal chlorine ligand is closer to the rhodium atom than the bridging chlorine ligand, as previously found for related rhodium complexes [11,25–27]. The Rh(1)–P bond distance 2.346(1) Å is comparable to those in the related μ-diphenyl-phosphido rhodium(III) complex [{(C_5Me_5)Rh}$_2$(μ-pz)$_2$(μ-PPh$_2$)]BF$_4$ [Rh–P = 2.334(1) Å (average)] [6]. If the centroid of the C_5Me_5 ring G is regarded either as a tetrahedral site or as the centre of a three *fac* octahedral site, the environment of the Rh(III) atom can be better regarded as octahedral. The Rh(I) atom (Rh(2)) displays a distorted square-planar coordination (the Cl(2)–Rh(2)–P and C(23,24)–Rh(2)–C(27,28) planes make an angle of 12.2(1)°).

The Rh(2)–Cl(2) bond distance 2.456(1) Å falls in the range of Rh(I)–Cl bond distances usually observed in related structures with bridging chlorine atoms (range 2.35–2.69 Å) [9]. As reported for the related μ-pyrazolate dirhodium complex [(C_5Me_5)ClRh(μ-Cl)(μ-pz)Rh(TFB)] [11] the Rh(I)–Cl and Rh(I)–P bonds are slightly shorter than the corresponding ones for the Rh(III) atom, in contradiction of the respective ionic radii. The Rh(2)–P bond is significantly shorter than those found for related Rh(I)–PR$_2$ bonds *trans* to 1,5-cyclooctadiene ligands [1,28].

As expected, the rhodium–olefin bond *trans* to the phosphorus atom (Rh(2)–C(27–28) = 2.101(4) Å) is longer than that *trans* to the chlorine atom (Rh(2)–C(23,24) = 1.986(4) Å) [28]. The dihedral angle between the Rh(2)–P–Cl(2) and Rh(1)–P–Cl(2) planes is 134.8(1)°. The cyclooctadiene ligand is in the boat config-uration, as is commonly observed for this ligand, and the structural parameters of this group are normal.

Experimental

C and H analyses were carried out with a Perkin–Elmer 240B microanalyser. IR spectra were recorded on a Perkin–Elmer 1330 (Nujol mulls). ^{1}H NMR and ^{31}P NMR spectra were recorded in $CDCl_3$ at ambient temperature on a Varian XL 200 spectrometer and are in ppm referenced to $SiMe_4$ (δ 0.00, ^{1}H) and 85% H_3PO_4 (aq.) (δ, 0.0, ^{31}P). Conductivities were measured in 10^{-4} N acetone solutions with a Crison 525 conductimeter.

All reactions were performed at room temperature under nitrogen.

Preparation of [(C$_5$Me$_5$)IrCl$_2$(HPPh$_2$)] (IV)

To a suspension of 420.8 mg (0.53 mmol) of [{(C$_5$Me$_5$)IrCl}$_2$(μ-Cl)$_2$] in 40 ml of dichloromethane was added HPPh$_2$ (0.185 ml; 1.06 mmol). After 1 h stirring the suspension was vacuum-concentrated to ca. 2 ml. Addition of hexane completed the precipitation of a yellow solid, which was filtered off, washed with hexane, and air dried. Yield 550.0 mg.

Complexes I–III and V–IX were prepared analogously, starting from the appropriate dimeric compound and phosphine ligand.

Preparation of [(C$_5$Me$_5$)RhCl(HPPh$_2$)$_2$]BF$_4$ (X)

To a solution of [(C$_5$Me$_5$)RhCl(acac)] (523.9 mg, 1.40 mmol) in acetone (15 ml) was added HBF$_4$ (0.280 ml, 35% w/w, 1.40 mmol). After 10 min stirring HPPh$_2$ (0.490 ml; 2.81 mmol) was added. The resulting reddish-orange solution was stirred for 2 h and vacuum-concentrated to ca. 2 ml. Addition of diethyl ether gave a yellow solid, which was filtered off, washed with diethyl ether, and air dried. Yield 962.0 mg.

Complexes XI–XIII were prepared by an analogous method.

Reaction between [(p-Cymene)RuCl(acac)], HBF$_4$ and HPPh$_2$

To a suspension of [(p-Cymene)RuCl(acac)] (256.5 mg, 0.69 mmol) in acetone (20 ml) were added HBF$_4$ (0.138 ml, 35% w/w, 0.69 mmol) and HPPh$_2$ (0.241 ml, 1.38 mmol). After 2 h stirring a red solid was filtered off anc characterized as [(p-Cymene)RuCl$_2$(HPPh$_2$)] (VII) from its analytical and spectroscopic data. Yield: 93.8 mg (30% based on the metal).

A yellow solid was isolated by addition of diethyl ether to the filtrate, and was formulated as [(p-Cymeme)Ru(acac)(HPPh$_2$)]BF$_4$ (XVIII) by comparison of their spectroscopic data with those of an authentic sample prepared as described below. Yield: 287.6 mg (68% based in the metal).

Preparation of [(C$_5$Me$_5$)Rh(acac)(HPPh$_2$)](BF$_4$) (XIV)

A mixture of 473.0 mg (1.27 mmol) of [(C$_5$Me$_5$)RhCl(acac)], 0.220 ml (1.27 mmol) of HPPh$_2$ and 142.2 mg (1.27 mmol) of NaBF$_4$ in acetone (25 ml) was stirred for 2 h. The orange solution was taken to dryness under vacuum and the residue was extracted with dichloromethane (15 ml). The NaCl was filtered off, and the filtrate vacuum-concentrated to dryness. The complex was obtained by recrystallization from acetone–diethyl ether. Yield 641.0 mg.

Complexes XV–XIX were prepared analogously.

Preparation of [(C₅Me₅)ClRh(μ-Cl)(μ-PPh₂)Rh(COD)] (XXI)

To a suspension of [(C₅Me₅)RhCl₂(HPPh₂)] (1) (154.2 mg, 0.310 mmol) in acetone (20 ml) was added [Rh(OMe)(COD)]₂ (75.4 mg, 0.160 mmol). After 6 h stirring, the brown solid formed, was filtered off and washed with hexane. The filtrate was vacuum-concentrated to ca. 2 ml; slow addition of hexane gave an additional amount of the complex. Yield 168.9 mg.

Single crystals of this compound suitable for the diffraction study, were obtained by slow diffusion of hexane into a diethyl ether solution, at −20°C.

Complexes XX and XXII–XXV were prepared analogously.

Crystal data for [(C₅Me₅)ClRh(μ-Cl)(μ-PPh₂)Rh(COD)] · ½Et₂O (XXI). Crystals are triclinic, space group $P\bar{1}$, with a 8.8947(6), b 9.6647(7), c 19.0620(15) Å, α 96.31(1), β 92.02(1), γ 104.17(1)°, V 1575.9(2) Å^3, $Z = 2$, $M = 742.374$, D_c 1.564 g cm^{-3}, $F(000) = 754$, μ(Mo-K_α) 12.735 cm^{-1}, $\lambda \# 0.71069$ Å, T 295 K.

Data were measured with a Stoe–Siemens AED-2 diffractometer for a crystal of size 0.56 × 0.23 × 0.20 mm. Intensities for 8680 reflections with $3 \leqslant 2\theta \leqslant 50°$ were measured with a $\omega/2\theta$ scan technique. Three standard reflections monitored every hour showed no change. After Lorentz, polarization and absorption effects [29] were corrected, a total of 4348 reflections with $F \geqslant 5\sigma(F)$ were considered observed out of 5326 unique reflections (R_{int} 0.0236). The positions of both independent rhodium atoms were obtained from a Patterson map. Successive Fourier syntheses allowed location of all the remaining non-hydrogen atoms. Some hydrogens were found in difference Fourier maps and others were included in calculated positions; all were refined riding on their carbon atoms with a common thermal parameter. A disordered diethyl ether molecule (occupancy factor 0.5) was included in the last cycles of refinement to compensate the residual electronic density observed. Full matrix least-squares refinement, with anisotropic temperature factors for all non-hydrogen atoms, except those of the solvent molecule, converged at $R = 0.038$ and $R_w = 0.0334$. The weighting scheme used was $w = 1.3753/(\sigma^2(F) + 0.000462 F^2)$. The final difference map was everywhere $\leqslant 0.5$ e Å^{-3}. Most of the calculations were carried out with program SHELX76 [30].

A list of observed and calculated structure factors is available from the authors.

Acknowledgments

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