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The synthesis, structure and selected reactivity of a series of tricarbonyl ruthenium complexes with 1,3-dienes and heterodienes

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Abstract

Displacement of the weakly ligated ethylene ligands in the complex Ru(CO)$_3${η^2-C$_2$H$_4$}$_2$ has been used to synthesise a series of tricarbonyl ruthenium compounds of η^4-coordinated 1,3-dienes and 1,3-heterodienes. Complexes of η^4-coordinated 1,3-heterodienes could not be isolated due to their extreme reactivity. Selected reactions were performed to replace a carbonyl at the metal centre with a phosphite, or to modify the coordinated ligand by standard methodologies. Single crystal X-ray analyses have been performed on the complexes [Ru(CO)$_3${(*E*,*E*)-1,4-diphenylbuta-1,3-diene}], [Ru(CO)$_3${ethyl(*E*,*E*)-5-phenylpenta-2,4-dien-1-oate}], [Ru(CO)$_3${(*E*,*E*)-5-phenylpenta-2,4-dienal}] and [Ru(CO)$_3${(*E*,*E*)-5-phenylpenta-2,4-dienol}] and indicate a change in electronic environment within the diene moiety on coordination. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Tricarbonyl; Dienes; Heterodienes

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1. Introduction

Tricarbonyl(η^4-1,3-diene) iron complexes have been widely utilised as intermediates for organic synthesis [1–3]. The bulky tricarbonyliron moiety is an effective stereo-directing group and can function as a chiral auxilliary when complexed to prochiral dienes [4–10]. In comparison, the analogous ruthenium complexes are not so readily available and as such have received relatively little attention to date [11–14]. This may reflect the lack of an easily accessible and high yielding synthetic strategy. Generally these compounds have been synthesised by the photolysis or thermolysis of Ru$_3$(CO)$_{12}$ in the presence of an excess of the diene and usually require more forcing conditions than their iron analogues. These vigorous conditions commonly give rise to the formation of products containing metal–metal bonds [15], or those in which C–H bond activation has occurred [16] and subsequently the desired mononuclear compounds are produced in low yields or not at all [17]. The use of pre-formed mononuclear species with readily displaceable ligands, such as Ru(CO)$_3${η^4-cycloocta-1,5-diene} [18,19] or Ru(CO)$_4${η^2-methyl acrylate} [20] have been used to avoid many of the synthetic problems mentioned above. A more attractive synthetic intermediate is the bis(ethylene) complex Ru(CO)$_3${η^2-C$_2$H$_4$}$_2$, which can be quantitatively generated in situ by photolysis of an ethylene saturated hydrocarbon solution of Ru$_3$(CO)$_{12}$ [21]. This complex has the distinct advantage that it need not be isolated. In addition, any excess ethylene may be readily purged from the reaction mixture. In this paper we report the synthesis, structure and reactivity of a series of tricarbonyl{η^4-1,3-diene} ruthenium complexes generated via the displacement of the labile ethylene ligands in Ru(CO)$_3${η^2-C$_2$H$_4$}$_2$.

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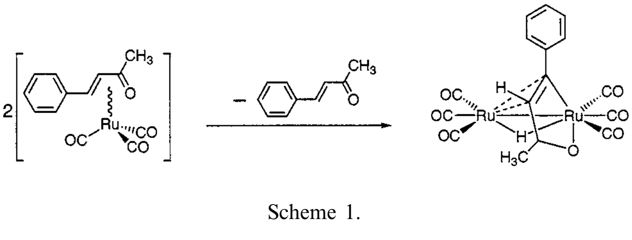
2. Results and discussion

From the reaction of a pentane solution of photochemically generated $Ru(CO)_3\{\eta^2\text{-}C_2H_4\}_2$ with an excess of cyclohexa-1,3-diene, was isolated the known compound $Ru(CO)_3\{\eta^4$-cyclohexa-1,3-diene$\}$(**1**) [22] in high yield. The formation of products containing more than one ruthenium atom was not observed, which is in contrast to the reported synthesis of **1** by the thermolysis of $Ru_3(CO)_{12}$ [22]. It was also observed that the isomerisation of cyclohexa-1,4-diene occurs on reaction with $Ru(CO)_3\{\eta^2\text{-}C_2H_4\}_2$ at ambient temperature to give the complex **1**. This observation is in accord with that reported for the reaction between $Ru(CO)_3\{\eta^4$-cycloocta-1,5-diene$\}$ and cyclohexa-1,4-diene [18]. Reaction between $Ru(CO)_3\{\eta^2\text{-}C_2H_4\}_2$ and (*E*,*E*)-hexa-2,4-dienal yielded $[Ru(CO)_3\{$(*E*,*E*)-hexa-2,4-dienal$\}]$ (**2**) in a reasonable yield as a moderately air-sensitive pale yellow oil. Although the latter compound has been reported in the literature [23], to our knowledge no synthetic or spectroscopic data have been published. As expected, **1** and **2** are significantly more sensitive to oxidation upon exposure to the atmosphere than their iron analogues. We reasoned that the replacement of the alkyl group on the diene moiety with an aromatic substituent would result in complexes that would be less susceptible to oxidation due to enhanced electronic delocalisation. Indeed, reaction between $Ru(CO)_3\{\eta^2\text{-}C_2H_4\}_2$ and (*E*,*E*)-1,4-diphenylbuta-1,3-diene gave the air-stable pale yellow crystalline material $[Ru(CO)_3\{$(*E*,*E*)-1,4-diphenylbuta-1,3-diene$\}]$ (**3**) in good yield. This compound has previously been isolated, together with a series of di- and tri-ruthenium species, from the thermolysis of $Ru_3(CO)_{12}$ and (*E*,*E*)-1,4-diphenylbuta-1,3-diene [11]. The complexes $[Ru(CO)_3\{$methyl (*E*,*E*)-5-phenylpenta-2,4-dien-1-oate$\}]$ (**4**), $[Ru(CO)_3\{$ethyl (*E*,*E*)-5-phenylpenta-2,4-dien-1-oate$\}]$ (**5**) and $[Ru(CO)_3\{$(*E*,*E*)-5-phenylpenta-2,4-dienal$\}]$ (**6**) were also isolated in good yields as air stable crystalline materials from the reactions between $Ru(CO)_3\{\eta^2\text{-}C_2H_4\}_2$ and the appropriate ligands. In contrast, the heterodienes (*E*,*E*)-1,4-diphenyl-1-azabuta-1,3-diene and (*E*)-4-phenyl-3-buten-2-one reacted with $Ru(CO)_3\{\eta^2\text{-}C_2H_4\}_2$ to form the complexes $[Ru(CO)_3\{$(*E*,*E*)-1,4-diphenyl-1-azabuta-1,3-diene$\}]$ (**7**) and $[Ru(CO)_3\{$(*E*)-4-phenyl-3-buten-2-one$\}]$ (**8**), respectively but could not be isolated due to their instability. Compound **7** was characterised on the basis of its ^{1}H-NMR and IR spectra and the comparison of these with the related compounds $[Ru(CO)_2L\{$(*E*,*E*)-1-phenyl-4-tolyl-1-azabuta-1,3-diene$\}]$ ($L = CO$, PPh_3) and $[Fe(CO)_3\{$(*E*,*E*)-1,4-diphenyl-1-azabuta-1,3-diene$\}]$ [24,25]. It is noteworthy that von Philipsborn et al. reported that all attempts to synthesise **8** by the replacement of ethylene in $Ru(CO)_4\{\eta^2\text{-}C_2H_4\}$ by the heterodiene and subsequent decarbonylation failed. Whilst we found that **8** may be synthesised from $Ru(CO)_3\{\eta^2\text{-}C_2H_4\}_2$, it readily decomposes to the known di-ruthenium complex $(\mu_2\text{-}H)Ru_2(CO)_6\{\mu_2\text{-}C_{10}H_9O\}$, obtained by C–H bond activation of the bound olefin (Scheme 1) [16]. Due to the lack of stability of **8** it was characterised solely by comparison of its IR spectrum to that reported for the related iron compound $[Fe(CO)_3\{$(*E*)-4-phenyl-3-buten-2-one$\}]$ [19]. The synthesis of complexes **1**–**8** from $Ru(CO)_3\{\eta^2\text{-}C_2H_4\}_2$ is summarised in Scheme 2.

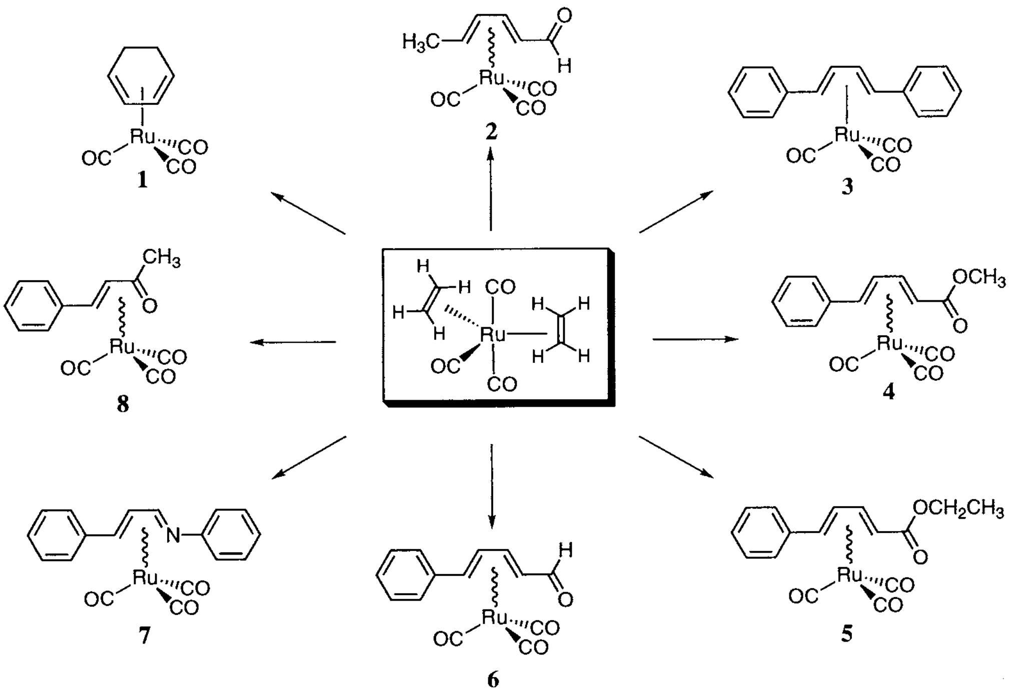
Replacement of a carbonyl group in **3** with a phosphite ligand is readily achieved by the addition of 1.3 equivalents of trimethylamine-*N*-oxide to a dichloromethane solution of **3** containing an excess of $P(OCH_3)_3$. After purification by column chromatography, a pale yellow crystalline material was obtained in moderate yield, which was formulated as $[Ru(CO)_2P(OCH_3)_3\{$(*E*,*E*)-1,4-diphenylbuta-1,3-diene$\}]$ (**9**) on the basis of spectroscopic data (Scheme 3). The replacement of a carbonyl ligand with the weaker π-acceptor phosphite results in a greater degree of back-donation into the π^* orbitals of the two remaining carbonyl groups. This is exemplified by a shift in the observed IR frequency of the C≡O groups to lower wavenumbers for **9** and demonstrates that the replacement of a carbonyl with a suitable phosphine or phosphite allows the electronic and steric properties of these molecules to be subtly modified.

Reduction of the ester functionality of **5** was readily achieved by reaction of a THF solution of **5** with 2.2 equivalents of diisobutylaluminium hydride. Purification by preparative thin layer chromatography yielded a white crystalline material in good yield, that on the basis of spectroscopic and analytical data was formulated as $[Ru(CO)_3\{$(*E*,*E*)-5-phenyl-2,4-pentadienol$\}]$ (**10**) (Scheme 4).

Complexation of the $Ru(CO)_3$ moiety with prochiral dienes produces a racemic mixture and the use of these complexes in asymmetric synthesis demands efficient resolution of their enantiomers [2,26]. Racemic mixtures of $Fe(CO)_3\{\eta^4$-diene$\}$ complexes have previously been resolved by the fractional crystallisation of oxazolidines, formed on reaction with (–)-(1*R*,2*S*)-ephedrine [27]. Attempts were made to separate a racemic mixture of **6** by this method. Although formation of diastereomers was observed by ^{1}H-NMR, separation by



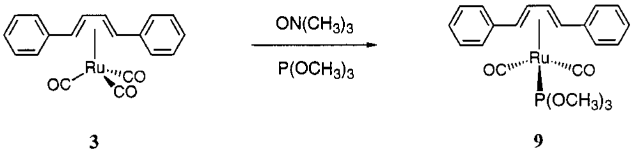
Scheme 1.



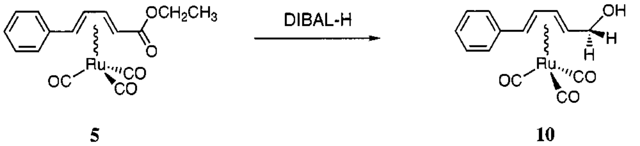
Scheme 2.

fractional crystallisation or thin layer chromatography proved unsuccessful. The development of suitable preparative methods for enantiopure complexes will be the focus of further work.

Single crystal X-ray structure determinations were performed on compounds **3**, **5**, **6** and **10**. Complex **3** can be obtained in two distinct crystal forms. The first form has half an equivalent of the uncoordinated ligand present in the crystal lattice, whereas the second form does not [28]. The structure of **3** described is for the first form, with both found to be isomorphous to their respective iron analogues [29,30]. The molecular structure of **3** is depicted in Fig. 1, with selected bond lengths presented in Table 1. The ruthenium tricarbonyl moiety coordinates to the diene in the expected η^4 fashion, with the 'outer' carbon atoms approximately 0.06 Å further from the metal centre than the 'inner' carbon atoms. The presence of the uncoordinated ligand in the crystal lattice allows a direct comparison of bond lengths within the diene functionality upon coordination. The 'outer' bonds C(07)–C(08) and C(09)–C(010) are 1.433(4) and 1.432(4) Å, respectively and these are significantly longer than the analogous bonds in the uncoordinated ligand (1.310(4) Å). In addition to the lengthening of these 'outer' bonds, there is a concomitant decrease in the 'inner' carbon–carbon bond length on coordination from 1.437(5) to 1.408(4) Å. It is of some note that there is no significant change on coordination for the bond lengths between the diene moiety and the phenyl substituents. The variation of the diene bond lengths on coordination can be traced to the partial population of the Lowest Unoccupied Molecular Orbital (LUMO) of the diene in the coordinated ligand [31]. This orbital is antibonding with respect to the 'outer' carbon–carbon bonds, but bonding with respect to the 'inner' bond. The most notable change in the overall configuration of the ligand upon coordination is the expected transformation from the *transoid* to the *cisoid* conformation. Whilst relatively uncommon, there are examples of ruthenium(II) complexes with dienes coordinated in the *transoid* form [32,33], whereas only the *cisoid* conformation is known for ruthenium(0) complexes. The diene carbon atoms C(07), C(08), C(09) and C(010) lie in a plane, but overall there is a considerable distortion from planarity of the coordinated ligand, with the diene plane making angles of 21.2(1) and 25.9(1)°, respectively to the phenyl rings C(01)–C(06) and C(011)–C(016). In contrast to the 'inner' diene hydrogen atoms H(08) and H(09),



Scheme 3.



Scheme 4.

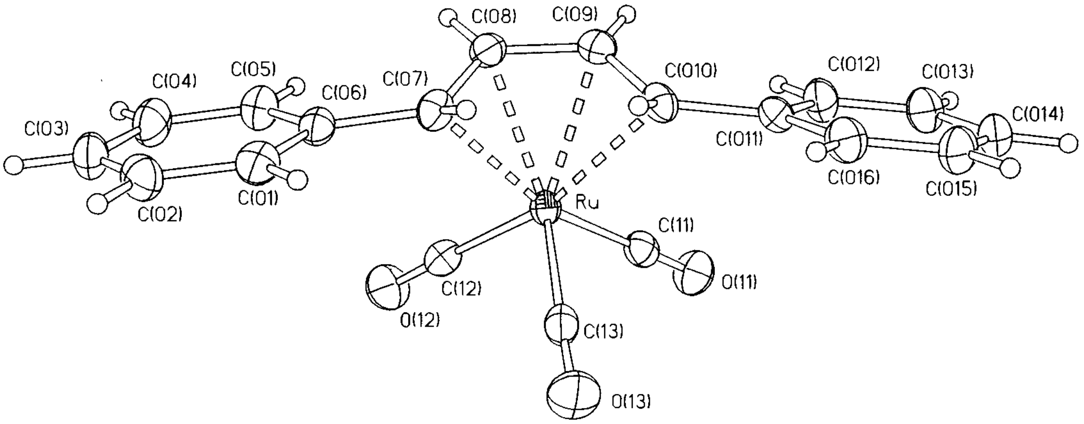


Fig. 1. Molecular structure of $[Ru(CO)_3\{(E,E)\text{-1,4-diphenylbuta-1,3-diene}\}]$ **3**.

which do not deviate significantly from the diene plane, the 'outer' hydrogen atoms H(07) and H(010) both lie above this plane by 0.50(3) Å. This displacement of the 'outer' diene protons from the plane of the diene carbon atoms, increases the overlap of metal- and ligand-based orbitals and also stabilises the ligand LUMO [34]. The molecular structure of **3** is markedly similar to the previously reported iron analogue [29], with the only significant variation in bond lengths observed for the metal–carbon distances, which are approximately 0.1 Å shorter in the iron derivative as might be expected.

The molecular structures of **5** and **6** are depicted in Figs. 2 and 3, with selected bond lengths presented in Tables 2 and 3, respectively. The metal centre in **5** and **6** coordinates to the respective diene ligands in a η^4 manner as was observed for **3**. There are however some small differences in the bond lengths between the metal and the diene carbon atoms and within the diene moiety, with these differences likely to be attributable to the asymmetric nature of the ligands. The ruthenium centre appears to make a stronger interaction with the double bond attached to the carbonyl substituent in both **5** and **6**. For example the metal is 2.217(3) Å away from the 'outer' carbon C(04) that is adjacent to the ester substituent in **5**. In comparison the ruthenium–carbon bond length for the 'outer' carbon adjacent to the aromatic substituent {Ru–C(07), 2.261(3) Å} is 0.044(6) Å longer. A similar observation is made for **6** where the 'outer' ruthenium–carbon distances are 2.270(2) and 2.222(2) Å, the latter being the bond length for the carbon adjacent to the aldehyde substituent. This asymmetry in bond lengths is also noted within the diene moiety, with 'outer' diene bond distances of 1.439(4) and 1.417(4) Å being observed for C(04)–C(05) and C(06)–C(07), respectively in **5**. Whilst these variations in bond length are relatively small and close to the level of statistical significance, a similar observation is made for **6**, with the 'outer' diene bonds C(02)–C(03) and C(04)–C(05) being of length 1.445(3) and 1.425(3) Å, respectively. Electronic delocalisation between the carbonyl substituent and the diene results in a stabilisation of the ligand LUMO and therefore an increase in the partial population of this orbital, which as described above is antibonding with respect to the 'outer' diene bonds and bonding with respect to the 'inner' diene bond. The molecular structure of **10** is depicted in Fig. 4, with selected bond lengths presented in Table 4. Structurally, **10** is similar to **5** and **6**, with asymmetric 'outer' ruthenium–carbon bonds. The lower degree of accuracy for the crystal structure determination of **10**, relative to the determinations performed for **3**, **5** and **6**, precludes a detailed comparison of bond parameters within the coordinated diene fragments.

Table 1
Selected bond lengths (Å) for complex **3**

Ru–C(07)	2.250(2)	C(07)–C(08)	1.433(4)
Ru–C(08)	2.196(2)	C(08)–C(09)	1.408(4)
Ru–C(09)	2.202(2)	C(09)–C(010)	1.432(4)
Ru–C(010)	2.262(2)	C(010)–C(011)	1.481(3)
C(06)–C(07)	1.484(3)		

In conclusion we have shown that tricarbonyl ruthenium complexes of η^4-coordinated 1,3-dienes and 1,3-heterodienes may be readily synthesised via the reactive compound $Ru(CO)_3\{\eta^2\text{-}C_2H_4\}_2$. Tricarbonyl ruthenium complexes of η^4-coordinated 1,3-heterodienes could not be isolated due to their extreme reactivity, but were characterised by IR spectroscopy. Complexes containing coordinated alkyl substituted 1,3-dienes were found to be moderately sensitive to air, whilst those with aromatic substituents were isolated as air stable solids. Selected reactions were performed that indicated it was possible to replace a carbonyl at the metal centre, or to modify the coordinated ligand by standard methodologies. Present studies are focused on the development of efficient synthetic strategies for the preparation of enantiopure complexes. Single crystal structural analyses indicate that the η^4-coordination of 1,3-dienes by the ruthenium tricarbonyl group gives complexes with simi-

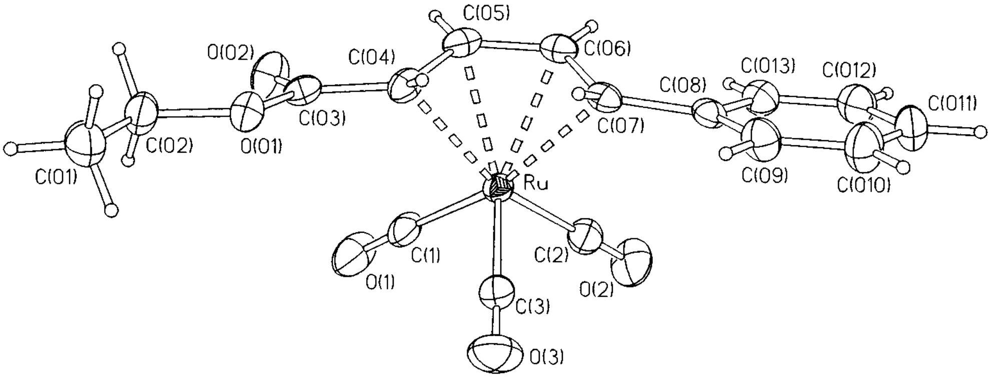


Fig. 2. Molecular structure of [Ru(CO)$_3${ethyl (*E*,*E*)-5-phenylpenta-2,4-dien-1-oate}] **5**.

lar structural parameters to their iron analogues and the bonding within these molecules may be largely described in terms of back donation from the metal into a ligand based LUMO [33].

3. Experimental

All reactions were performed under an atmosphere of purified dinitrogen by standard Schlenk and vacuum line techniques [35]. Subsequent work-up of products was carried out without precautions to exclude air. Solvents used were distilled from appropriate drying agents under dinitrogen [36]. Routine separations of products were performed by column chromatography using Merck Kieselgel 60 (230–400 mesh) and thin layer chromotography using commercially available glass plates, precoated to 0.25 mm thickness with Merck Kieselgel 60 PF$_{254}$. IR spectra were recorded as pentane solutions on a Perkin-Elmer 1710 Fourier Transform spectrometer. ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectra were recorded on a Bruker AC-250 spectrometer and were referenced to external TMS (^{1}H and ^{13}C{^{1}H}) or 85% H_3PO_4 (^{31}P{^{1}H}). ^{13}CO resonances for complexes **2** and **6** were not observed. Positive ion fast atom bombardment mass spectra were recorded on a Kratos MS-50 mass spectrometer, using *m*-nitrobenzyl alcohol as a matrix. Elemental analyses were performed in this department by standard techniques. The compound [Ru(CO)$_3${C_2H_4}$_2$] was generated in situ by the photolysis of $Ru_3(CO)_{12}$ as previously described [37]. The ligands methyl (*E*,*E*)-5-phenylpenta-2,4-dien-1-oate, ethyl (*E*,*E*)-5-phenylpenta-2,4-dien-1-oate and (*E*,*E*)-5-phenylpenta-2,4-dienal were synthesised according to literature preparations [38,39].

*3.1. [Ru(CO)$_3${cyclohexa-1,3-diene}] (**1**)*

To a colourless solution of [Ru(CO)$_3${C_2H_4}$_2$] prepared from $Ru_3(CO)_{12}$ (0.256 g, 0.40 mmol) in pentane (150 cm^{-3}) was added an excess (1 cm^{-3}) of cyclohexa-1,3-diene and the solution purged with dinitrogen for ca. 30 min. The resulting pale yellow solution was stirred at room temperature (r.t.) overnight and then filtered through a pad of silica. Removal of the solvent and unreacted cyclohexa-1,3-diene at reduced pressure yielded 0.248 g (78%) of a pale yellow oil, identified as the desired compound on the basis of previously reported spectroscopic evidence [40]. $\tilde{\nu}_{max}$ cm^{-1} (pentane) 2062s, 1994vs and 1989vs (CO).

*3.2. [Ru(CO)$_3${(E,E)-hexa-2,4-dienal}] (**2**)*

The synthesis of this compound has appeared in the literature [23], however no spectroscopic data were reported. A synthesis analogous to that used for **1** was employed. Purification was performed by filtration through celite to yield 54% of the desired product as a moderately air-sensitive pale yellow oil. $\tilde{\nu}_{max}$ cm^{-1} (pentane) 2078s, 2018vs and 2002vs (CO); δ_H(CDCl$_3$) 9.19 (1 H, d, $J = 4.1$ Hz, CHO), 5.77 (1 H, dd, $J = 5.2$, 6.9 Hz, C*H*=CH–CHO), 5.36 (1 H, dd, $J = 5.0$, 8.1 Hz, C*H*=CH–CH$_3$), 1.80–1.93 (1 H, m, C*H*–CH$_3$), 1.74 (1 H, dd, $J = 4.2$, 7.1 Hz, C*H*–CHO), 1.54 (3 H, d, $J = 6.0$ Hz, CH$_3$); δ_C(CDCl$_3$) 195.3 (1 C, CHO), 92.3 (1 C, *C*H=CH–CH$_3$), 81.3 (1 C, *C*H=CH–CHO), 52.6 (1 C, *C*H–CH$_3$), 52.3 (1 C, *C*H–CHO), 19.8 (3 C, CH$_3$); *m*/*z* 282 [MH]$^+$. $C_9H_8O_4Ru$ requires *M* (based on ^{101}Ru) 281.

*3.3. [Ru(CO)$_3${(E,E)-1,4-diphenylbuta-1,3-diene}] (**3**)*

The synthesis of this compound has appeared in the literature [11], however no ^{13}C{^{1}H}-NMR data was reported. A synthesis analogous to that used for **1** was employed. The crude product readily crystallises, with this material shown by ^{1}H-NMR to contain 0.5 equivalents of the uncoordinated ligand. Purification was performed by column chromatogra-

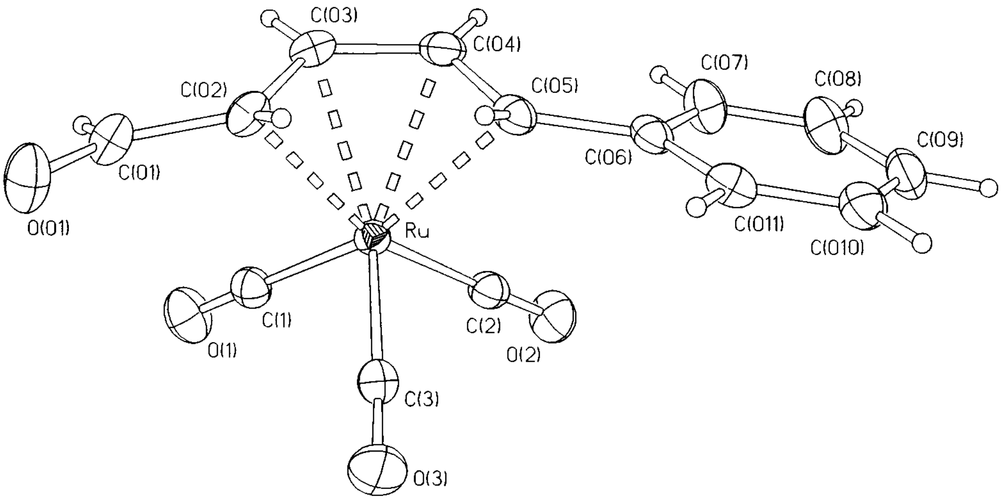


Fig. 3. Molecular structure of [Ru(CO)$_3${(*E*,*E*)-5-phenylpenta-2,4-dienal}] **6**.

phy eluting with a 10% dichloromethane–hexane mixture to afford the desired product as an air stable pale yellow crystalline material ($R_f = 0.36$, 42.6%). $\tilde{\nu}_{max}$ cm^{-1} (pentane) 2078s, 2018vs and 2002vs (CO); δ_C(CDCl$_3$) 225.9 (3 C, CO), 141.3 (2 C, *ipso*-Ar), 128.5 (4 C, *o*-Ar), 125.7 (2 C, *p*-Ar), 125.5 (4 C, *m*-Ar), 82.5 (2 C, CH=*C*H–*C*H=CH), 54.3 (2 C, *C*H=CH–CH=*C*H).

3.4. [Ru(CO)$_3${methyl (E,E)-5-phenylpenta-2,4-dien-1-oate}] (4)

A synthesis analogous to that used for **1** was employed. Purification was performed by column chromatography eluting with dichloromethane to afford a pale yellow air stable crystalline material. ($R_f = 0.67$, 61.8%) [Found: C, 48.2; H 3.2; *m*/*z* 373. $C_{15}H_{12}O_5Ru$ requires C, 48.26; H, 3.24%; *M* (based on ^{101}Ru) 373], $\tilde{\nu}_{max}$ cm^{-1} (pentane) 2078s, 2017vs, 2007s (CO); δ_H(CDCl$_3$) 7.09–7.28 (5 H, m, Ar), 5.94–6.01 (2 H, m, CH=C*H*–C*H*=CH), 3.67 (3 H, s, CH$_3$), 2.64–2.69 (1 H, m, Ar–C*H*), 1.66–1.72 (1 H, m, C*H*–CO$_2$CH$_3$); δ_C(CDCl$_3$) 198.9 (1 C, CO), 194.4 (1 C, CO), 193.3 (1 C, CO), 173.2 (1 C, *C*O$_2$CH$_3$), 140.5 (1 C, *ipso*-Ar), 128.7 (2 C, *o*-Ar), 126.2 (1 C, *p*-Ar), 125.5 (2 C, *m*-Ar), 86.0 (1 C, Ar–CH=*C*H), 84.2 (1 C, *C*H=CH–CO$_2$CH$_3$), 56.0 (1 C, Ar–*C*H), 51.5 (1 C, CH$_3$), 41.5 (1 C, *C*H–CO$_2$CH$_3$).

Table 2
Selected bond lengths (Å) for complex **5**

Ru–C(04)	2.217(3)	C(04)–C(05)	1.439(4)
Ru–C(05)	2.176(3)	C(05)–C(06)	1.408(4)
Ru–C(06)	2.203(3)	C(06)–C(07)	1.417(4)
Ru–C(07)	2.261(3)	C(07)–C(08)	1.486(4)
C(03)–C(04)	1.473(4)		

3.5. [Ru(CO)$_3${ethyl (E,E)-5-phenylpenta-2,4-dien-1-oate}] (5)

A synthesis analogous to that used for **1** was employed. Purification was performed by column chromatography eluting with dichloromethane to afford a pale yellow air stable crystalline material. ($R_f = 0.71$, 56.3%) [Found: C, 49.6; H 3.5; *m*/*z* 387. $C_{16}H_{14}O_5Ru$ requires C, 49.61; H, 3.64%; *M* (based on ^{101}Ru) 387], $\tilde{\nu}_{max}$ cm^{-1} (pentane) 2077s, 2017vs, 2007s (CO); δ_H(CDCl$_3$) 7.10–7.28 (5 H, m, Ar), 5.94–6.01 (2 H, m, CH=C*H*–C*H*=CH), 4.06–4.19 (2 H, m, CH$_2$), 2.63–2.69 (1 H, m, Ar–C*H*), 1.66–1.72 (1 H, m, C*H*–CO$_2$CH$_2$CH$_3$), 1.26 (3 H, t, $J = 7.1$ Hz, CH$_3$); δ_C(CDCl$_3$) 199.0 (1 C, CO), 194.5 (1 C, CO), 193.3 (1 C, CO), 172.7 (1 C, *C*O$_2$CH$_2$CH$_3$), 140.6 (1 C, *ipso*-Ar), 128.7 (2 C, *o*-Ar), 126.1 (1 C, *p*-Ar), 125.6 (2 C, *m*-Ar), 85.9 (1 C, Ar–CH=*C*H), 84.3 (1 C, *C*H=CH–CO$_2$CH$_2$CH$_3$), 60.3 (1 C, CH$_2$), 55.9 (1 C, Ar–*C*H), 42.1 (1 C, *C*H–CO$_2$CH$_2$CH$_3$), 14.2 (1 C, CH$_3$).

3.6. [Ru(CO)$_3${(E,E)-5-phenylpenta-2,4-dienal}] (6)

A synthesis analogous to that used for **1** was employed. Purification was performed by column chromatography eluting with dichloromethane to afford a pale yellow air stable crystalline material. ($R_f = 0.47$; 50.5%) [Found: C, 49.1; H 2.9; *m*/*z* 344 [MH]$^+$.

Table 3
Selected bond lengths (Å) for complex **6**

Ru–C(02)	2.222(2)	C(02)–C(03)	1.445(3)
Ru–C(03)	2.175(2)	C(03)–C(04)	1.411(3)
Ru–C(04)	2.209(2)	C(04)–C(05)	1.425(3)
Ru–C(05)	2.270(2)	C(05)–C(06)	1.485(2)
C(01)–C(02)	1.458(3)		

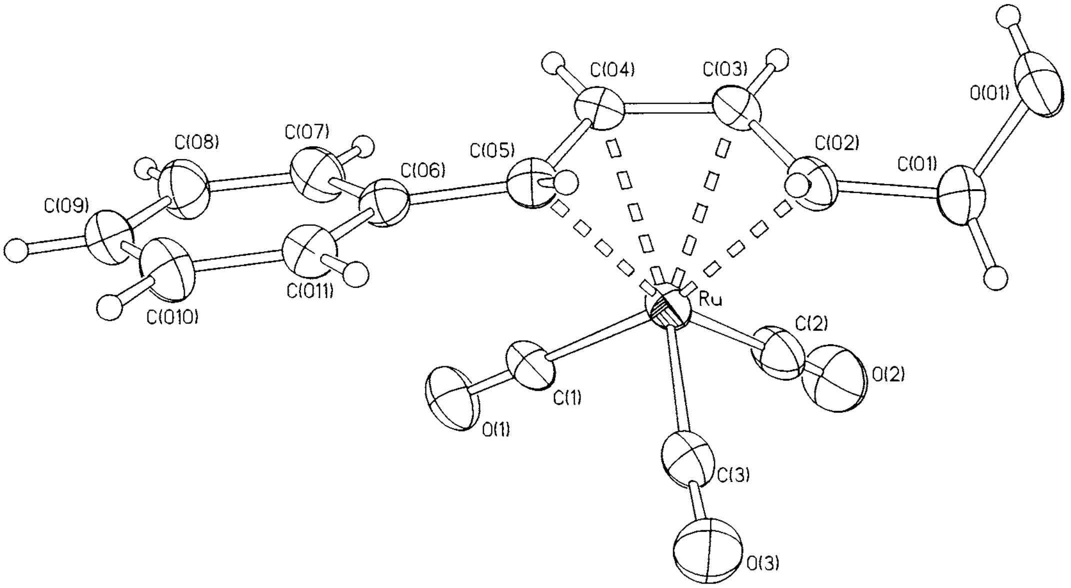


Fig. 4. Molecular structure of $[Ru(CO)_3\{(E,E)\text{-5-phenylpenta-2,4-dienol}\}]$ **10**.

$C_{14}H_{10}O_4Ru$ requires C, 48.98; H, 2.94%; *M* (based on ^{101}Ru) 343], $\tilde{\nu}_{max}$ cm^{-1} (pentane) 2080s, 2021vs, 2010s (CO); $\delta_H(CDCl_3)$ 9.34 (1 H, d, $J = 3.8$ Hz, CHO), 7.12–7.38 (5 H, m, Ar), 5.95–6.08 (2 H, m, CH=C*H*–C*H*=CH), 2.92 (1 H, d, $J = 8.5$ Hz, Ar–C*H*), 2.06 (1 H, dd, $J = 7.2$, 3.8 Hz, C*H*–CHO); $\delta_C(CDCl_3)$ 195.1 (1 C, CHO), 139.8 (1 C, *ipso*-Ar), 128.7 (2 C, *o*-Ar), 126.4 (1 C, *p*-Ar), 125.5 (2 C, *m*-Ar), 87.1 (1 C, Ar–CH=*C*H), 81.7 (1 C, *C*H=CH–CHO), 56.8 (1 C, Ar–*C*H), 52.3 (1 C, *C*H–CHO).

3.7. $[Ru(CO)_3\{(E,E)\text{-1,4-diphenyl-1-azabuta-1,3-diene}\}]$ (*7*)

A synthesis analogous to that used for **1** was employed. Attempts to isolate this compound in a pure form were not successful due to its lack of stability and therefore this compound was characterised by comparison of its ^{1}H-NMR and IR spectra to that reported for the related compounds $[Ru(CO)_3\{(E,E)\text{-1-phenyl-4-tolyl-1-azabuta-1,3-diene}\}]$, $[Ru(CO)_2(PPh_3)_2\{(E,E)\text{-1-phenyl-4-tolyl-1-azabuta-1,3-diene}\}]$ and $[Fe(CO)_3\{(E,E)\text{-1,4-diphenyl-1-azabuta-1,3-diene}\}]$ [24,25] $\tilde{\nu}_{max}$ cm^{-1} (pentane) 2073s, 2012vs, 2000s (CO); $\delta_H(CDCl_3)$ 7.12–7.44 (10 H, m, Ar), 7.00 (1 H, dd, $J = 3.2$, 1.0 Hz, CH=N), 5.53 (1 H, dd, $J = 8.4$, 3.1 Hz, CH=C*H*–CH), 3.62 (1 H, dd, $J = 8.4$, 1.0 Hz, Ph–CH).

Table 4
Selected bond lengths (Å) for complex **10**

Ru–C(02)	2.211(9)	C(02)–C(03)	1.409(13)
Ru–C(03)	2.195(8)	C(03)–C(04)	1.417(11)
Ru–C(04)	2.204(8)	C(04)–C(05)	1.423(11)
Ru–C(05)	2.257(8)	C(05)–C(06)	1.490(12)
C(01)–C(02)	1.509(12)		

3.8. $[Ru(CO)_3\{(E)\text{-4-phenyl-3-buten-2-one}\}]$ (*8*)

A synthesis analogous to that used for **1** was employed. This compound readily decomposes at ambient temperatures and therefore was characterised solely by comparison of its IR spectrum to that reported for the related iron(0) compound $[Fe(CO)_3\{(E)\text{-4-phenyl-3-buten-2-one}\}]$ [19]. $\tilde{\nu}_{max}$ cm^{-1} (pentane) 2068s, 2008vs, 1988s (CO).

3.9. $[Ru(CO)_2P(OCH_3)_3\{(E,E)\text{-1,4-diphenylbuta-1,3-diene}\}]$ (*9*)

To a solution of **3** (0.100 g, 0.256 mmol) in dichloromethane (50 cm^{-3}) at r.t. was added in succession an excess of $P(OCH_3)_3$ (0.2 cm^{-3}) and $(CH_3)_3NO$ (0.250 g, 0.333 mmol). The resulting solution was stirred for 4 h, at which point complete consumption of **3** was indicated by IR spectroscopy. Removal of solvent and excess $P(OCH_3)_3$, followed by column chromatography eluting with a 25% dichloromethane–hexane mixture afforded the desired product as a pale yellow micro-crystalline material ($R_f = 0.25$, 0.047 g, 37.6%). *m*/*z* 488 $[MH]^+$; $C_{21}H_{23}O_5PRu$ requires *M* (based on ^{101}Ru) 487, $\tilde{\nu}_{max}$ cm^{-1} (pentane) 2010vs, 1952s (CO); $\delta_H(CDCl_3)$ 6.99–7.43 (10 H, m, Ar), 5.85–5.92 (2 H, m, CH=C*H*–C*H*=CH), 3.34 (9 H, d, $J_{PH} = 12.4$ Hz, CH_3), 2.00–2.06 (2 H, m, C*H*=CH–CH=C*H*);

Table 5
Summary of crystallographic data for complexes **3**, **5**, **6** and **10**[a]

	3	**5**	**6**	**10**
Empirical formula	$C_{27}H_{21}O_3Ru$	$C_{16}H_{14}O_5Ru$	$C_{14}H_{10}O_4Ru$	$C_{14}H_{12}O_4Ru$
Formula weight	494.51	387.34	343.29	345.31
Crystal size (mm)	0.47, 0.31, 0.19	0.42, 0.35, 0.20	0.47, 0.39, 0.08	0.27, 0.23, 0.12
Crystal class	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$\mathrm{P}\bar{1}$	$C2/c$
a (Å)	9.311(2)	7.3735(9)	7.133(1)	27.464(5)
b (Å)	10.178(2)	10.044(1)	9.927(2)	15.796(2)
c (Å)	12.415(3)	21.617(3)	10.029(2)	7.755(1)
α (°)	75.75(2)	90	70.80(1)	90
β (°)	89.49(2)	98.60(1)	74.35(1)	94.11(2)
γ (°)	71.81(1)	90	85.44(1)	90
V (Å^3)	1080.4(4)	1582.9(4)	645.8(2)	3355.5(10)
Z	2	4	2	8
$D_{\mathrm{calc.}}$ (Mg m^{-3})	1.520	1.625	1.766	1.367
μ(Mo–K$_\alpha$) (mm^{-1})	0.752	1.010	1.219	0.939
F(000)	502	776	340	1376
θ range (°)	2.6–25.0	2.8–25.0	3.0–27.5	2.6–22.5
Min/max transmission	0.801, 0.871	0.546, 0.641	0.690, 0.921	0.297, 0.391
No. reflections collected	3842	3463	3778	2872
Unique reflections	3818	2788	2633	2201
R_{int}	0.025	0.019	0.009	0.024
Observed reflections [$F_o > 4\sigma(F_o)$]	3624	2492	2541	1543
R_1 [$F_o > 4\sigma(F_o)$]	0.026	0.027	0.016	0.049
wR_2 (all data)	0.069	0.086	0.043	0.169
Goodness-of-fit	1.074	1.073	1.085	1.090
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	1.02, −0.69	0.77, −0.80	0.31, −0.46	0.708, −0.624

[a] Details in common: Stoè Stadi-4 diffractometer operating at 150(2) K{220(2)K for **10**}; ω-θ scan mode with learnt profile fitting (ω scan mode for **10**); graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å); absorption corrections from semi-empirical ψ scans; full-matrix least-squares refinement on F_o^2 where the function minimised was

$$\Sigma w(F_o^2 - F_c^2)^2;\quad R_1 = \frac{\sum\|F_o| - |F_c\|}{\sum|F_o|}$$

$$wR_2 = \sqrt{\frac{[\Sigma w(F_o^2 - F_c^2)^2]}{\Sigma w F_o^4}},$$

where $w^{-1} = \sigma^2(F_o^2) + (xP)^2 + yP$ and $P = (F_o^2 + 2F_c^2)/3$.

δ_P(CDCl$_3$) 166.8; δ_C(CDCl$_3$) 200.2 (2 C, d, $J_{PC} = 7.5$ Hz, CO), 143.1 (2 C, *ipso*-Ar), 128.1 (4 C, *o*-Ar), 125.3 (2 C, *m*-Ar), 124.6 (4 C, *p*-Ar), 82.1 (2 C, CH=*C*H–*C*H=CH), 54.6 (2 C, *C*H=CH–CH=*C*H), 51.2 (3 C, d, $J_{PC} = 1.6$ Hz, CH$_3$).

3.10. [Ru(CO)$_3${(E,E)-5-phenylpenta-2,4-dienol}] (**10**)

To a solution of **5** (0.100 g, 0.258 mmol) in THF (50 cm^{-3}) at −78°C was added diisobutylaluminium hydride (0.57 cm^{-3}; 1 M in hexane, 0.568 mmol). The resulting solution was allowed to warm to r.t. and stirred for 1 h, at which point complete consumption of **5** was indicated by thin layer chromatography. The reaction mixture was quenched with water and the organic layer washed successively with 2 M HCl and a saturated NaCl solution. The organic phase was dried and the solvent removed to yield a pale yellow oil, which was purified by preparative thin layer chromatography eluting with a 30% ethyl actetate–hexane mixture to afford the desired product as a white crystalline material ($R_f = 0.37$, 0.075 g, 83.7%) [Found: C, 48.8; H 3.4; m/z 346 [MH]$^+$. $C_{14}H_{12}O_4Ru$ requires C, 48.70; H, 3.50%; M (based on ^{101}Ru) 345], $\tilde{\nu}_{\max}$ cm^{-1} (pentane) 2067s, 2005vs, 1993s (CO); δ_H(CDCl$_3$) 7.06–7.26 (5 H, m, Ar), 5.84–5.89 (1 H, m, Ar–CH=C*H*), 5.42–5.47 (1 H, m, C*H*=CH–CH$_2$OH), 3.60–3.83 (2 H, m, CH$_2$), 2.52 (1 H, d, $J = 8.6$ Hz, Ar–C*H*), 1.62–1.71 (1 H, m, C*H*–CH$_2$OH), 1.46 (1 H, s, br, OH); δ_C(CDCl$_3$) 141.0 (1 C, *ipso*-Ar), 128.5 (2 C, *o*-Ar), 125.7 (1 C, *p*-Ar), 125.4 (2 C, *m*-Ar), 84.6 (1 C, Ar–CH=*C*H), 84.0 (1 C, *C*H=CH–CH$_2$OH), 65.2 (1 C, CH$_2$), 55.1 (1 C, Ar–*C*H), 54.1 (1 C, *C*H–CH$_2$OH).

4. Crystallography

A summary of crystal data and parameters associated with data collection, structure solution and refinement is given in Table 5. The structures were solved by a combination of Patterson methods and Fourier techniques. Hydrogen atoms of the coordinated diene moieties (and aldehyde hydrogen for **6**) were located from Fourier difference electron density syntheses and allowed to refine without constraint. All remaining hydrogen atoms were placed in calculated positions and refined using a riding model with individual isotropic thermal parameters allowed to refine freely. Anisotropic thermal motion was assumed for all non-hydrogen atoms. The crystallographic computing programs SHELXS-86 and SHELXL-93 were used throughout the structure solution and refinement process [41,42]. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

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