Substituted *o*-Quinodimethane Complexes of Ruthenium(0)

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Reactions of $[RuCl_2L_4]$ ($L = PMe_3$ or $PMePh_2$) with the lithium salts of 1,2,3-trimethyl-, 1,2,3,4-tetramethyl-, or 1,2,4,5-tetramethyl-benzene lead to complexes which contain co-ordinated methyl substituted *o*-xylidene moieties. Spectroscopic studies confirm the metal-ligand interaction as intermediate between (σ^2,π) and (π^2) and the *o*-xylidene moieties can be better described as methyl substituted *o*-quinodimethanes. By contrast reaction of the lithium salt of *o*-xylene with $[RuCl_2\{P(OPh)_3\}_4]$ gives the *o*-metallated compound $[RuH(C_6H_4OPOPh)_2)\{P(OPh)_3\}_3]$ whilst reaction of the lithium salt of 3,4-dimethylanisole with $[RuCl_2(PMe_3)_4]$ gives $[Ru(CH_2OC_6H_2Me_2)(PMe_3)_4]$ with binding through a phenyl carbon atom. The structures of these complexes have been assigned by spectroscopic means.

The use of transition metals to stabilize otherwise unstable organic molecules is an important area of research and, in recent years, a number of research groups have reported the stabilization of *o*-quinodimethanes by co-ordination.[1–7] The reactions that have been employed (reactions of $o\text{-}C_6H_4X_2$; $X = CH_2Br$, CH_2Cl, or CH_2MgCl; or deprotonation of co-ordinated C_6Me_6) are usually not very useful for general studies of these compounds since only rather specific compounds in the desired class are available. We have reported[5] that $[Ru(CH_2C_6H_4CH_2)(PMe_3)_3]$ can be prepared directly from *o*-xylene by deprotonation with $LiBu^n{\cdot}tmen$ (tmen = *NNN'N'*-tetramethylethylenediamine), followed by reaction with $[RuCl_2(PMe_3)_4]$. We have argued that since methyl substituted aromatic systems are commonly available, this should provide a more general route to substituted *o*-quinodimethane complexes and have demonstrated this potential in the synthesis of 1,2- and 2,3-naphthoquinodimethane complexes of ruthenium.[8] We now report our studies on a range of polymethylbenzenes which in general give substituted *o*-quinodimethane complexes. In addition we reformulate one of the products obtained from the reaction of $[RuCl_2(PMe_3)_4]$ with lithiated 1,2-dimethylnaphthalene.

Results and Discussion

Preparation of Lithium Reagents.—Lithium reagents derived from 1,2,3-trimethyl-, 1,2,3,4-tetramethyl-, and 1,2,4,5-tetramethyl-benzene were prepared by reaction of the parent compound with 1 equivalent of $LiBu^n$ in the presence of 2 equivalents of tmen.

Previous studies have shown[9] that, in general, monolithiation occurs, although in some cases dilithiation is a significant reaction. For example, 1,2,3-trimethylbenzene has been shown to give 1-lithiomethyl-2,3-dimethylbenzene (30%), 1-lithiomethyl-2,6-dimethylbenzene (16%), and 1,2-bis(lithiomethyl)-3-methylbenzene (31%). By analogy it would be expected that a range of different mono- and di-lithiated products should be formed from 1,2,3,4-tetramethylbenzene. The presence of the strongly *ortho*-directing methoxy group in 3,4-dimethylanisole suggested that deprotonation would occur on the ring rather than on the methyl groups and interestingly therefore a quinodimethane should not be formed.

Preparation of Ruthenium Complexes.—Reaction of a 2 molar excess of the lithium reagents, derived from the methyl substituted benzenes described above, with $[RuCl_2L_4]$ ($L = PMe_3$ or $PMePh_2$) leads smoothly after work-up to orange microcrystalline solids which can be identified as *o*-quinodimethane complexes by their spectroscopic properties (Tables 1 and 2). It proved extremely difficult to remove the last traces of the high-boiling parent organic hydrocarbons so that often microanalytical data for these compounds are not as accurate as desired. The presence of traces of the parent organic hydrocarbons was confirmed in many cases by ^1H n.m.r. spectroscopy although the amounts were very small. Although substituted *o*-quinodimethanes can be prepared for $L = PMe_3$ or $PMePh_2$ in which bonding is intermediate between (σ^2,π) and (π^2), attempts to extend the chemistry to prepare purely π^2 complexes using auxiliary ligands which can be classed as better π acceptors, *e.g.* $L = P(OPh)_3$, were unsuccessful. The product of reaction of the tmen adduct of 1-lithiomethyl-2-methylbenzene with $[RuCl_2\{P(OPh)_3\}_4]$ did not contain the *o*-quinodimethane ligand. Spectroscopic properties suggest that it is $[RuH\{C_6H_4OP(OPh)_2\}\{P(OPh)_3\}_3]$ containing an ortho-metallated triphenyl phosphite ligand.

Reaction of the lithium salt of 3,4-dimethylanisole with $[RuCl_2(PMe_3)_4]$ yields a white crystalline compound of stoicheiometry $[Ru(C_6H_2Me_2OCH_2)(PMe_3)_4]$. The n.m.r. spectra clearly indicate that it is not an *o*-quinodimethane complex but rather that it contains a metallacycle with binding through a ring carbon and the carbon of the CH_2O group. A similar product has been obtained from the reaction of $Mg(2\text{-}MeOC_6H_4)_2$, $[Ru(CO_2Me)_4Cl]$, and PMe_3.[10]

Spectroscopic Properties.—(a) o-*Quinodimethane complexes.* The ^{31}P n.m.r. data for the new complexes are collected in Table 1 and for the complexes derived from 1,2,4,5-tetramethylbenzene show two resonances indicating a plane of symmetry through the molecule as expected for the only possible *o*-quinodimethane [structure (**1**)]. For the complexes derived from 1,2,3-trimethylbenzene there is no plane of symmetry [structure (**2**)] so that all the phosphorus atoms are inequivalent. It is interesting that this complex is rendered chiral by the additional ring methyl group since it is not superimposable on its mirror image. Of the various *o*-quinodimethane complexes that we have examined only those derived from 1,2,3,4-tetramethylbenzene have the possibility of giving more than one product, either symmetrical (1—α,2—α'-η^4-3,6-dimethylquinodimethane), (**3**), or unsymmetrical (1—α,2—α'-η^4-3,4-dimethylquinodimethane), (**4**). Examination of the ^{31}P n.m.r. spectrum of the

Table 1. ^{31}P N.m.r. data for the new quinodimethane complexes

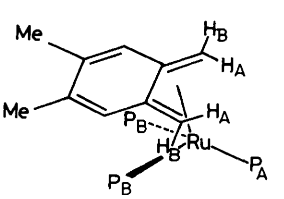
Compound	Chemical shifts* (δ)			Coupling constants (J/Hz)		
	P_A	P_B	P_C	P_AP_B	P_AP_C	P_BP_C
$[Ru\{CH_2(C_6H_2Me_2\text{-}2,3)CH_2\}(PMePh_2)_3]$	35.18 (s)	21.45 (d)		<2	—	—
$[Ru\{CH_2(C_6H_2Me_2\text{-}2,3)CH_2\}(PMe_3)_3]$	13.97(t)	−5.46 (d)		7.27	—	—
$[Ru\{CH_2(C_6H_3Me\text{-}1)CH_2\}(PMePh_2)_3]$	35.82 (s)	17.87 (d)	16.40 (d)	<2	<2	22.51
$[Ru\{CH_2(C_6H_3Me\text{-}1)CH_2\}(PMe_3)_3]$	14.25 (t)	−7.60 (dd)	−11.25 (dd)	8.48	8.37	29.46
$[Ru\{CH_2(C_6H_2Me_2\text{-}1,4)CH_2\}(PMe_3)_3]$	14.25 (t)	−10.85 (d)		7.92	—	—
$[Ru\{CH_2(C_6H_2Me_2\text{-}1,2)CH_2\}(PMe_3)_3]$	14.79 (t)	−7.62 (dd)	−7.89 (dd)	7.36	8.01	29.13

* Chemical shifts in p.p.m. to high frequency of external 85% H_3PO_4, measured in[$^2H_6$]benzene at 298 K.

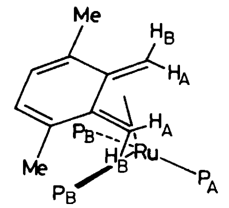
Table 2. Selected proton n.m.r. data for the new quinodimethane complexes[a]

Compound	δ(J_{PH}/Hz)					J(HH)
	P_AMe	P_BMe	P_CMe	CH_{exo}	CH_{endo}	
$[Ru\{CH_2(C_6H_2Me_2\text{-}2,3)CH_2\}(PMePh_2)_3]$	2.24 (d) (7.0)	1.73 (vd) (4.4)[b]		1.96 (dd) (6.1)	0.73 (dd) (7.1)	3.4
$[Ru\{CH_2(C_6H_2Me_2\text{-}2,3)CH_2\}(PMe_3)_3]$	1.45 (d) (7.3)	1.03 (vd) (5.3)[b]		1.95 (dd) (5.6)	0.00 (dd) (7.0)	3.5
$[Ru\{CH_2(C_6H_3Me\text{-}1)CH_2\}(PMePh_2)_3]$	2.28 (d) (7.1)	1.71 (d) (5.2)	1.51 (d) (5.2)	2.33 (m), 1.98 (m)	0.64 (m), 0.27 (m)	
$[Ru\{CH_2(C_6H_2Me\text{-}1)CH_2\}(PMe_3)_3]$	1.44 (d) (7.8)	1.07 (d) (6.1)	1.04 (d) (6.1)	2.17 (m), 1.91 (m)	−0.16 (m), −0.22 (m)	
$[Ru\{CH_2(C_6H_2Me_2\text{-}1,2)CH_2\}(PMe_3)_3]$	1.42 (d) (7.8)	1.03 (d) (5.8)	0.95 (d) (6.0)	2.21 (m), 1.88 (m)	−0.23 (br m)	

[a] Chemical shifts to high frequency of $SiMe_4$, measured in C_6D_6 at 298 K using C_6D_5H (δ 7.27) as internal reference; s = singlet, d = doublet, t = triplet, m = multiplet, and v = virtual. [b] $J_{PH} + J_{P'H}$.



(1)



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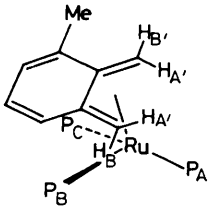

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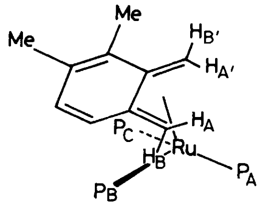

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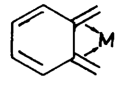
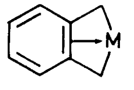


π^2

(I)

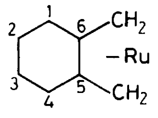


σ^2,π

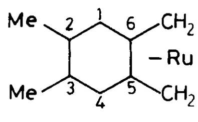
(II)

reaction solution shows the presence of both products in the approximate ratio 1:2, suggesting therefore that neither the deprotonation of 1,2,3,4-tetramethylbenzene nor the subsequent metallation reaction show any regiospecificity. Crystallization yields only the unsymmetrical complex, the symmetrical complex remaining in solution. The ^{1}H n.m.r. spectra (Table 2)

Table 3. ^{13}C N.m.r. shifts for ring C atoms of *o*-quinodimethane complexes



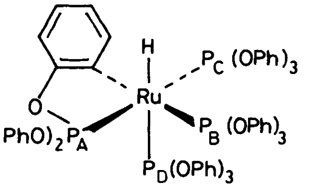
(III)



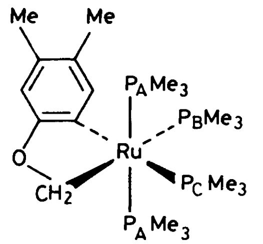
(IV)

Carbons	δ (p.p.m.)	
	(III)	(IV)
C^5,C^6	101.65	100.32
C^1,C^4	131.65	131.06
C^2,C^3	122.97	130.64

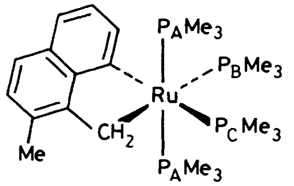
of all the products show the high-field multiplet or multiplets arising from the *endo* hydrogens of the CH_2 groups together with a multiplet (or multiplets) near δ 2.0 arising from the *exo* CH_2 groups. In addition singlets are observed for the methyl groups on the ring and doublets and virtual doublets (from $H_nPP'H'_n$ type spin systems[11]) from the methyl groups of phosphorus. In the ^{13}C n.m.r. spectra the chemical shifts of the quaternary carbon atoms of the *o*-xylidene moieties attached to the metal (*ca.* 100 p.p.m.) suggest that the bonding is similar to that in the unsubstituted *o*-xylidene complexes of ruthenium[5] and therefore the metal–ligand interaction can be described as intermediate between pure diene-like bonding (π^2), (**I**), and bonding *via* two localized M–C bonds and a localized double bond in the *o*-xylidene ring (σ^2,π), (**II**). Comparison of the ^{13}C n.m.r. spectrum of $[Ru(CH_2C_6H_4CH_2)(PMe_3)_3]$ with that of $[Ru\{CH_2(C_6H_2Me_2\text{-}2,3)CH_2\}(PMe_3)_3]$ allows the unequivocal assignment of all the resonances of the ring carbon atoms



(5)



(6)



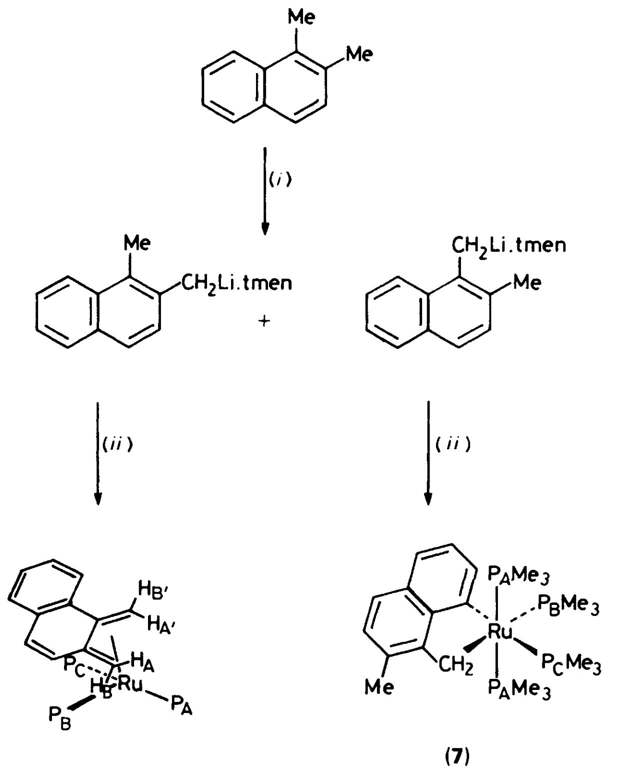
(7)

which was not possible from the data for the unsubstituted *o*-quinodimethane complex alone.

These arguments are displayed in Table 3 and are based on the fact that the C^2 and C^3 carbons for the complex derived from 1,2,4,5-tetramethylbenzene are quaternary C atoms. The upfield shift of these resonances on substitution of Me for H is expected on account of the mesomeric effects in the aromatic ring.

(b) [$RuH\{C_6H_4OP(OPh)_2\}\{P(OPh)_3\}_3$]. The second-order ^{31}P n.m.r. spectrum of the product obtained from the reaction of the tmen adduct of 1-lithiomethyl-2-methylbenzene and [$RuCl_2\{P(OPh)_3\}_4$] (see Experimental section) can be simulated with resonances from four inequivalent phosphorus atoms, two of them mutually *trans*. One of these must be the resonance from the phosphorus of the *o*-metallated phosphite and because of the expected high-frequency shift for a phosphorus atom in a five-membered ring[12] we assign this as giving rise to the resonance at δ 163.3 p.p.m. In the ^1H n.m.r. spectrum the hydride resonates as a doublet of quartets with a large coupling to one of the phosphorus atoms and hence the complex has structure (5). As expected then the phosphorus atom *trans* to H resonates to higher field than any of the others in the ^{31}P n.m.r. spectrum.[13]

(c) [$Ru(CH_2OC_6H_2Me_2)(PMe_3)_4$]. The complex obtained from reaction of the lithiated form of 3,4-dimethylanisole with [$RuCl_2(PMe_3)_4$] (see Experimental section) has spectroscopic properties very similar to those reported for [$Ru(CH_2OC_6H_4)(PMe_3)_4$],[10] suggesting structure (6). The ^1H n.m.r. spectrum shows methylene hydrogens giving a well defined first-order pattern of a 1:2:1 triplet ($^3J_{PH}$ = 14.28 Hz) of doublets of doublets ($^3J_{PH}$ = 3.67 and 1.70 Hz respectively). The triplet structure can be ascribed to splitting by the two mutually *trans* phosphorus atoms and the doublet of doublets from the two *cis* non-equivalent atoms. The *cis*-P coupling with CH_2 is thus apparently greater than the *trans*-P coupling. The ^{31}P n.m.r. spectrum is consistent with structure (6), and has two triplets of doublets arising from the *cis* non-equivalent phosphines. The two *trans* equivalent phosphines give a doublet of doublets ($^2J_{PP}$ = 24.52 and 28.10 Hz) as coupling to each of the mutually *cis* phosphorus atoms is slightly different.



Scheme. Proposed mechanism for the formation of observed products from [$RuCl_2(PMe_3)_4$] and lithiated 1,2-dimethylnaphthalene. For conditions see ref. 8. (*i*) LiBu^n·tmen, (*ii*) [$RuCl_2(PMe_3)_4$]

(d) *Product from the reaction of lithiated* 1,2-*dimethylnaphthalene with* [$RuCl_2(PMe_3)_4$]. We have previously reported that lithiated 1,2-dimethylnaphthalene reacts with [$RuCl_2(PMe_3)_4$] to give two products, one of which contains co-ordinated 1,2-naphthoquinodimethane. The other product was formulated as the metallacycle [$Ru(CH_2C_{10}H_6CH_2)(PMe_3)_4$] in which the *o*-naphthoquinodimethane was co-ordinated by two σ bonds to the metal. However close study of the ^1H n.m.r. parameters of a recrystallized sample of this compound shows that this formulation is incorrect. In particular, the multiplet observed at δ 1.99 is not present for the purified sample whilst a single at δ 2.84 (intensity 3 H), which was originally thought to arise from an impurity, is retained. In addition, the aromatic region of the spectrum has resonances from only five hydrogens.

The spectra of the purified sample are clearly more consistent with the structure (7), which could readily be formed by initial lithiation of the 1-methyl group, metathesis with the Ru–Cl bond, and subsequent metallation (possibly *via* deprotonation) of the C–H bond on C^8. A similar metallacycle formation from a naphthylmethyl platinum complex has previously been reported.[14] The 1,2-naphthoquinodimethane complex obtained in the ruthenium system probably arises from initial lithiation on the 2-methyl group. These reactions are outlined in the Scheme.

Experimental

Microanalyses were carried out by St. Andrews University Laboratories. N.m.r. spectra were recorded on Bruker WP-80, AM-300, and Varian CFT-20 spectrometers. All manipulations were carried out under dry deoxygenated nitrogen using standard Schlenk-line and catheter-tubing techniques. All solvents were thoroughly dried by distillation from sodium diphenylketyl and degassed before use. The light petroleum had a boiling range of 40—60 °C.

The compounds trimethylphosphine,[15] methyldiphenylphosphine,[16] $[\mathrm{RuCl_2(PPh_3)_3}]$,[17] $[\mathrm{RuCl_2(PPh_2Me)_4}]$,[18] $[\mathrm{RuCl_2(PMe_3)_4}]$,[19,20] and $[\mathrm{RuCl_2\{P(OPh)_3\}_4}]$[21] were prepared by standard literature methods.

Preparation of Lithium Reagents.—To a stirred solution of $\mathrm{LiBu^n}$ in hexane (6 cm^3, 1.6 mol dm^{-3}, 9.6×10^{-3} mol) cooled to 0 °C was added tmen (3.0 cm^3, 19.8×10^{-3} mol). After 15 min the appropriate organic precursor (10×10^{-3} mol) was added in light petroleum (40 cm^3). After a further 15 min the ice-bath was removed and the mixture allowed to stir for a further 24 h. Where possible the light petroleum was removed by filtration and the lithium salt dissolved in diethyl ether.

(5—α,6—α′-η-2,3-*Dimethyl*-5,6-*dimethylenecyclohexa*-1,3-*diene*)*tris*(*methyldiphenylphosphine*)*ruthenium*(0).—The complex $[\mathrm{RuCl_2(PMePh_2)_4}]$ (1.0 g, 1.028×10^{-3} mol) was stirred with a solution of the tmen adduct of 1-lithiomethyl-2,4,5-trimethylbenzene (2.5×10^{-3} mol) in diethyl ether. After 24 h, water (20 cm^3) was added and after shaking vigorously and allowing to settle the ether layer was decanted and dried over anhydrous magnesium sulphate. The diethyl ether was removed *in vacuo*. Excess of 1,2,4,5-tetramethylbenzene and methyldiphenylphosphine were removed by sublimation *in vacuo* at 120 °C onto a cold-finger (−78 °C). The resulting orange gum was dissolved in hot light petroleum (b.p. 80—100 °C). After filtration and concentration the product separated as a yellow-orange powder which was collected and dried *in vacuo*. Yield 0.27 g (31%). ^{1}H N.m.r. ([^{2}H$_6$]benzene, 298 K):* δ 7.83—6.70 (complex, aromatic); 2.24 (d, $^2J_{\mathrm{PH}}$ 6.97, P$_\mathrm{A}$Me), 2.22 (s, CH$_3$), 1.96 (dd, $^2J_{\mathrm{HH}}$ 3.44, $^3J_{\mathrm{PH}}$ 6.13, H$_\mathrm{B}$), 1.73 (vd, $^2J_{\mathrm{PH}} + {}^4J_{\mathrm{PH}}$ 4.37, P$_\mathrm{B}$Me), and 0.73 (ddd, $^2J_{\mathrm{HH}}$ 3.44, $^3J_{\mathrm{PH}}$ 7.08 Hz, H$_\mathrm{A}$) (Found: C, 69.25; H, 6.10. $\mathrm{C_{49}H_{51}P_3Ru}$ requires C, 70.55; H, 6.15%).

The following complexes were similarly prepared.

(5—α,6—α′-η-2,3-*Dimethyl*-5,6-*dimethylenecyclohexa*-1,3-*diene*)*tris*(*trimethylphosphine*)*ruthenium*(0).—From $[\mathrm{RuCl_2(PMe_3)_4}]$ (0.55 g, 1.155×10^{-3} mol) and the tmen adduct of 1-lithiomethyl-2,4,5-trimethylbenzene (3.0×10^{-3} mol). After work-up the yellow gum was dissolved in light petroleum. After filtration, concentration, and cooling to −30 °C the product separated as yellow crystals, which were collected and dried *in vacuo*. Yield 0.19 (36%). ^{1}H N.m.r. ([^{2}H$_6$]benzene, 298 K): δ 7.22 (s, 2 H), 2.28 (s, CH$_3$), 1.95 (dd, $^2J_{\mathrm{HH}}$ 3.52, $^3J_{\mathrm{PH}}$ 5.58, H$_\mathrm{B}$), 1.45 (d, $^2J_{\mathrm{PH}}$ 7.34, P$_\mathrm{A}$Me), 1.03 (vd, $^2J_{\mathrm{PH}} + {}^4J_{\mathrm{PH}} = 5.28$, P$_\mathrm{B}$Me), and 0.00 (dd, $^2J_{\mathrm{HH}}$ 3.52, $^3J_{\mathrm{PH}}$ 7.04 Hz, H$_\mathrm{A}$) (Found: C, 50.85; H, 8.85. $\mathrm{C_{19}H_{39}P_3Ru}$ requires C, 49.45; H, 8.5%).

(5—α,6—α′-η-1-*Methyl*-5,6-*dimethylenecyclohexa*-1,3-*diene*)*tris*(*methyldiphenylphosphine*)*ruthenium*(0).—From $[\mathrm{RuCl_2(PMePh_2)_4}]$ (1.0 g, 1.028×10^{-3} mol) and the lithium salt of 1,2,3-trimethylbenzene (2.5×10^{-3} mol). After work-up the orange gum was dissolved in toluene. After filtration and concentration the product separated as orange crystals, which were collected and dried *in vacuo*. Yield 0.41 g (40%). ^{1}H N.m.r. ([^{2}H$_6$]benzene, 298 K): δ 7.80—6.55 (complex, aromatic), 2.33 (br m, H$_\mathrm{B}$), 2.28 (d, $^2J_{\mathrm{PH}}$ 7.10, P$_\mathrm{A}$Me), 2.22 (s, CH$_3$), 1.98 (m br, H$_\mathrm{B}'$), 1.71 (d, $^2J_{\mathrm{PH}}$ 5.17, P$_\mathrm{B}$Me), 1.51 (d, $^2J_{\mathrm{PH}}$ 5.24 Hz, P$_\mathrm{C}$Me), 0.64 (br m, H$_\mathrm{A}'$), and 0.27 (m br, H$_\mathrm{A}$) (Found: C, 71.40; H, 6.25. $\mathrm{C_{48}H_{49}P_3Ru}$ requires C, 70.30; H, 6.05%).

(5—α,6—α′-η-1-*Methyl*-5,6-*dimethylenecyclohexa*-1,3-*diene*)-*tris*(*trimethylphosphine*)*ruthenium*(0).—From $[\mathrm{RuCl_2(PMe_3)_4}]$ (0.55 g, 1.155×10^{-3} mol) and the lithium salt of 1,2,3-trimethylbenzene (3.0×10^{-3} mol). After work-up the yellow oil was dissolved in light petroleum. After filtration, concentration, and cooling to −30 °C the product separated as yellow crystals which were collected and dried *in vacuo*. Yield 0.21 g (41%). ^{1}H N.m.r. ([^{2}H$_6$]benzene, 298 K): δ 7.44—6.98 (3 H), 2.27 (s, CH$_3$), 2.17 (br m, H$_\mathrm{B}$), 1.91 (br m, H$_\mathrm{B}'$), 1.44 (d, $^2J_{\mathrm{PH}}$ 7.81, P$_\mathrm{A}$Me), 1.07 (d, $^2J_{\mathrm{PH}}$ 6.10, P$_\mathrm{B}$Me), 1.04 (d, $^2J_{\mathrm{PH}}$ 6.10 Hz, P$_\mathrm{C}$Me), −0.16 (br m, H$_\mathrm{A}'$), and −0.22 (br m, H$_\mathrm{A}$) (Found: C, 49.00; H, 8.65. $\mathrm{C_{18}H_{37}P_3Ru}$ requires C, 48.30; H, 8.35%).

(5—α,6—α′-η-1,2-*Dimethyl*-5,6-*dimethylenecyclohexa*-1,3-*diene*)*tris*(*trimethylphosphine*)*ruthenium*(0).—From $[\mathrm{RuCl_2(PMe_3)_4}]$ (0.55 g, 1.155×10^{-3} mol) and the lithium salt of 1,2,3,4-tetramethylbenzene (3.0×10^{-3} mol). After work-up the yellow oil was examined by ^{31}P n.m.r. spectroscopy and shown to contain both the required compound and (5—α,6—α-η-1,4-dimethyl-5,6-dimethylenecyclohexa-1,3-diene)tris(trimethylphosphine)ruthenium(0) in the approximate ratio 2:1. The yellow oil was dissolved in light petroleum. After filtration, concentration and cooling to −30 °C, the product separated as yellow crystals which were collected and dried *in vacuo*. Yield 0.12 g (23%). ^{1}H N.m.r. ([^{2}H$_6$]benzene, 298 K); δ 7.44—6.84 (2 H); 2.40 (s, CH$_3$), 2.28 (s, CH$_3$), 2.21 (br m, H$_\mathrm{B}$), 1.88 (br m, H$_\mathrm{B}'$), 1.42 (d, $^2J_{\mathrm{PH}}$ 7.8, P$_\mathrm{A}$Me), 1.03 (d, $^2J_{\mathrm{PH}}$ 5.8, P$_\mathrm{B}$Me), 0.95 (d, $^2J_{\mathrm{PH}}$ 6.0 Hz, P$_\mathrm{C}$Me), and −0.23 (br m, H$_\mathrm{A}'$, H$_\mathrm{A}$) (Found: C, 49.65; H, 8.85. $\mathrm{C_{19}H_{39}P_3Ru}$ requires C, 49.45; H, 8.50%).

$[\mathrm{RuH\{C_6H_4OP(OPh)_2\}\{P(OPh)_3\}_3}]$.—From $[\mathrm{RuCl_2\{P(OPh)_3\}_4}]$ (1.412 g, 1.0×10^{-3} mol) and the tmen adduct of 1-lithiomethyl-2-methylbenzene. After 24 h, water (20 cm^3) was added to the solution and after shaking vigorously and allowing to stand the ether layer was decanted and dried over anhydrous magnesium sulphate. The diethyl ether was removed *in vacuo*. The residual pale orange oil was dissolved in toluene. After filtration and addition of light petroleum a grey-white powder was obtained. Recrystallization from toluene yielded a white crystalline solid which was collected and dried *in vacuo*. Yield 0.83 g (62%), ν(Ru–H) 1910 cm^{-1}. N.m.r. ([^{2}H$_6$]benzene, 298 K): ^{1}H, δ 8.82—6.68 (complex, aromatic), 2.3 (s, toluene of crystallization), and −7.8 (dq, $^2J_{\mathrm{PH}}$ 129.79, 21.65, 25.79, 21.95 Hz, Ru–H); ^{31}P-{^{1}H}, δ 163.28 [ddd, ^2J(P$_\mathrm{A}$P$_\mathrm{C}$) 641.95, ^2J(P$_\mathrm{A}$P$_\mathrm{B}$) 57.91, ^2J(P$_\mathrm{A}$P$_\mathrm{D}$) 39.09, P$_\mathrm{A}$], 138.96 [pq, ^2J(P$_\mathrm{B}$P$_\mathrm{A}$) 57.91, ^2J(P$_\mathrm{B}$P$_\mathrm{C}$) 49.06, ^2J(P$_\mathrm{B}$P$_\mathrm{D}$) 46.16, P$_\mathrm{B}$], 138.38 [ddd, ^2J(P$_\mathrm{C}$P$_\mathrm{A}$) 641.95, ^2J(P$_\mathrm{C}$P$_\mathrm{B}$) 49.06, ^2J(P$_\mathrm{C}$P$_\mathrm{D}$) 46.25, P$_\mathrm{C}$], and 126.69 p.p.m. [q, ^2J(P$_\mathrm{D}$P$_\mathrm{A}$) 39.09, ^2J(P$_\mathrm{D}$P$_\mathrm{C}$) 46.25, ^2J(P$_\mathrm{D}$P$_\mathrm{B}$) 46.16 Hz, P$_\mathrm{D}$] (Found: C, 66.25; H, 4.25. $\mathrm{C_{72}H_{60}O_4P_4Ru{\cdot}C_6H_5CH_3}$ requires C, 66.15; H, 4.80%).

$[\mathrm{Ru(CH_2OC_6H_2Me_2)(PMe_3)_4}]$.—From $[\mathrm{RuCl_2(PMe_3)_4}]$ (0.55 g, 1.155×10^{-3} mol) and the lithium salt of 3,4-dimethylanisole (3.0×10^{-3} mol). After 24 h, water (20 cm^3) was added to the solution and after shaking vigorously and allowing to stand the ether layer was decanted and dried over anhydrous magnesium sulphate. Concentration of the ether solution yielded a white-grey solid. Upon recrystallization from diethyl ether white crystals were obtained which were collected and dried *in vacuo*. Yield 0.29 g (47%). N.m.r. ([^{2}H$_6$]benzene, 298 K): ^{1}H, δ 7.56 (s br, aromatic H), 7.00 (s, aromatic H), 5.29 (tdd, $^3J_{\mathrm{PH}}$ 14.28, 3.67, 1.70, OCH$_2$), 1.31 (d, $^2J_{\mathrm{PH}}$ 4.64, PMe), 1.17 (pt, $^2J_{\mathrm{PH}} + {}^4J_{\mathrm{PH}}$ 5.37, PMe), and 1.05 (d, $^2J_{\mathrm{PH}}$ 5.37 Hz, PMe); ^{31}P-{^{1}H}, δ −5.39 [dd, ^2J(P$_\mathrm{A}$P$_\mathrm{B}$) 24.52, ^2J(P$_\mathrm{A}$P$_\mathrm{C}$) 28.10, P$_\mathrm{A}$], −13.22 [dt, ^2J(P$_\mathrm{B}$P$_\mathrm{A}$) 24.52 Hz, ^2J(P$_\mathrm{B}$P$_\mathrm{C}$) 14.70, P$_\mathrm{B}$], −19.13

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* p = Pseudo, referring to an accidental equivalence of coupling constants; v = virtual, referring to a second-order spectrum.

[dt, ${}^2J(P_CP_A)$ 28.10, ${}^2J(P_CP_B)$ 14.70 Hz, P_C] (Found: C, 47.00; H, 8.95. $C_{21}H_{46}OP_4Ru$ requires C, 46.75; H, 8.60%).

$[Ru\{C_{10}H_5MeCH_2\}(PMe_3)_4]$.—The experimental details have previously been documented.[8] Yield 0.07 g (11%). N.m.r. ($[{}^2H_6]$benzene, 298 K): ${}^1H$, δ 7.96—7.41 (5 aromatic H), 2.84 (s, CH_3), 2.41 (m, ${}^3J_{PH}$ 4.67, 4.67, 8.27, 8.82, CH_2), 1.37 [d, ${}^2J_{PH}$ 4.64, $P_C(CH_3)_3$], 1.23 [d, ${}^2J_{PH}$ 5.37, $P_B(CH_3)_3$], and 0.81 [pt, ${}^2J_{PH} + {}^4J_{PH}$ 5.13 Hz, $P_A(CH_3)_3$]; ${}^{13}C$-$\{{}^1H\}$, δ 26.25 [d, ${}^1J_{PC}$ 14.08, $P_C(CH_3)_3$], 24.40 [d, ${}^1J_{PC}$ 15.26, $P_B(CH_3)_3$], 22.19 (pdq, ${}^2J_{PC}$ 9.24, 9.23, 9.23, 52.98, CH_2), 20.51 (s, CH_3), 20.13 [pt, ${}^1J_{PC} + {}^3J_{PC}$ 36.38 Hz, $P_A(CH_3)_3$], ${}^{31}P$-$\{{}^1H\}$, δ −4.59 [pt, ${}^2J(P_AP_C)$ 27.5, ${}^2J(P_AP_B)$ 25.5 Hz, P_A], −13.13 [dt, ${}^2J(P_BP_C)$ 13.8, ${}^2J(P_BP_A)$ 25.5, P_B], −19.27 [dt, ${}^2J(P_CP_B)$ 13.8, ${}^2J(P_CP_A)$ 27.5 Hz, P_C] (Found: C, 51.8; H, 8.2. $C_{24}H_{46}P_3Ru$ requires C, 51.5; H, 8.3%).

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References

1 W. Roth and J. D. Meier, *Tetrahedron Lett.*, 1967, 2053.
2 M. A. Bennett, I. J. McMahon, and T. W. Turney, *Angew. Chem., Int. Edn. Engl.*, 1982, **21**, 379.
3 W. H. Hersch, F. J. Hollander, and R. G. Bergman, *J. Am. Chem. Soc.*, 1983, **105**, 5834.
4 J. W. Hull and W. L. Gladfelter, *Organometallics*, 1982, **1**, 1761.
5 S. D. Chappell, D. J. Cole-Hamilton, A. M. R. Galas, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1982, 1867.
6 J-M. Grosselin, H. Le Bozec, C. Moinet, F. Kohler, L. Toupet, and P. H. Dixneuf, *Organometallics*, 1988, **7**, 88.
7 D. Astruc, *Acc. Chem. Res.*, 1986, **19**, 377.
8 N. J. Simpson and D. J. Cole-Hamilton, *Polyhedron*, 1988, **7**, 1945.
9 J. Klein and A. Medlik-Balan, *J. Am. Chem. Soc.*, 1977, **99**, 1473.
10 R. A. Jones and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1979, 472.
11 R. K. Harris, *Can. J. Chem.*, 1964, **42**, 2275.
12 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.
13 T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335.
14 J. A. Duff, B. L. Shaw, and B. L. Turtle, *J. Organomet. Chem.*, 1974, **66**, C18.
15 W. Wolfsberger and H. Schmidbaur, *Synth. React. Inorg. Metal-Org. Chem.*, 1974, **4**, 149.
16 M. A. Mathur, W. H. Myers, H. H. Sisler, and G. E. Ryschkewitsch, *Inorg. Synth.*, 1974, **15**, 129.
17 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945.
18 P. W. Armit and T. A. Stephenson, *J. Organomet. Chem.*, 1973, **57**, C80.
19 R. A. Jones, F. Mayor Real, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, and K. M. Abdul Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 511.
20 J. S. Bradley, S. J. Simpson, and G. Wilkinson, unpublished work.
21 J. J. Levinson and S. D. Robinson, *J. Chem. Soc. A*, 1970, 639.

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