

Preparation of $\eta^2 : \eta^2$ -*o*-Xylylene Complexes of Ruthenium(0) via Facile δ -Hydrogen Abstraction Reactions. The Crystal and Molecular Structure of $[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{PMe}_2\text{Ph})_3]^\dagger$

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Reactions of *cis*- or *trans*- $[\text{RuCl}_2\text{L}_4]$ (L = PMe_2Ph , PMePh_2 , or PEt_3) with *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{MgBr}$ produce $[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{L}_3]$ as the only isolable product at temperatures down to -30°C , presumably by δ -hydrogen-abstraction reactions. For L = PMe_3 no reaction is observed but

$[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{PMe}_3)_3]$ may be synthesised from $[\text{RuCl}_2(\text{PMe}_3)_4]$ and *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{Li}^\dagger\text{tmen}$ (tmen = $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$) in toluene. The yellow colour of the complexes, as well as their ^1H and ^{31}P n.m.r. spectra and their reaction with CO to give substitution products rather than adducts, suggest a diene like ($\eta^2 : \eta^2$) binding of the xylylene ligand. This is fully confirmed by an X-ray study of

$[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{PMe}_2\text{Ph})_3]$ which is monoclinic, space group $P2_1/c$, with $a = 15.919(2)$, $b = 11.643(2)$, $c = 16.674(3)\text{\AA}$, $\beta = 104.60(30)^\circ$, and $Z = 4$. The structure was determined with 3 098 observed intensities measured on an automatic diffractometer and refined to an R value of 0.029. The co-ordination geometry can be considered as distorted square pyramidal with the diene molecule occupying two basal sites and bound through its exocyclic double bonds. The C-C distances suggest localisation of bonding in the xylylene ring and the angle between the plane containing Ru, C(1), C(4) and the extension of that of C(1), C(2), C(3), C(4) is 93° , confirming the $\eta^2 : \eta^2$ binding of the xylylene ligand.

We have recently reported¹ that decomposition of bis(*o*-methylbenzyl) complexes of platinum occurs *via* hydrogen abstraction from the δ -carbon atom of one alkyl group to give 2,3-benzoplatinacyclopentene complexes, although forcing conditions (refluxing in xylene for 16 h) are required. This δ -hydrogen abstraction from a carbon donor ligand, although known,²⁻⁵ is considerably less usual than abstraction from α ,⁶ β ,⁷ or γ ^{8,9} carbon atoms.

We now report that such δ -hydrogen abstraction reactions on ruthenium are so facile that dialkyl complexes cannot be isolated even at low temperature. Similar marked differences in reactivity between platinum⁹ and ruthenium⁸ have been observed in the formation of 2,3-dimethylmetallacyclobutane complexes *via* γ -hydrogen abstraction reactions in bis-(neopentyl) complexes. A preliminary communication of our results has appeared.¹⁰

Results and Discussion

Preparation of *o*-Xylylene Complexes of Ruthenium.—Reactions of *cis*- or *trans*- $[\text{RuCl}_2\text{L}_4]$ (L = PMe_2Ph , PMePh_2 , or PEt_3) with two or more mol equivalents of *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{MgBr}$ in diethyl ether at temperatures down to -30°C lead to orange solutions from which compounds analysing (Table 1) as $[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{L}_3]$ may be isolated in high yield, although for L = PEt_3 we have not obtained the pure complex. Below -30°C no reaction occurs and we have been

[†] Tris(dimethylphenylphosphine)(1- α - η : 2- α' - η -*o*-phenylene-dimethylene)ruthenium.

Supplementary data available (No. SUP 23361, 16 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: atm = 101 325 Pa.

unable to isolate any intermediates in the reactions. We believe that the reactions proceed *via* $[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{Me})_2\text{L}_n]$ ($n = 3$ or 4) followed by loss of *o*-xylene rather than *via* loss of HCl from $[\text{RuCl}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_3)\text{L}_n]$ since reaction of $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]$ with 1 mol equivalent of *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{MgBr}$ leads to $[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{PMe}_2\text{Ph})_3]$ and unreacted $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]$.

Somewhat surprisingly, $[\text{RuCl}_2(\text{PMe}_3)_4]$ does not react with *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{MgBr}$ even on warming but the complex $[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{PMe}_3)_3]$ can be prepared from $[\text{RuCl}_2(\text{PMe}_3)_4]$ and *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{Li}^\dagger\text{tmen}$ [tmen = 1,2-bis(dimethylamino)ethane] in toluene solution. This difference in reactivity suggests that, for the Grignard reaction, prior dissociation of a phosphine molecule, which is facile for L = PMe_2Ph , PMePh_2 , or PEt_3 ,¹¹ but not for PMe_3 , may be required. One of us¹² has previously isolated a complex containing a Ru(MeMgCl) unit which lends support to the view that Grignard alkylations may occur *via* a four-centred transition state such as $[\text{Ru}\{\text{RMg}(\text{Br})\text{Cl}\}]$.

Table 1. Analytical data (%) for new ruthenium complexes

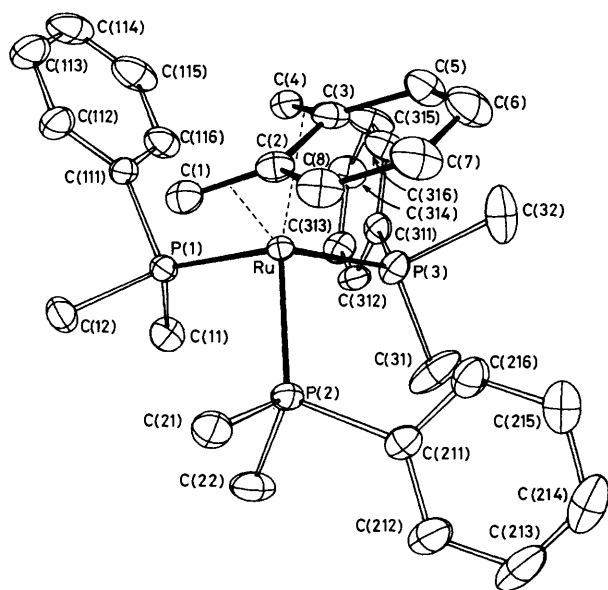
Complex	Analysis ^a		
	C	H	P
<i>trans</i> - $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]^b$	53.3 (53.0)	6.2 (6.1)	16.9 (17.1)
$[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{PMe}_2\text{Ph})_3]$	62.4 (62.0)	6.8 (6.6)	
$[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{PMePh}_2)_3]$	69.0 (70.1)	5.9 (5.8)	11.0 (11.5)
$[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{PMe}_3)_3]$	47.2 (47.1)	8.0 (8.1)	

^a Calculated values are given in parentheses. ^b Cl 10.4 (9.8)%.

Table 2. Proton n.m.r. data ^a for new ruthenium compounds measured in C₆D₆ using C₆D₅H (δ 7.27) as internal standard

Compound	P ² Me + P ³ Me		P ¹ Me		CH _{exo}		CH _{endo}		
	δ	$J(\text{PH}) + J(\text{PH}')$	δ	$J(\text{PH})$	δ	$J(\text{PH})$	δ	$J(\text{PH})$	$J(\text{HH})$
[Ru(CH ₂ C ₆ H ₄ CH ₂)(PMe ₂ Ph) ₃] ^b	1.21 (d) ^c 1.29 (d) ^c	5 5	1.73 (d)	7	1.90 (dd)	6	-0.15 (dd)	8	4
[Ru(CH ₂ C ₆ H ₄ CH ₂)(PMePh ₂) ₃] ^b	1.7 (d) ^c	5	2.22 (d)	6	1.99 (dd)	6	0.63 (dd)	8	4
[Ru(CH ₂ C ₆ H ₄ CH ₂)(PMe ₃) ₃]	0.98 (d) ^c	6	1.37 (d)	8	1.89 (dd)	6	-0.13 (dd)	8	4
[Ru(CH ₂ C ₆ H ₄ CH ₂)(PEt ₃) ₃]	<i>d</i>	<i>d</i>	<i>d</i>		<i>d</i>		-0.04 (dd)	8	4

^a *J* values in Hz. ^b Phenyl resonances near δ 7.5. ^c Virtual doublet with intensity between outer lines. ^d Not analysed.

**Figure.** Solid-state structure and atomic numbering scheme for [Ru(CH₂C₆H₄CH₂)(PMe₂Ph)₃]

During the course of this work, Bennett and co-workers^{13,14} have prepared very similar complexes by deprotonation of [Ru(η -C₆Me₆)L₃] [L = P(OMe)₃, PMe₂Ph, or P(OCH₂)₃-CMe].

Mass spectroscopic studies on [Ru(CH₂C₆H₄CH₂)(PMe₂Ph)₃] show a parent ion at *m/e* 620 (¹⁰²Ru) and a fragmentation pattern arising from loss of phosphines and the *o*-xylylene unit, confirming the monomeric nature of the complex. If the xylylene group were bound as a two-electron donor in these molecules, they would be five-co-ordinate 16-electron complexes of ruthenium(II). However, their spectroscopic and chemical properties (see below and Table 2) suggest that they are 18-electron complexes and that the xylylene moiety is bound as a diene ($\eta^2 : \eta^2$ co-ordination). This conclusion is confirmed by X-ray diffraction studies on [Ru(CH₂C₆H₄CH₂)(PMe₂Ph)₃].

The Solid-state Structure of [Ru(CH₂C₆H₄CH₂)(PMe₂Ph)₃].—A diagram of the molecule is shown in the Figure, whilst selected bond lengths and angles are given in Table 3. The representation of the ligand binding as a four-electron, diene system is confirmed in a number of ways. First of all it is quite symmetrically bonded, with the molecule possessing an

Table 3. Selected bond lengths and angles

(a) Bond lengths (Å)			
Ru-P(1)	2.242(1)	Ru-P(2)	2.323(1)
Ru-P(3)	2.316(1)	Ru-C(1)	2.168(4)
Ru-C(2)	2.290(4)	Ru-C(3)	2.305(4)
Ru-C(4)	2.179(5)	Ru-C(1.2)*	2.115(4)
Ru-C(3.4)*	2.122(4)		
P(1)-C(11)	1.835(5)	P(1)-C(12)	1.835(5)
P(1)-C(111)	1.834(4)	P(2)-C(21)	1.821(5)
P(2)-C(22)	1.830(8)	P(2)-C(211)	1.859(4)
P(3)-C(31)	1.831(8)	P(3)-C(32)	1.844(9)
P(3)-C(311)	1.843(4)		
C(1)-C(2)	1.415(7)	C(4)-C(3)	1.456(6)
C(2)-C(3)	1.440(5)	C(3)-C(5)	1.414(7)
C(5)-C(6)	1.362(7)	C(6)-C(7)	1.394(7)
C(7)-C(8)	1.352(8)	C(8)-C(2)	1.426(6)
(b) Bond angles (°)			
P(1)-Ru-P(2)	96.7(0)	P(1)-Ru-P(3)	102.0(0)
P(1)-Ru-C(1)	87.6(1)	P(1)-Ru-C(4)	96.1(1)
P(2)-Ru-P(3)	94.6(0)	P(2)-Ru-C(1)	94.8(1)
P(2)-Ru-C(4)	164.2(1)	P(3)-Ru-C(1)	165.6(1)
P(3)-Ru-C(4)	91.7(1)	C(1)-Ru-C(4)	76.5(2)
P(1)-Ru-C(1.2)	106.0(1)	P(2)-Ru-C(1.2)	97.2(1)
P(3)-Ru-C(1.2)	148.0(1)	P(1)-Ru-C(3.4)	113.4(1)
P(2)-Ru-C(3.4)	144.9(1)	P(3)-Ru-C(3.4)	96.3(1)
C(1.2)-Ru-C(3.4)	58.4(1)		
Ru-P(1)-C(11)	124.1(2)	Ru-P(2)-C(21)	116.8(2)
Ru-P(1)-C(12)	116.4(2)	Ru-P(2)-C(22)	120.0(2)
Ru-P(1)-C(111)	113.9(1)	Ru-P(2)-C(211)	117.8(1)
C(11)-P(1)-C(12)	97.3(3)	C(21)-P(2)-C(22)	98.2(3)
C(11)-P(1)-C(111)	100.1(2)	C(21)-P(2)-C(211)	99.0(2)
C(12)-P(1)-C(111)	101.3(2)	C(22)-P(2)-C(211)	101.2(3)
Ru-P(3)-C(31)	120.6(2)		
Ru-P(3)-C(32)	116.1(2)	C(1)-C(2)-C(8)	126.3(4)
Ru-P(3)-C(311)	118.9(1)	C(4)-C(3)-C(5)	125.7(4)
C(31)-P(3)-C(32)	98.8(3)	C(3)-C(5)-C(6)	121.1(4)
C(31)-P(3)-C(311)	99.5(2)	C(6)-C(7)-C(8)	120.5(5)
C(32)-P(3)-C(311)	98.8(3)	C(7)-C(8)-C(2)	117.2(4)
C(1)-C(2)-C(3)	116.4(3)		
C(4)-C(3)-C(2)	115.3(4)		
C(2)-C(3)-C(5)	118.8(4)		
C(5)-C(6)-C(7)	120.5(5)		
C(7)-C(8)-C(2)	121.9(4)		

* C(1.2) and C(3.4) refer to the centres of the bonds C(1)-C(2) and C(3)-C(4) respectively.

approximate mirror plane bisecting the CH₂C₆H₄CH₂ ligand and containing Ru and P(1). This is well demonstrated by the similarity in bond angles from P(1)-Ru to atoms on each side of this approximate plane. In fact, if the midpoints of the exocyclic double bonds are taken as co-ordination points, the co-ordination geometry can be regarded as square pyramidal, with P(1) axial and P(2), P(3) and the two centre points form-

ing the base, see Table 3. This representation correlates with the differences in Ru-P distances, where Ru-P(1) is distinctly different from Ru-P(2) and Ru-P(3). A second confirmation of the diene bonding mode is given by the orientation of the plane of the ligand relative to the RuP₃ unit. The angle of fold at C(1),C(4), that is the dihedral angle between the plane containing Ru,C(1),C(4), and the extension of that of C(1),C(2),C(3),C(4), is 93°, much larger than the value of 40° found in complexes where the xylylene ligands are acting as two-electron donors^{15,16} or even in complexes where some degree of π interaction is suggested (53.1,¹⁷ 66°¹⁶). Only for the complex

[W(CH₂C₆H₄CH₂)₃] has an angle near 90° been observed.¹⁸

Additionally, the Ru-C(2) and Ru-C(3) distances are only slightly larger than Ru-C(1) and Ru-C(4), a difference which could be due to steric crowding.

The geometry of the CH₂C₆H₄CH₂ ligand is final confirmation of the proposed electronic structure, with strong indications of π -bond localisation. The C(5)-C(6) and C(7)-C(8) lengths are considerably shorter than the others and show that the aromaticity of the six-membered ring has been removed. Broadly similar bond lengths and angles have been observed¹⁹ in the C₈H₈ ring of [Fe(C₈H₈)(CO)₂(PPh₃)], the only other example of a truly $\eta^2 : \eta^2$ xylylene complex whose structure has been crystallographically determined. Similarly, the C(3)-C(4) and C(1)-C(2) distances of 1.456 and 1.415 Å are similar to those found¹⁹ in the iron complex and are significantly shorter than those observed¹⁷ in [Zr(CH₂C₆H₄CH₂)(C₅H₅)₂], where only a small amount of π interaction between the metal and the xylylene group is suggested.

In [W(CH₂C₆H₄CH₂)₃], where the ligands are significantly distorted¹⁸ so that substantial interaction between the metal and the phenyl rings probably occurs, the C-C distances are much more like those found in [Ru(CH₂C₆H₄CH₂)(PMe₂-Ph)₃].

The phosphine ligands of [Ru(CH₂C₆H₄CH₂)(PMe₂Ph)₃] are unexceptional, being similar to those in other dimethylphenylphosphine complexes of ruthenium, except that the same deviations from tetrahedral geometry at phosphorus, leading to one Ru-P-C(methyl) angle of ca. 120° for each phosphine, that has been observed for [Ru₂Cl₃(PMe₂Ph)₃]²⁰ and [RuH(C₄H₆)(PMe₂Ph)₃]²¹ are also observed in [Ru(CH₂C₆H₄CH₂)(PMe₂Ph)₃]. The origin of these deviations has been discussed²² and attributed to steric interaction between the phosphine ligands. Overall, the structure of [Ru(CH₂C₆H₄CH₂)(PMe₂Ph)₃] is very similar²¹ to that of [RuH(C₄H₆)(PMe₂Ph)₃]⁺, with bond distances and angles about the ruthenium atom, as well as in the co-ordinated C₄ fragment, being almost identical, despite the presence of an hydrido-ligand in the butadiene complex. The ruthenium atom of [Ru(CH₂C₆H₄CH₂)(PMe₂Ph)₃] thus has 18 electrons, consistent with the yellow colour of the complex, red being a more usual colour for 16-electron ruthenium complexes.²³

Spectroscopic Properties of [Ru(CH₂C₆H₄CH₂)L₃].—The n.m.r. spectroscopic properties of [Ru(CH₂C₆H₄CH₂)L₃] are entirely consistent with the compounds retaining their solid-state structure in solution. Thus, in the proton n.m.r. spectrum two signals are observed from the phosphine methyl groups (relative intensity 2 : 1). The methyl groups on the unique phosphorus atom resonate as a doublet [$J(\text{PH}) = 7$ Hz] whilst those on the other phosphorus atoms give a doublet with some intensity between the outer lines, a signal typical²⁴

Table 4. Atom co-ordinates ($\times 10^4$)

Atom	x	y	z
Ru *	2 196(*)	1 592(*)	2 065(*)
P(1)	3 001(1)	3 008(1)	1 732(1)
P(2)	1 911(1)	645(1)	800(1)
P(3)	3 246(1)	299(1)	2 734(1)
C(1)	1 088(3)	2 733(4)	1 711(3)
C(2)	797(2)	1 848(4)	2 158(3)
C(3)	1 325(2)	1 622(4)	2 980(2)
C(4)	2 100(3)	2 331(4)	3 240(3)
C(5)	1 099(3)	696(4)	3 432(3)
C(6)	384(3)	41(5)	3 111(3)
C(7)	-134(3)	258(5)	2 318(3)
C(8)	63(3)	1 125(5)	1 856(3)
C(11)	4 071(3)	2 794(5)	1 529(4)
C(12)	2 510(4)	3 821(5)	788(3)
C(111)	3 259(3)	4 161(3)	2 505(3)
C(112)	2 743(4)	5 121(4)	2 463(4)
C(113)	2 940(5)	5 969(5)	3 052(5)
C(114)	3 639(6)	5 865(6)	3 701(5)
C(115)	4 162(4)	4 907(6)	3 773(3)
C(116)	3 969(3)	4 057(5)	3 182(3)
C(21)	990(4)	1 157(5)	-6(3)
C(22)	2 722(4)	641(6)	193(4)
C(211)	1 623(3)	-904(4)	780(3)
C(212)	1 706(4)	-1 674(5)	186(4)
C(213)	1 437(4)	-2 794(5)	192(5)
C(214)	1 060(4)	-3 165(5)	792(5)
C(215)	975(3)	-2 417(5)	1 391(4)
C(216)	1 256(3)	-1 303(4)	1 393(3)
C(31)	3 692(4)	-760(6)	2 141(5)
C(32)	2 931(5)	-681(6)	3 476(5)
C(311)	4 265(3)	855(3)	3 409(3)
C(312)	5 025(3)	933(4)	3 151(3)
C(313)	5 765(3)	1 420(4)	3 648(3)
C(314)	5 771(3)	1 816(5)	4 415(3)
C(315)	5 045(3)	1 725(5)	4 693(3)
C(316)	4 299(3)	1 263(5)	4 201(3)

* Estimated standard deviations of x, y, and z co-ordinates are 0.2, 0.3, and 0.2 referred to the last significant figures.

of an H₂PP'H₂ spin system with $J(\text{PP})$ being small but non-zero and $J(\text{PH}) + J(\text{PH}') = 5$ Hz. For L = PMe₂Ph, the lack of a plane of symmetry through the phosphorus atoms of the two chemically equivalent phosphines renders the two methyl groups on each phosphorus atom diastereotopic and hence two second-order doublets of equal intensity are observed in this case.

The resonances from the xylylene group are also more consistent with $\eta^2 : \eta^2$ binding than simple metallocyclic coordination since, although the two methylene groups are equivalent, the two hydrogens on each are substantially different, resonating as doublets of doublets at near δ 0 and 2. Homonuclear decoupling experiments show that the two protons of each methylene group are coupled to one another [$J(\text{HH}) = 4$ Hz] and that the other coupling is to phosphorus [$J(\text{PH}) = 6$ Hz for the low-field signal and 8 Hz for the high-field signal]. Apart from the coupling to phosphorus, spectra are extremely similar to those reported^{25,26} for [Fe(C₈H₈)(CO)₃] which can be prepared from [Fe₂(CO)₉] or [Fe(CO)₄]²⁻ and α, α' -dibromoxylene, and for the recently prepared²⁷ [Co(C₈H₈)(C₅H₅)], both of which contain an η^4 -xylylene ligand. The very high-field shift of one of the protons of each methylene group is also similar to those found in diene complexes,²⁸ but complexes in which the xylylene ligand is bound as a dialkyl do not show this high-field shift.^{1,15-18}

The ¹³C n.m.r. spectrum of [Ru(CH₂C₆H₄CH₂)(PMe₂Ph)₃] (see Experimental section) is unexceptional, with the methyl-

ene carbon atom resonating as a doublet of triplets. However, the ^{31}P n.m.r. spectra of the complexes with $\text{L} = \text{PMe}_2\text{Ph}$ or PMePh_2 both show two singlet resonances of intensity ratio 1:2. These clearly must be assigned to the unique and symmetry-related phosphorus atoms respectively but the lack of coupling between the two sets of atoms is surprising, usual values for $J(\text{PP})_{\text{cis}}$ being >20 Hz for five-co-ordinate complexes of ruthenium(0)²⁹ or -(II).¹¹

Very low P-P couplings have been observed for other diene complexes of ruthenium and iron^{14,29} and zero couplings occur³⁰ in $[\text{Ru}(\text{C}_4\text{H}_8\text{R})(\text{PPh}_3)_2\text{L}']$ ($\text{L}' = \text{styrene}$, $\text{R} = \text{H}$ or Et). Although the two singlet resonances in the ^{31}P n.m.r. spectra of these complexes were originally assigned³⁰ to their existing in two different isomeric forms of equal population, we now believe that only one isomer is present and that $J(\text{PP}) = 0$.

These very low couplings presumably reflect the P-Ru-P angles which for $[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{PMe}_2\text{Ph})_3]$ will be close to their solid-state values of ca. 100° and probably similar to those found³¹ in tetrahedral complexes of nickel(0), for which $J(\text{PP})$ is also zero. In other five- and six-co-ordinate complexes of ruthenium(0) or -(II), angles of ca. 90° (octahedral, trigonal bipyramidal, square pyramidal) or 120° (trigonal bipyramidal) would be expected and would give rise to the observed higher values of the coupling constants.

Reaction of $[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{PMePh}_2)_3]$ with Carbon Monoxide.—Were $[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{L}_3]$ simple five-co-ordinate complexes containing the xylylene ligand bound as a dialkyl, they should readily add small donor molecules such as carbon monoxide to give $[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{L}_3(\text{CO})]$. The fact that no reaction is observed under mild conditions is further evidence in favour of the $\eta^2 : \eta^2$ mode of bonding.

Under more forcing conditions (80 atm, 80°C , 16 h), mass spectral studies show a range of products to be produced, which we have been unable to separate. These include $[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{CO})_2(\text{PMePh}_2)_2]$ and $[\text{Ru}(\text{CO})_3(\text{PMePh}_2)_2]$ but no simple addition product. The fate of the displaced xylylene molecule has not been established.

Under u.v. irradiation, carbonylation occurs at 1 atm and room temperature but we have again been unable to isolate a pure product. Mass spectroscopic studies show that the main product is $[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{CO})(\text{PMePh}_2)_2]$.

Experimental

Microanalyses were by Berhardt Analytische Laboratories and Elemental Microanalyses Ltd. N.m.r. spectra were recorded on Perkin-Elmer R12B and R34 (^1H) or JEOL FX90Q (^{13}C and ^{31}P) spectrometers. Melting points were obtained in an electrothermal melting-point apparatus in sealed capillaries *in vacuo* and are uncorrected.

All solvents were thoroughly dried by distillation from sodium-benzophenone ketyl and degassed before use. The light petroleum had a boiling range of $60\text{--}80^\circ\text{C}$. All manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk-line and catheter-tubing techniques. The compounds $[\text{RuCl}_2(\text{PPh}_3)_3]$,³² *cis*- $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]$,¹¹ $[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\text{Cl}$,³³ *trans*- $[\text{RuCl}_2(\text{PMe}_3)_4]$,³⁴ *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{MgBr}$,³⁵ and *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{Li}^+\text{tmen}^-$ ³⁶ were prepared by standard literature methods.

***trans*-Dichlorotetrakis(dimethylphenylphosphine)ruthenium(II).**—The compounds $[\text{RuCl}_2(\text{PPh}_3)_3]$ (1.0 g) and PMe_2Ph

(1.0 cm^3) were stirred in light petroleum (75 cm^3) for 16 h. The resulting mustard yellow solid was collected, washed with light petroleum, and dried *in vacuo*. Yield ca. 90%. The compound is considerably more stable than the *cis* isomer,¹¹ being recovered unchanged as orange crystals on recrystallisation from toluene-light petroleum. I.r.: $\nu(\text{Ru-Cl})$ 302 cm^{-1} . N.m.r.: ^{31}P , * $\delta -7.7$ (s); ^1H , δ 1.8 (s, br).

Dichlorotetrakis(triethylphosphine)ruthenium(II) was similarly prepared as pale yellow crystals from the reaction of $[\text{RuCl}_2(\text{PPh}_3)_3]$ (1.0 g) and PET_3 (1.0 cm^3) for 96 h.

Tris(dimethylphenylphosphine)(1- α - η : 2- α' -*o*-phenylenedimethylene)ruthenium(0).—(i) The compound *cis*- $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]$ (0.5 g) was stirred with *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{MgBr}$ (1.5 cm^3 , 1.0 mol dm^{-3}) in diethyl ether (20 cm^3) for 1 h. The clear orange solution was evaporated to dryness and the resulting orange oil extracted into toluene (15 cm^3) before filtration, evaporation to 4 cm^3 , and addition of light petroleum (10 cm^3). The solution was filtered to remove precipitated Grignard reagent and magnesium halides (this often required more than one filtration) and cooled to -30°C for 16 h to give yellow-orange crystals which were collected and dried *in vacuo*. M.p. $180\text{--}182^\circ\text{C}$ (decomp.).

(ii) As above but using *trans*- $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]$ (0.5 g).

(iii) As above but using $[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\text{Cl}$ (0.6 g). Yield ca. 60%.

(iv) As (ii) above but at -30°C ; below this temperature no reaction was observed.

(v) As (ii) above but using *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{MgBr}$ (0.7 cm^3 , 1.0 mol dm^{-3}) gave an orange solution with a yellow solid. These were separated by filtration and the solid identified as unreacted *trans*- $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]$. Treatment of the orange solution, as described above, afforded the complex as yellow-orange crystals. Yield ca. 30%.

N.m.r.: ^{31}P , 25.71 (s, rel. int. 1), 5.05 (s, 2); ^{13}C (alkyl region), δ 35.40 [d, $J(\text{P}^1\text{C}) = 4$, of t, $J(\text{P}^2\text{C}) + J(\text{P}^3\text{C}) = 15$ (CH_2)], 26.02 [d, $J(\text{PC}) = 24$ (CH_3)], 24.71 [t, $J(\text{PC}) + J(\text{PC}') = 22$ (CH_3)], 23.63 [t, $J(\text{PC}) + J(\text{PC}') = 22$ Hz (CH_3)].

The following compounds were similarly prepared.

Tris(methylphenylphosphine)(1- α - η : 2- α' -*o*-phenylenedimethylene)ruthenium(0) from $[\text{RuCl}_2(\text{PMePh}_2)_4]$ (0.6 g) and *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{MgBr}$ (1.3 cm^3 , 1.0 mol dm^{-3}). ^{31}P N.m.r.: 35.71 (s, 1), 19.71 (s, 2). M.p. $200\text{--}203^\circ\text{C}$ (decomp.).

(1- α - η : 2- α' -*o*-Phenylenedimethylene)tris(triethylphosphine)ruthenium(0) from $[\text{RuCl}_2(\text{PET}_3)_4]$ (0.5 g) and *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{MgBr}$ (1.6 cm^3 , 1.0 mol dm^{-3}). The orange ethereal solution was evaporated to dryness and extracted with light petroleum. Attempts to obtain crystals from this solution were unsuccessful, but evaporation to dryness afforded an orange oil which was identified as containing the product by its high-field ^1H resonance (see Table 1).

(1- α - η : 2- α' -*o*-Phenylenedimethylene)tris(trimethylphosphine)ruthenium(0).—The compound $[\text{RuCl}_2(\text{PMe}_3)_4]$ (0.4 g) in toluene (75 cm^3) was stirred with *o*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{Li}^+\text{tmen}^-$ (1.7 cm^3 , 1.0 mol dm^{-3} in diethyl ether) for 16 h. The resulting orange-red solution was evaporated to dryness and the oil so formed extracted with light petroleum. After filtration and evaporation to dryness, the yellow-orange solid was obtained analytically pure after heating at 120°C *in vacuo* for 16 h to remove solvent, tmen, and 2,2'-dimethylbibenzyl.

Reaction of $[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{PMePh}_2)_3]$ with Carbon Monoxide.—(i) **Thermal.** The compound $[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)$

* Chemical shifts in p.p.m. to high frequency of external 85% H_3PO_4 .

(PMePh₂)₃] (0.25 g) in benzene (5 cm³) was heated to 80 °C for 16 h under carbon monoxide (80 atm). The resulting orange solution was evaporated to dryness and mass spectral studies

showed a mixture of mainly [Ru(CH₂C₆H₄CH₂)(CO)₂(PMePh₂)₃] (*m/e* = 462, ¹⁰²Ru) and a little [Ru(CO)₃(PMePh₂)₂] (*m/e* = 586, ¹⁰²Ru). Attempts to separate these products were unsuccessful. At 100 °C the products were the same but [Ru(CO)₃(PMePh₂)₂] was the major product.

(ii) *Photochemical*. The compound [Ru(CH₂C₆H₄CH₂)(PMePh₂)₃] (0.3 cm³) was photolysed in benzene in a silica reaction vessel under carbon monoxide with light from a medium-pressure mercury lamp for 96 h. Evaporation of the resulting solution to dryness followed by mass spectral analysis showed that the major product was [Ru(CH₂C₆H₄CH₂)(CO)₂(PMePh₂)₂] (*m/e* = 634, ¹⁰²Ru).

Crystallography.—*Crystal data*. C₃₂H₄₁P₃Ru, *M* = 619.70, Monoclinic, *a* = 15.919(2), *b* = 11.643(2), *c* = 16.674(3) Å, β = 104.60(30)°, *U* = 2 990.6 Å³ space group *P*₂₁/*c*, *D*_m not measured, *Z* = 4, *D*_c = 1.38 g cm⁻³, μ(Mo-*K*_α) = 6.23 cm⁻¹, *F*(000) = 1 288.

Data collection.³⁷ CAD4 diffractometer, ω—2θ scan mode, ω scan width = 0.8 + 0.35 tanθ, ω scan speed = 1.27—6.77° min⁻¹, Mo-*K*_α radiation (λ = 0.710 69 Å), 1.5 ≤ θ ≤ 25.0°. 4 163 Unique measured data, 3 098 of which were considered observed [*I* > 1.5σ(*I*)].

Structure solution and refinement.³⁷ Standard heavy-atom method, full-matrix least-squares refinement; non-hydrogen atoms anisotropic, hydrogen atoms given individual isotropic thermal parameters; weighting scheme *w* = 1/[σ²(*F*_o) + 0.0003 *F*_o²] with σ(*I*) from counting statistics. Final *R*(= Σ|Δ*F*|/Σ|*F*_o|) and *R*'(= Σ*w*Δ*F*²/Σ*wF*_o²) were 0.029 and 0.028. Final atomic co-ordinates are listed in Table 4.

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References

- 1 S. D. Chappell and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 1980, 238.
- 2 J. A. Duff, B. L. Shaw, and B. L. Turtle, *J. Organomet. Chem.*, 1974, **66**, C18.
- 3 R. A. Jones and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1979, 472.
- 4 G. M. Whitesides, *Pure Appl. Chem.*, 1981, **53**, 287.
- 5 T. H. Tulip, Int. Conf. on Chem. of Platinum Group Metals, Bristol, July 1981, Poster C36.
- 6 R. R. Schrock, *Acc. Chem. Res.*, 1979, **12**, 98 and refs. therein.

- 7 G. W. Parshall and J. J. Mrowca, *Adv. Organomet. Chem.*, 1968, **7**, 157 and refs. therein.
- 8 R. A. Andersen, R. A. Jones, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1978, 446.
- 9 P. Foley, R. DiCosimo, and G. M. Whitesides, *J. Am. Chem. Soc.*, 1980, **102**, 6713.
- 10 S. D. Chappell and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 1981, 319.
- 11 P. W. Armit, A. S. F. Boyd, and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 1975, 1663.
- 12 D. J. Cole-Hamilton and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1977, 797.
- 13 M. A. Bennett, Int. Conf. on Chem. of Platinum Group Metals, Bristol, July 1981, Paper C2.
- 14 M. A. Bennett, I. J. McMahon, and T. W. Turney, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 379 and refs. therein.
- 15 M. F. Lappert, T. R. Martin, C. R. C. Milne, J. L. Atwood, W. E. Hunter, and R. E. Pentilla, *J. Organomet. Chem.*, 1980, **192**, C35.
- 16 M. F. Lappert, C. L. Raston, G. L. Rowbottom, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1981, 6.
- 17 M. F. Lappert, T. R. Martin, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 1980, 476.
- 18 M. F. Lappert, C. L. Raston, B. W. Skelton, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1981, 485.
- 19 J. D. Oliver, Ph.D. Thesis, Austin, Texas, 1971 (*Chem. Abstr.*, 1972, **77**, 106413).
- 20 M. Laing and L. Pope, *Acta Crystallogr., Sect. B*, 1976, **32**, 1547.
- 21 T. V. Ashworth, E. Singleton, M. Laing, and L. Pope, *J. Chem. Soc., Dalton Trans.*, 1978, 1032.
- 22 T. V. Ashworth, M. J. Nolte, E. Singleton, and D. M. Laing, *J. Chem. Soc., Dalton Trans.*, 1977, 1816.
- 23 B. N. Chaudret, D. J. Cole-Hamilton, R. S. Nohr, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1977, 1546.
- 24 R. Harris, *Can. J. Chem.*, 1964, **42**, 2275.
- 25 W. R. Roth and J. D. Meier, *Tetrahedron Lett.*, 1967, 2053.
- 26 B. F. G. Johnson, J. Lewis, and D. J. Thompson, *Tetrahedron Lett.*, 1974, 3789.
- 27 W. H. Hersh and R. G. Bergman, *J. Am. Chem. Soc.*, 1981, **103**, 6992.
- 28 D. J. Cole-Hamilton and G. Wilkinson, *Nouveau J. Chim.*, 1977, **1**, 141.
- 29 D. J. Cole-Hamilton and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1979, 1283.
- 30 B. N. Chaudret, D. J. Cole-Hamilton, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1979, 1739.
- 31 P. S. Pregosin and R. W. Kunz, ' ³¹P and ¹³C N.M.R. of Transition Metal Phosphine Complexes,' Springer, Berlin, 1979, p. 120.
- 32 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945.
- 33 J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 896.
- 34 R. A. Jones, F. Mayor Real, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 511.
- 35 K. Jacob, K.-H. Thiele, Ch. Keilberg, and R. Niebuhr, *Z. Anorg. Allg. Chem.*, 1975, **415**, 109.
- 36 J. Klein, A. Medlik, and A. Y. Meier, *Tetrahedron*, 1976, **32**, 51.
- 37 M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1978, 1334.

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