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Cyclopentadienyl-ruthenium and -osmium chemistry

XXXVI *. Oligomerisation of phenylacetylide residues on ruthenium. Crystal structures of $\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_8Ph_4)$ and $\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2\{\mu\text{-}C_{10}Ph_4(C_6H_4)\}$

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Abstract

Reactions between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and AgC_2Ph afforded a deep blue binuclear complex, shown by X-ray crystallography to contain a planar tricyclic diruthenadicyclobutadieno[*a*,*c*]benzene system, formed by tetramerisation of phenylacetylide residues at the ruthenium centres. A deep purple complex, isolated in small yield from the same reaction, was similarly shown to contain a diruthenapentacyclic system, formed by an unprecedented oligomerisation of five phenylacetylide units. Related reactions have given $[\{Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)\}_2Ag][PF_6]$ and the divinylidene $[\{Ru(PPh_3)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_4Ph_2)][PF_6]_2$.

Introduction

Transition metal-induced oligomerisation reactions of alkynes have been known for many years and have proved to be a continuing source of exotic complexes containing ligands formed from the alkynes, sometimes with incorporation of other groups present on the metal, such as CO or isocyanides [2]. Development of many of these reactions into sources of organic materials often followed, and sometimes preceded, an understanding of the mechanisms of the metal-based reactions. Few of these reactions resulted in combination of more than three molecules of alkyne, although the tetramerisation to cyclooctatetraenes is an old example, only relatively recently understood [3]. We have described well-characterised tri- and tetra-mers of $C_2(CO_2Me)_2$ formed at an $Ru(\eta\text{-}C_5H_5)$ centre [4], while related reactions at dinuclear centres have also been reported [5].

The oxidative coupling of acetylide groups, usually using a copper(I) intermediate, is a well established synthetic method, either as the Glaser reaction [6] or

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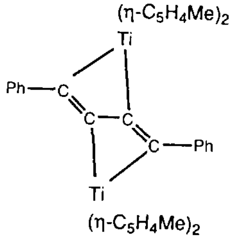
* For Part XXXV, see ref. 1.



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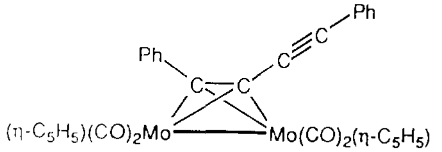

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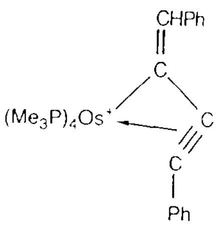
later, the Cadiot–Chodkiewicz modification [7]. There is an increasing number of transition metal-centred couplings of acetylide fragments, which have also given unusual unsaturated C_4 ligands. The reaction between NaC_2Ph and $TiCl_2(\eta\text{-}C_5H_4Me)_2$ gave complex **1** containing two $Ti(\eta\text{-}C_5H_4Me)_2$ moieties attached to 1,4-diphenyl-1,3-butadiyne [8]; the same diyne was found in **2**, which was formed when $Mo(C_2Ph)(CO)_3(\eta\text{-}C_5H_5)$ was heated [9]. Oxidative coupling of two PhC_2 ligands was observed on osmium, the reaction between *cis*-$Os(C_2Ph)_2(PMe_3)_4$ with $AgPF_6$ affording $Os(\eta^3\text{-}PhC{\equiv}CC{=}CHPh)(PMe_3)_4$ (**3**) [10]. Similar products have been obtained from reactions between 1-alkynes and $FeX_2(dmpe)_2$ ($X_2 = Cl_2$ [11], $[H(H_2)]^+$ [12]) or $RuH_4(cyttp)$ (cyttp = $PPh\{(CH_2)_3PCy_2\}_2$) [13]. Related reactions are also suggested as an alternative explanation for the formation of the cumulene derivative **4** from HC_2CF_3 and a ruthenium precursor [14]. Nickel acetylide complexes have been found to undergo thermally induced rearrangements in which three acetylide residues have combined [15]. Thus, oxidative addition of ClC_2SiMe_3 to Ni^0 complexes gave $NiCl(C_2SiMe_3)(PMe_3)_2$, which, after halide exchange, afforded $NiX\{C(C_2SiMe_3){=}C(SiMe_3)(C_2SiMe_3)\}(PMe_3)_2$ (**5**) (Scheme 1) on heating in the solid state. Interestingly, substitution of halide by $LiC_2{}^tBu$ gave *trans*-$Ni(C^tBu)\{C(C_2SiMe_3){=}C(SiMe_3)(C_2SiMe_3)\}(PMe_3)_2$ (**6**), which under CO reductively eliminated the unusual olefin $(Me_3Si)(Me_3SiC_2)C{=}C(C_2{}^tBu)(C_2SiMe_3)$ (**7**) by coupling of *sp* and sp^2 carbons. Simple coupling of acetylide and vinyl ligands has been known since 1977 when vinylacetylide ligands were obtained from $MX(O_2CCF_3)(CO)(PPh_3)_2$ (M = Ru, Os; X = H or CF_3CO_2) and phenylacetylene, possibly by reaction of $M(C_2Ph)(O_2CCF_3)(CO)(PPh_3)_2$ with more HC_2Ph [16]; these complexes were also obtained from the hydride and PhC_2C_2Ph. However, to our knowledge there are no examples of reactions in which more than three acetylide moieties have been oligomerised at a transition metal centre.



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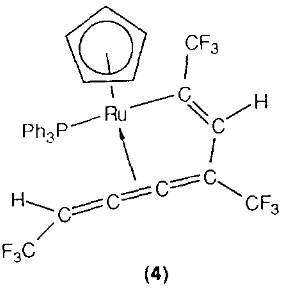

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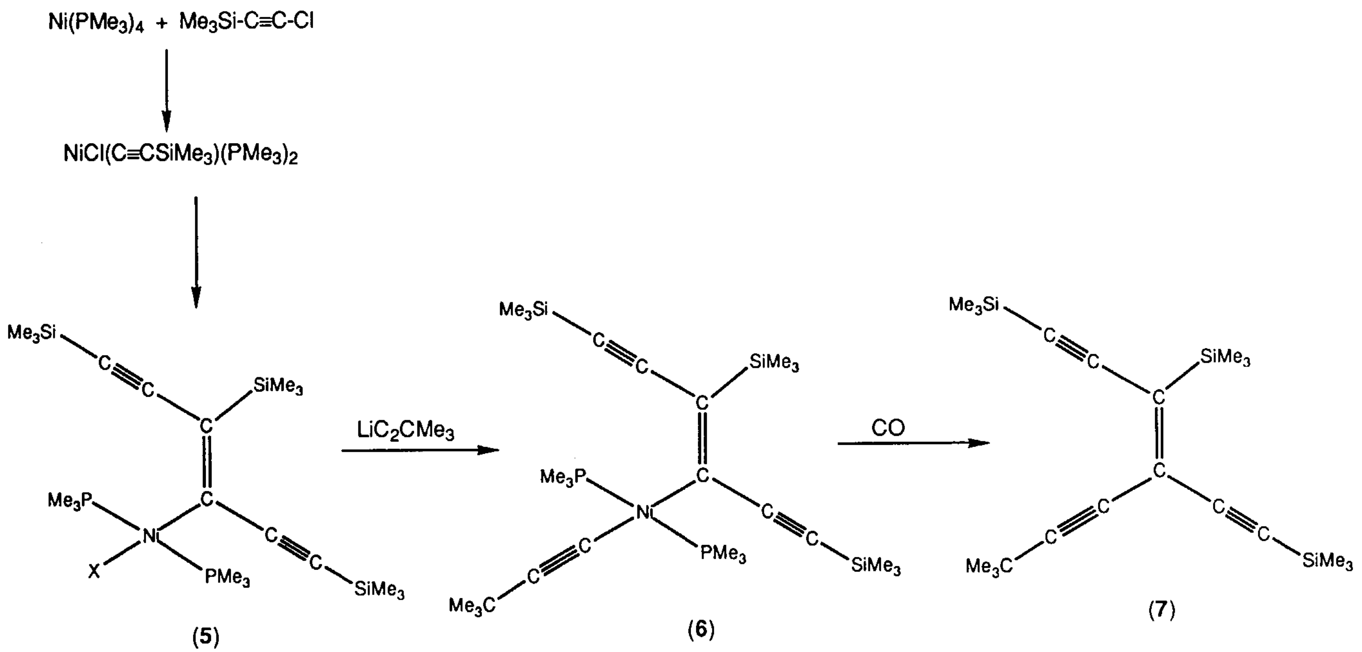
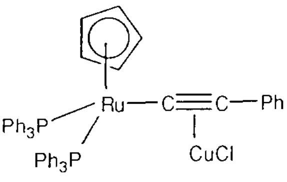

Ni(PMe3)4 + Me3Si-C≡C-Cl
NiCl(C≡CSiMe3)(PMe3)2
LiC2CMe3
CO
Me3Si
SiMe3
Me3P
PMe3
X
Ni
Me3C
(5)
(6)
(7)

Scheme 1

Several years ago, we described the reactions of copper(I) acetylides with a variety of transition metal halide complexes [17]. Among these were reactions with $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ which gave the first examples of η^2-alkyne-copper(I) complexes **8**, subsequently obtained by direct reactions between the acetylides and copper(I) halides [18]. We have now investigated similar reactions of silver(I) phenylacetylide and found that these take a completely different course to afford unusual dimetalla-polycyclic systems which form the subject of this paper.



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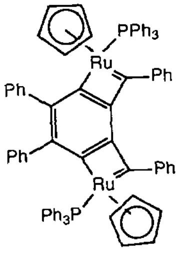
Results and discussion

The reaction between AgC_2Ph and $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ in refluxing toluene gave a dark coloured solution over a silver mirror. Chromatographic separation afforded several products, of which dark blue **9** and dark purple **10** have been crystallographically characterised. The best yields of **9** were obtained by quenching the reaction when spot TLC analysis showed that all the chloro complex had been consumed. Continued heating of **9** in refluxing toluene resulted in complete decomposition after 30 min, as shown independently; the products were not identified. Complex **10** was always obtained as a minor product from the synthesis of **9**.

The molecular structure of **9** is shown in Fig. 1 and important bond distances are collected in Table 1. Two $Ru(PPh_3)(\eta\text{-}C_5H_5)$ moieties are bridged by a C_8Ph_4 ligand, being attached to it by Ru–C single bonds from the central six-membered ring [Ru(1)–C(11) 2.062(7), Ru(2)–C(14) 2.051(7) Å] and by Ru–C carbene interactions from the side chains [Ru(1)–C(17) 1.982(7), Ru(2)–C(24) 1.997(7) Å]. The small bite of the ligand results in severe distortions within the four-membered RuC_3 rings as shown by the inter-ring angles at Ru(1) and Ru(2) of 64.8(3)°, which results in angles of between 96–100° at the carbon atoms. The Ru_2C_8 skeleton forms a planar 4/6/4 tricyclic unit which can be described as a diruthenadicyclobutadiene[*a*,*c*]benzene. The $Ru(PPh_3)(\eta\text{-}C_5H_5)$ units have conventional geometries, each metal having approximately octahedral coordination, with Ru–C(cp) 2.26 Å (av.), Ru–P 2.309 Å (av.).

The spectroscopic properties of **9** can be interpreted with the aid of the molecular structure. The ^{13}C NMR spectrum contains resonances at δ 87.0 and 138.3 for the C_5H_5 and σ-carbons, respectively; all other carbons resonate as a series of multiplets between δ 125–134.5. The resonances of the carbenic carbons were not observed, perhaps because of slow decomposition in solution. An exhaustive search of the ^1H NMR spectrum failed to reveal any hydrogens other than those of the phenyl (δ 6.4–7.3) and C_5H_5 groups (δ 4.7). The FAB mass spectrum contains a molecular ion centred on m/z 1262, which fragments mainly by loss of



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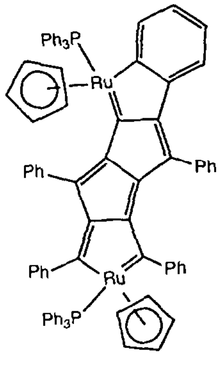


(10)

Ph, PPh_3 and $Ru(PPh_3)(C_5H_5)$ groups; the usual strong ion at m/z 429 confirms the presence of the $Ru(PPh_3)(\eta\text{-}C_5H_5)$ moiety.

The purple complex **10** was identified as containing one more C_2Ph group than **9** by mass spectrometry, having a molecular ion at m/z 1363; the only other prominent ions are $[Ru(PPh_3)(C_5H_5)]^+$ and the organic fragment $[C_7Ph_3(C_6H_4)]^+$ at m/z 391. The X-ray structure (Fig. 2) shows that this complex also contains two

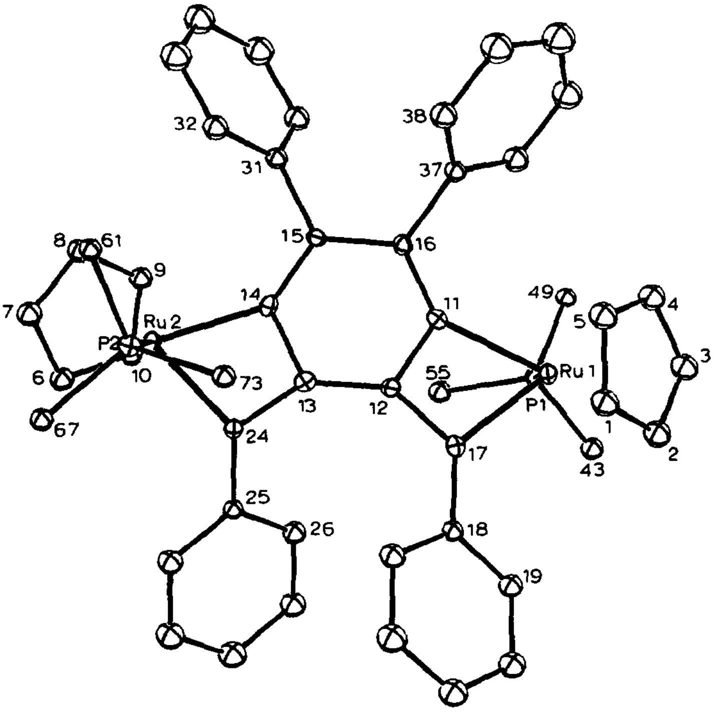


Fig. 1. Molecular structure of $\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_8Ph_4)$ (**9**) showing atom numbering scheme. For reasons of clarity only the *ipso* C atoms of the PPh_3 groups are shown.

Table 1

Selected bond distances (Å) and angles (deg.) in **9** and **10**

	9	**10**
Ru(1)-P(1)	2.308(2)	2.310(5)
Ru(2)-P(2)	2.310(2)	2.321(5)
Ru(1)-C(σ)	2.062(7)	2.04(1)
Ru(2)-C(σ)	2.051(7)	2.06(2)
Ru(1)-C(carb)	1.982(7)	1.96(2)
Ru(2)-C(carb)	1.997(7)	1.91(2)
Ru(1)-C(cp)	2.239-2.270(9)	2.26-2.33(2)
(av.)	2.257	2.29
Ru(2)-C(cp)	2.232-2.269(8)	2.23-2.35(2)
(av.)	2.253	2.29
C(11)-C(12)	1.411(9)	1.44(2)
C(11)-C(16)	1.40(1)	
C(12)-C(13)	1.44(1)	1.47(2)
C(12)-C(17)	1.44(1)	1.41(2)
C(13)-C(14)	1.41(1)	1.37(2)
C(13)-C(15)		1.44(2)
C(13)-C(24)	1.432(9)	
C(14)-C(15)	1.419(9)	
C(15)-C(16)	1.43(1)	1.38(2)
C(16)-C(17)		1.45(2)
C(16)-C(20)		1.49(2)
C(17)-C(18)		1.49(2)
C(18)-C(19)		1.42(2)
C(19)-C(20)		1.52(2)
C(19)-C(21)		1.46(2)
C(21)-C(22)		1.41(2)
P(1)-Ru(1)-C(σ)	90.1(2)	90.3(4)
P(2)-Ru(2)-C(σ)	90.9(2)	83.9(4)
P(1)-Ru(1)-C(carb)	92.2(2)	95.8(5)
P(2)-Ru(2)-C(carb)	93.1(2)	100.4(5)
C(σ)-Ru(1)-C(carb)	64.8(3)	80.6(6)
C(σ)-Ru(2)-C(carb)	64.8(3)	80.8(6)

In **9**, C(σ) are C(11), C(14), C(carb) are C(17), C(24); in **10**, C(σ) are C(14), C(22), C(carb) are C(11), C(20).

Ru(PPh_3)(η-C_5H_5) groups attached via Ru–C single [Ru(1)–C(14) 2.04(1), Ru(2)–C(22), 2.06(2) Å] and multiple bonds [Ru(1)–C(11) 1.96(2), Ru(2)–C(20) 1.91(2) Å] to a polycyclic ligand formed from five phenylacetylide residues. The central feature is a pentalene fused to a ruthenacyclopentadiene ring; in the latter, localised multiple bonds are found between Ru(1)–C(11) and C(13)–C(14) [1.44(2) Å], the metal also being σ-bonded to C(14). The second ruthenium is multiply-bonded to C(20) of the pentalene and metallates one of the phenyl rings at C(22). Overall, the pentacyclic 5/5/5/5/6 system is planar; the maximum deviation from the mean plane defined by Ru(1)Ru(2)C(11)–C(26) is 0.18 Å for C(23); alternatively, Ru(1) and Ru(2) are 0.016 and 0.112 Å out of the C(11)–C(26) plane.

The ring system combines the structural features of a methylenepentalene fused to a metallacyclopentadiene; it is the first example of a pentalene-metal complex which does not involve stabilisation of this sytem by π-complexation to the metal.

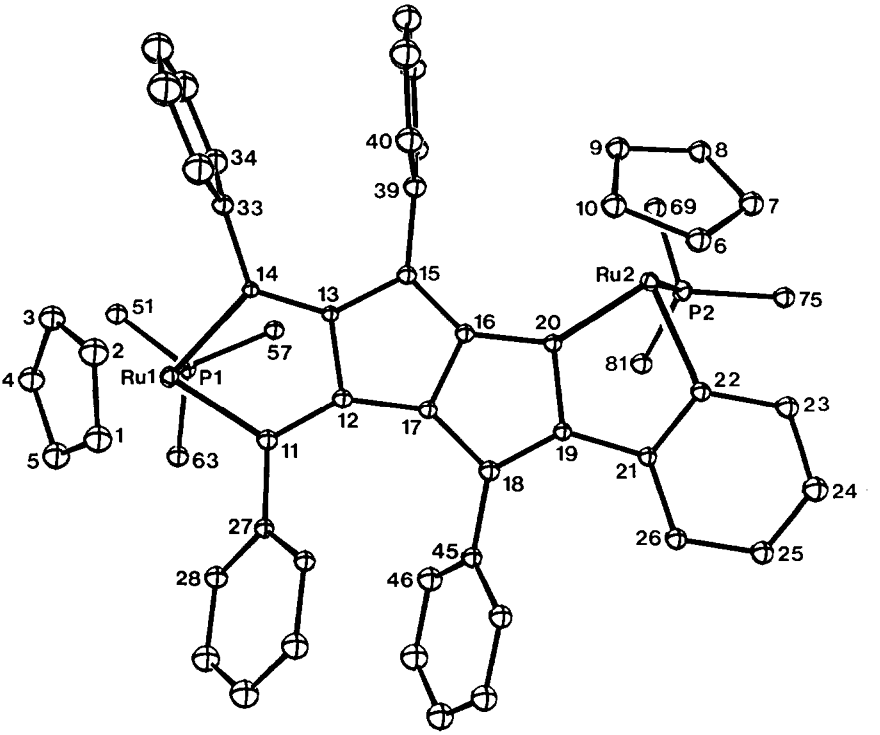


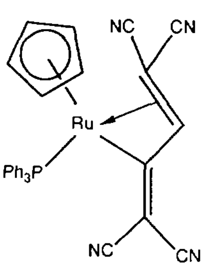
Fig. 2. Molecular structure of $\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2\{\mu\text{-}C_{10}Ph_4(C_6H_4)\}$ (**10**) showing atom numbering scheme. For reasons of clarity only the *ipso* C atoms of the PPh_3 groups are shown.

It is of interest that the conjugated system is fixed; although the precision of the X-ray determination scarcely enables C–C single and C=C double bonds to be distinguished, the different Ru–C distances are well established.

The Ru–C multiple bonds found in **9** and **10** are further examples to add to the growing number of such features found in other ruthenium complexes recently described. These include the η^3(4e)-butadienyl ligands found in $Ru\{\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2\}(PPh_3)(\eta\text{-}C_5H_5)$ (**11**) and related complexes [19], the η^4(5e)-butadienyl ligand in $Ru(\eta^4\text{-}CPhCPhCPhCHPh)(\eta\text{-}C_5H_5)$ (**12**) [20] and the metallacyclopentatriene ring in $RuBr(\eta^2\text{-}CPhCHCHCPh)(\eta\text{-}C_5H_5)$ (**13**) [21].

The routes by which these unusual complexes are formed are presently matters of speculation. Qualitative experiments have established the formation of complexes analogous to **9** in reactions involving $AgC_2(C_6H_4X\text{-}p)$ (X = H, Me) and $RuCl\{P(C_6H_4R\text{-}p)_3\}_2(\eta\text{-}C_5H_4R')$ (R, R′ = H, Me); other silver(I) acetylides reacted to give $Ru(C_2R)(PPh_3)_2(\eta\text{-}C_5H_5)$. The intermediacy of species such as, or related to, PhC_2C_2Ph or $[\{Ru(PPh_3)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_4Ph_2)]^{2+}$, formed by oxidative coupling of either the C_2Ph fragments or the ruthenium σ-phenylacetylide, is supported by the deposition of silver metal during the reactions.

On paper, reaction schemes can be described which allow construction of these complexes with surprisingly little rearrangement. Scheme 2 is an example. Initial formation of the σ-phenylacetylide complex is followed by oxidative coupling to form the divinylidene complex. Related complexes have been described [22]. Further coupling with 1,4-diphenylbuta-1,3-diyne, also formed by oxidative coup-



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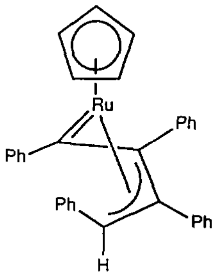

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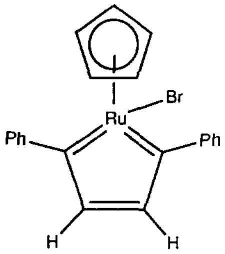

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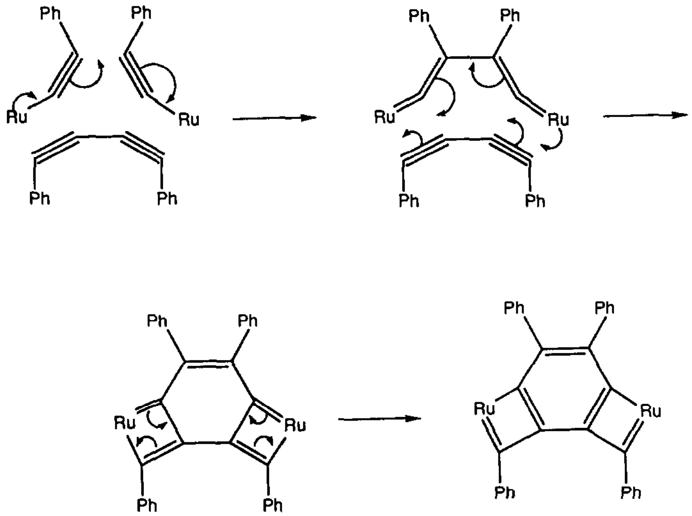

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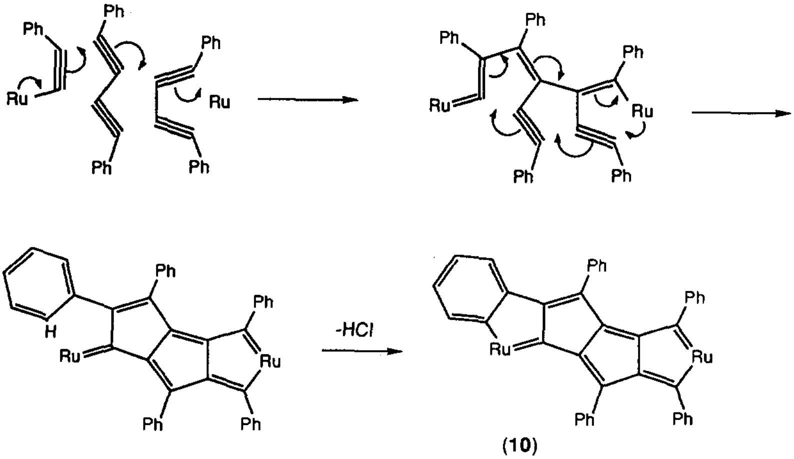
Scheme 2



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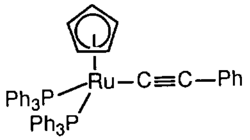
Scheme 3



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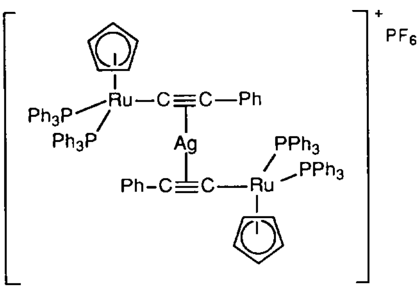


(15)

ling of phenylacetylide residues, could lead to **9** in the manner shown. However, we have not been successful in making **9** from either of these precursors; these processes may be concerted.

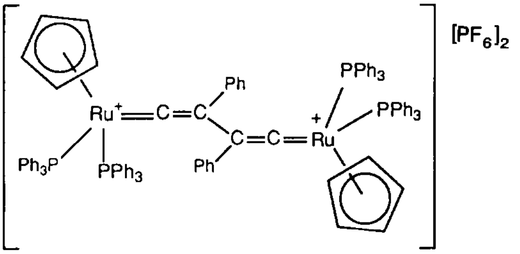
In the case of **10**, a more tentative scheme is illustrated as Scheme 3. A concerted rearrangement of two molecules of 1,4-diphenylbuta-1,3-diyne with the σ-phenylacetylide and a second ruthenium centre, followed by a conventional cyclometallation reaction, is required to generate **10**. Of interest is the attachment of Ru(1) to two carbons bearing phenyl groups, indicating that the σ-phenylacetylide complex is unlikely to be directly involved.

Some related reactions

Addition of $AgPF_6$ to two equivalents of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (**14**) in toluene at 0 °C resulted in the immediate precipitation of $[\{Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)\}_2Ag][PF_6]$ (**15**) in quantitative yield. This air-stable yellow complex decomposes on attempted purification by chromatography on silica, and was identified from its spectroscopic and analytical properties. In the IR spectrum of **15**, the $\nu(C{\equiv}C)$ modes are found at 1984 and 1943 cm^{-1}, compared with 2068 cm^{-1} in **14**; there is also the strong $\nu(PF)$ band associated with the counterion. The NMR spectra contained the anticipated resonances from the C_5H_5 and Ph groups, and a ^{13}C resonance at δ 91.1 is assigned to C_β. The FAB mass spectrum contained a parent ion at m/z 1692, which fragmented with competitive loss of Ag, PPh_3 and $Ru(C_2Ph)(PPh_3)_2(C_5H_5)$. An ion at m/z 529 loses C_6H_4, then C_2, to give the usual base peak at m/z 429, $[Ru(PPh_3)(C_5H_5)]^+$.

These data are accommodated by structure **15** for this complex, which is related to that found for $[\{Mn(C_2{}^tBu)(CO)_3(dppe)\}_2Cu][PF_6]$ as a representative of similar complexes formed by Cu, Ag and Au [23]. We have also described the closely related derivative $[\{Ru(C_2Ph)[P(OMe)_3]_2(\eta\text{-}C_5H_5)\}_2Cu][PF_6]$, which has a similar IR spectrum [24].

A similar reaction between equimolar amounts of AgC_2Ph and **14** also resulted in the formation of **15**. However, if CH_2Cl_2 was then added, the precipitate dissolved and the colour of the solution rapidly darkened to red. Work-up gave a pale apricot powder identified as $[\{Ru(PPh_3)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_4Ph_2)][PF_6]_2$ (**16**). In the IR spectrum, broad medium intensity bands at 1626 and 1587 cm^{-1} are characteristic of the vinylidene $\nu(C{=}C)$; the strong band at 840 cm^{-1} is $\nu(PF)$. In the ^1H NMR spectrum, two equal intensity resonances at δ 5.42 and 5.59 were assigned to inequivalent C_5H_5 resonances. Similarly, two peaks at δ 91.1 and 95.5 in the ^{13}C NMR spectrum were assigned to the C_5H_5 carbons, while a broad, low intensity signal at δ 347.6 is assigned to C_α. The highest mass ion in the FAB mass spectrum was at m/z 1729, assigned to $[M + PF_6]^+$; an ion at m/z 1583 corresponds to $[M - H]^+$, and $[Ru(C_4Ph_2)(PPh_3)(C_5H_5)]^+$ occurs at m/z 631. Complex **16** has the divinylidene structure illustrated, and is analogous to the crystallographically characterised $[\{Fe(dppe)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_4Me_2)][BF_4]_2$, which was obtained by oxidation of $[Fe(CCMe_2)(dppe)(\eta\text{-}C_5H_5)]^+$ [22]. More recently, the molybdenum complexes $[\{Mo(dppe)(\eta\text{-}C_7H_7)\}_2(\mu\text{-}C_4R_2)]^+$ have been described [25].



(16)

Work continues to uncover further and possibly more extensive systems available from metal-induced oxidative coupling of acetylide residues.

Experimental

General conditions

All reactions were carried out under dry, high purity nitrogen using standard Schlenk techniques. Solvents were dried and distilled before use. Elemental analyses were by the Canadian Microanalytical Service, Delta, B.C., Canada V4G 1G7. TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

Reagents. Complex **1** was prepared as previously described [8]. $Me_3NO \cdot 2H_2O$ (Aldrich) was dehydrated by sublimation (100 °C/0.1 mmHg).

Instrumentation. IR: Perkin-Elmer 1700X FT IR; 683 double beam, NaCl optics; NMR: Bruker CXP300 (^1H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz). Spectra recorded in non-deuterated solvents used an external concentric tube containing D_2O for field lock. FAB MS: VG ZAB 2HF (FAB MS, using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV).

Starting materials. Published methods were used to prepare $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ [26]. Silver phenylacetylide was obtained by addition of HC_2Ph in EtOH to an aqueous ammoniacal solution of $AgNO_3$; the product was filtered off, washed with EtOH and dried. $AgPF_6$ was used as received (Pennwalt Chemicals, Tulsa, OK).

Reaction between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and AgC_2Ph

A suspension of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (127 mg, 0.175 mmol) and AgC_2Ph (130 mg, 0.622 mmol) was heated in refluxing toluene (30 ml) for 1 h. The mixture was filtered, the filtrate was evaporated to dryness, and the residue was chromatographed (Florisil; 3 × 20 cm). Elution (acetone/light petroleum, 1/9) gave a blue-green fraction which was crystallised (CH_2Cl_2/EtOH) to give dark blue crystals of $\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_8Ph_4)$ (**9**) (27 mg, 24%), m.p. > 239 °C (dec.). Found: C, 70.5; H, 4.65; *M* (mass spectrometry), 1262. $C_{78}H_{60}P_2Ru_2 \cdot CH_2Cl_2$ calc.: C, 70.5; H, 4.65%; *M*, 1262. IR (Nujol): 1438m, 1089w, 790w, 740w, 720w, 645m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 4.69 (s, 10H, C_5H_5); 6.4–7.3 (m, 50H, Ph). $^{13}C\{^1H\}$ NMR: $\delta(CDCl_3)$ 87.0 (s, C_5H_5); 124.9–134.6 (m, Ph); 138.3 [d, *J*(PC) 37 Hz, Ru–C]; Ru=C not detected. FAB MS: 1262, $[M]^+$, 65; 1185, $[M-Ph]^+$, 0.7; 1000, $[M-PPh_3]^+$, 13; 833, $[M-Ru(PPh_3)(C_5H_5)]^+$, 4; 738, $[M-2PPh_3]^+$, 100; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 70. Further elution of the column afforded a purple fraction which was crystallised (CH_2Cl_2/EtOH) to give purple crystals of $\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2\{\mu\text{-}C_{10}Ph_4(C_6H_4)\}$ (**10**) (3 mg, 0.5%), m.p. > 250 °C (dec.). Found: *M* (mass spectrometry), 1363. $C_{86}H_{64}P_2Ru_2$ calc.: *M*, 1363. FAB MS: 1363, $[M]^+$, 1; 1101, $[M-PPh_3]^+$, 0.5; 839, $[M-2PPh_3]^+$, 3; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 5; 391, $[C_7Ph_3(C_6H_4)]^+$, 100.

Reaction between $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ *(14) and* $AgC_2Ph/AgCl$ *(by M.L. Williams)*

A suspension of **14** (500 mg, 0.632 mmol) and AgC_2Ph (140 mg, 0.498 mmol) in toluene (50 ml) was treated with AgCl (90 mg, 0.627 mmol) after 5 min reflux. After 15 min the dark blue suspension was cooled. Work-up as above gave **9** (35 mg, 9%) (TLC, FAB MS).

Reaction between $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ *and* $AgPF_6$

(a) In 2:1 ratio. A suspension of $AgPF_6$ (80 mg, 0.32 mmol) in toluene (10 ml) was added to a solution of **14** (500 mg, 0.632 mmol) also in toluene (50 ml). A yellow precipitate of $[\{Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)\}_2Ag][PF_6]$ (**15**) (436 mg, 75%) separated immediately. M.p. > 190 °C (dec.). Found: C, 63.3; H, 4.65; $(M+H)$ (mass spectrometry), 1692. $C_{98}H_{80}AgF_6P_5Ru_2$ calc.: C, 64.1; H, 4.4%; *M*, 1691. IR (Nujol): $\nu(C\equiv C)$ 1984m, 1943s; $\nu(PF)$ 839s (br); other bands at 1593m, 1570m, 1481s, 1433s, 1089s, 752s, 737s, 696vs, 557vs cm^{-1}. ^1H NMR: δ(acetone-d_6) 4.41 (s, 10H, C_5H_5); 7.25 (m, 70H, Ph). $^{13}C\{^1H\}$ NMR: δ(acetone-d_6) 86.2 (s, C_5H_5); 91.1 (s, C_β); 128.3–138.1 (m, Ph). FAB MS: 1692, $[M+H]^+$, 2; 901, $[M-Ru(C_2Ph)(PPh_3)_2(C_5H_5)]^+$, 23; 792, $[M-AgRu(C_2Ph)(PPh_3)_2(C_5H_5)]^+$, 16; 691, $[Ru(PPh_3)_2(C_5H_5)]^+$, 11; 639, $[M-Ru(C_2Ph)(PPh_3)_3(C_5H_5)]^+$, 24; 529, $[Ru(C_2C_6H_4)(PPh_3)(C_5H_5)]^+$, 31; 453, $[Ru(C_2)(PPh_3)(C_5H_5)]^+$, 61; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100.

(b) In 1:1 ratio. The yellow suspension obtained by adding $AgPF_6$ (33 mg, 0.13 mmol) to a solution of **14** (100 mg, 0.126 mmol) in toluene (22 ml) was stirred for 10 min, and CH_2Cl_2 (10 ml) was added. The colour of the solution gradually changed to red-pink and silver was deposited. After 30 min, the solution was filtered through Celite and the filtrate was evaporated to dryness. Extraction with CH_2Cl_2 (5 ml) and filtration into an excess of Et_2O gave a pale apricot precipitate of $[\{Ru(PPh_3)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_4Ph_2)][PF_6]_2$ (**16**) (93 mg, 82%), m.p. 150 °C (dec.). Found: C, 62.55; H, 4.35%; *M* (mass spectrometry), 1583. $C_{98}H_{80}F_{12}P_6Ru_2$ calc.: C, 62.8; H, 4.3%, *M*, 1583. IR (Nujol): $\nu(C=C)$ 1626m, 1587m; $\nu(PF)$ 841vs(br); other bands at 1437s, 1311m, 1187m, 1160m, 1091s, 744s, 723s, 696s cm^{-1}. ^1H

Table 2

Fractional atomic coordinates ($\times 10^5$ for Ru; $\times 10^4$ for remaining atoms) for $\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_8Ph_4)$ (**9**)

Ru(1)	30407(4)	9732(3)	38350(5)
Ru(2)	12532(4)	36836(3)	38955(5)
P(1)	3819(1)	1320(1)	2228(1)
P(2)	323(1)	3381(1)	5391(2)
C(1)	2261(6)	266(4)	4987(8)
C(2)	2586(6)	−91(4)	4120(8)
C(3)	3627(6)	61(4)	4331(8)
C(4)	3927(7)	502(4)	5326(8)
C(5)	3094(6)	625(4)	5748(8)
C(6)	891(6)	4392(4)	2462(8)
C(7)	1114(6)	4734(4)	3617(7)
C(8)	2076(6)	4720(4)	4153(7)
C(9)	2475(6)	4371(4)	3318(7)
C(10)	1766(6)	4170(4)	2289(7)
C(11)	2982(5)	1921(3)	4317(6)
C(12)	2070(5)	1937(3)	3597(6)
C(13)	1649(5)	2511(3)	3667(6)
C(14)	2153(5)	3042(3)	4459(7)
C(15)	3077(5)	3022(3)	5160(6)
C(16)	3454(5)	2430(3)	5156(6)
C(17)	1832(5)	1276(3)	3115(6)
C(18)	859(3)	895(2)	2638(5)
C(19)	772(3)	340(2)	1877(5)
C(20)	−146(3)	−38(2)	1466(5)
C(21)	−976(3)	138(2)	1817(5)
C(22)	−888(3)	693(2)	2578(5)
C(23)	30(3)	1071(2)	2989(5)
C(24)	890(5)	2807(3)	3028(6)
C(25)	299(3)	2570(3)	1834(5)
C(26)	6472(3)	2196(3)	1031(5)
C(27)	118(3)	1971(3)	−100(5)
C(28)	−811(3)	2120(3)	−428(5)
C(29)	−1184(3)	2494(3)	375(5)
C(30)	−630(3)	2719(3)	1506(5)
C(31)	3666(3)	3621(3)	5842(5)
C(32)	3274(3)	3970(3)	6666(5)
C(33)	3818(3)	4547(3)	7245(5)
C(34)	4755(3)	4776(3)	7002(5)
C(35)	5148(3)	4427(3)	6178(5)
C(36)	4603(3)	3849(3)	5599(5)
C(37)	4317(4)	2348(3)	6077(5)
C(38)	4294(4)	2459(3)	7314(5)
C(39)	5063(4)	2347(3)	8188(5)
C(40)	5855(4)	2124(3)	7825(5)
C(41)	5878(4)	2012(3)	6588(5)
C(42)	5110(4)	2124(3)	5714(5)
C(43)	3722(4)	705(3)	970(5)
C(44)	3215(4)	80(3)	1073(5)
C(45)	3158(4)	−401(3)	159(5)
C(46)	3608(4)	−257(3)	−857(5)
C(47)	4115(4)	368(3)	−960(5)
C(48)	4172(4)	850(3)	−46(5)
C(49)	5171(3)	1558(2)	2533(5)

Table 2 (continued)

C(50)	5685(3)	1200(2)	3357(5)
C(51)	6703(3)	1329(2)	3568(5)
C(52)	7208(3)	1816(2)	2955(5)
C(53)	6694(3)	2174(2)	2130(5)
C(54)	5676(3)	2045(2)	1919(5)
C(55)	3465(4)	2026(3)	1434(4)
C(56)	3780(4)	2642(3)	2014(4)
C(57)	3549(4)	3187(3)	1423(4)
C(58)	3002(4)	3116(3)	252(4)
C(59)	2687(4)	2499(3)	−329(4)
C(60)	2919(4)	1954(3)	262(4)
C(61)	662(4)	3805(2)	6914(4)
C(62)	1057(4)	4467(2)	6992(4)
C(63)	1252(4)	4815(2)	8118(4)
C(64)	1052(4)	4501(2)	9165(4)
C(65)	657(4)	3839(2)	9087(4)
C(66)	462(4)	3491(2)	7961(4)
C(67)	−966(4)	3506(3)	5058(4)
C(68)	−1608(4)	3363(3)	5890(4)
C(69)	−2579(4)	3436(3)	5583(4)
C(70)	−2908(4)	3654(3)	4445(4)
C(71)	−2267(4)	3798(3)	3613(4)
C(72)	−1296(4)	3724(3)	3920(4)
C(73)	202(3)	2531(2)	5786(5)
C(74)	1022(3)	2307(2)	6364(5)
C(75)	961(3)	1652(2)	6599(5)
C(76)	80(3)	1220(2)	6257(5)
C(77)	−741(3)	1444(2)	5679(5)
C(78)	−680(3)	2099(2)	5443(5)
C(80)	3438(20)	5882(15)	1110(18)
Cl(1)	2366(7)	6144(4)	829(8)
Cl(2)	3900(7)	5996(7)	−246(10)

NMR: δ(acetone-d_6) 5.42 (s, 5H, C_5H_5); 5.59 (s, 5H, C_5H_5); 7.21 (m, 70H, Ph). $^{13}C\{^1H\}$ NMR: $\delta[CD_2Cl_2, Cr(acac)_3]$ 91.1, 95.5 (2 × s, C_5H_5); 129.0–134.0 (m, Ph); 347.6 (s(br), C_α). FAB MS: 1729, $[M + PF_6]^+$, 1; 1583, $[M - H]^+ \equiv [M']^+$, 23; 1321, $[M' - PPh_3]^+$, 1; 1059, $[M' - 2PPh_3]^+$, 2; 892, $[M' - Ru(PPh_3)(C_5H_5)]^+$, 7; 796, $[M' - 3PPh_3]^+$, 6; 691, $[Ru(PPh_3)_2(C_5H_5)]^+$, 20; 631, $[Ru(C_4Ph_2)(PPh_3)(C_5H_5)]^+$, 12; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100.

Crystallography

Intensity data for **9** and **10** were measured at room temperature on an Enraf–Nonius CAD4F diffractometer fitted with Mo-K_α (graphite monochromatised) radiation, $\lambda = 0.7107$ Å. The $\omega : 2\theta$ scan technique was employed to measure N_m reflections, N_u of which were unique and N_o were considered observed with $I \geqslant 2.5\sigma(I)$. Lorentz, polarisation and absorption (analytical procedure) corrections were applied [27]. The structures were each solved from a Patterson synthesis and each was refined by a block-matrix least-squares procedure with SHELX76 [27]. Phenyl groups were refined as hexagonal rigid groups. For **9**, the Ru, P and C atoms of the C_8 moiety and the CH_2Cl_2 solvent molecule were refined anisotropi-

Table 3

Fractional atomic coordinates ($\times 10^5$ for Ru; $\times 10^4$ for remaining atoms) for $\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2\{\mu\text{-}C_{10}Ph_4(C_6H_4)\}$ (**10**)

Ru(1)	−1151(11)	−34146(9)	25799(9)
Ru(2)	23295(11)	17173(9)	8923(8)
P(1)	1420(4)	−3026(3)	3667(3)
P(2)	3798(4)	2554(3)	1916(3)
C(1)	−1975(14)	−4271(12)	2123(16)
C(2)	−1342(18)	−4374(12)	1584(13)
C(3)	−582(16)	−4789(12)	2011(14)
C(4)	−733(16)	−4930(12)	2810(14)
C(5)	−1633(17)	−4644(11)	2893(13)
C(6)	1498(16)	1771(14)	−392(10)
C(7)	2567(16)	2481(11)	−279(10)
C(8)	3449(15)	2107(13)	−35(9)
C(9)	2889(16)	1128(12)	−60(10)
C(10)	1675(14)	916(13)	−255(9)
C(11)	−444(13)	−2327(10)	2610(10)
C(12)	217(12)	−1527(10)	2237(9)
C(13)	933(12)	−1731(9)	1802(9)
C(14)	896(12)	−2600(10)	1863(9)
C(15)	1539(12)	−924(11)	1412(10)
C(16)	1239(13)	−248(10)	1607(9)
C(17)	401(12)	−606(10)	2098(9)
C(18)	122(13)	110(11)	2316(9)
C(19)	690(13)	894(10)	1909(9)
C(20)	1497(12)	737(10)	1489(9)
C(21)	693(13)	1803(9)	1795(10)
C(22)	1404(12)	2314(11)	1283(9)
C(23)	1470(14)	3207(11)	1111(11)
C(24)	846(15)	3562(12)	1466(12)
C(25)	180(14)	3054(11)	1971(11)
C(26)	59(13)	2149(10)	2149(10)
C(27)	−1476(9)	−2354(7)	2851(5)
C(28)	−2248(9)	−2034(7)	2340(5)
C(29)	−3263(9)	−2139(7)	2542(5)
C(30)	−3506(9)	−2563(7)	3255(5)
C(31)	−2734(9)	−2883(7)	3766(5)
C(32)	−1719(9)	−2779(7)	3564(5)
C(33)	1450(8)	−2967(8)	1390(7)
C(34)	864(8)	−3362(8)	641(7)
C(35)	1357(8)	−3768(8)	237(7)
C(36)	2436(8)	−3778(8)	582(7)
C(37)	3021(8)	−3383(8)	1331(7)
C(38)	2528(8)	−2977(8)	1735(7)
C(39)	2346(7)	−890(7)	918(7)
C(40)	1922(7)	−1158(7)	117(7)
C(41)	2640(7)	−1253(7)	−321(7)
C(42)	3781(7)	−1080(7)	41(7)
C(43)	4204(7)	−812(7)	842(7)
C(44)	3487(7)	−717(7)	1280(7)
C(45)	−664(8)	−3(8)	2845(7)
C(46)	−389(8)	−283(8)	3631(7)
C(47)	−1109(8)	−391(8)	4145(7)
C(48)	−2104(8)	−218(8)	3872(7)
C(49)	−2379(8)	62(8)	3086(7)

Table 3 (continued)

C(50)	-1659(8)	170(8)	2572(7)
C(51)	2166(11)	-3808(8)	3951(7)
C(52)	2794(11)	-3824(8)	4729(7)
C(53)	3402(11)	-4390(8)	4919(7)
C(54)	3382(11)	-4942(8)	4330(7)
C(55)	2755(11)	-4926(8)	3552(7)
C(56)	2147(11)	-4360(8)	3362(7)
C(57)	2618(10)	-1946(6)	3671(7)
C(58)	3711(10)	-1909(6)	3698(7)
C(59)	4590(10)	-1080(6)	3651(7)
C(60)	4377(10)	-287(6)	3578(7)
C(61)	3284(10)	-325(6)	3552(7)
C(62)	2404(10)	-1154(6)	3599(7)
C(63)	980(10)	-3002(7)	4614(9)
C(64)	1304(10)	-2232(7)	5074(9)
C(65)	800(10)	-2268(7)	5710(9)
C(66)	-29(10)	-3073(7)	5886(9)
C(67)	-354(10)	-3843(7)	5427(9)
C(68)	151(10)	-3807(7)	4790(9)
C(69)	5130(7)	2396(7)	1968(7)
C(70)	5030(7)	1524(7)	1827(7)
C(71)	6006(7)	1327(7)	1931(7)
C(72)	7082(7)	2002(7)	2177(7)
C(73)	7181(7)	2874(7)	2318(7)
C(74)	6205(7)	3071(7)	2214(7)
C(75)	4283(10)	3784(8)	1828(6)
C(76)	4569(10)	4333(8)	2493(6)
C(77)	4996(10)	5269(8)	2413(6)
C(78)	5137(10)	5656(8)	1669(6)
C(79)	4851(10)	5107(8)	1004(6)
C(80)	4424(10)	4171(8)	1084(6)
C(81)	3667(9)	2375(8)	2962(9)
C(82)	4397(9)	2050(8)	3517(9)
C(83)	4268(9)	1889(8)	4305(9)
C(84)	3410(9)	2051(8)	4537(9)
C(85)	2680(9)	2375(8)	3982(9)
C(86)	2809(9)	2537(8)	3194(9)

cally; for **10**, non-phenyl atoms were refined anisotropically. Hydrogen atoms were not included in the structure factor calculations. A weighting scheme of the form $w = k/[\sigma^2(F) + g\,|F|^2]$ was applied and the refinement continued until convergence in each case. Fractional atomic coordinates are listed in Tables 2 and 3 and the crystallographic numbering schemes used are shown in Figs. 1 and 2 which were drawn with the ORTEP [28] program at 15% probability ellipsoids. Scattering factors for neutral Ru (corrected for f' and f'') were from ref. 29 and those for the remaining atoms were as incorporated in SHELX76 [27].

Crystal and refinement data

9: $\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2C_8Ph_4 \cdot CH_2Cl_2 \equiv C_{78}H_{60}P_2Ru_2 \cdot CH_2Cl_2$, M = 1346.3, triclinic, space group $P\bar{1}$, $a = 14.108(1)$, $b = 20.949(3)$, $c = 11.117(2)$ Å, $\alpha = 91.51(1)$, $\beta = 99.03(1)$, $\gamma = 100.14(1)°$, $V = 3189(4)$ Å^3, D_c $(Z = 2) = 1.402$ g

cm^{-3}. Crystal dimensions 0.16 × 0.18 × 0.42 mm, $N_m = 10449$, $\theta_{max} = 23°$, (ranges $\pm h$, $\pm k$, $-l$), $N_u = 8874$, $\mu = 6.10$ cm^{-1}, max/min transmission factors 0.953, 0.899, $R_{int} = 0.063$, $N_o = 6269$, $F(000) = 1426$, $R = 0.055$, $R_w = 0.058$, $k = 1.0$, $g = 0.0001$.

10: $\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2C_{10}Ph_4(C_6H_4) \equiv C_{86}H_{64}P_2Ru_2$, $M = 1361.5$, triclinic, space group $P\bar{1}$, $a = 13.056(8)$, $b = 16.08(1)$, $c = 17.219(7)$ Å, $\alpha = 84.85(4)$, $\beta = 104.01(4)$, $\gamma = 112.73(6)°$, $V = 3235(6)$ Å^3, D_c $(Z = 2) = 1.398$ g cm^{-3}. Crystal dimensions 0.06 × 0.26 × 0.17 mm, $N_m = 7021$, $\theta_{max} = 20°$, (ranges $\pm h$, $\pm k$, $-l$), $N_u = 6055$, $\mu = 5.21$ cm^{-1}, max/min transmission factors 0.968, 0.881, $R_{int} = 0.039$, $N_o = 3600$, $F(000) = 1396$, $R = 0.072$, $R_w = 0.071$, $k = 1.7$, $g = 0.0010$.

Supplementary material available. Tables of bond lengths and angles, thermal parameters, H atom parameters and structure factors may be obtained from ERTT.

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