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FULL PAPER

Bis(acetylacetonato)bis(cyclooctene)ruthenium(II), *cis*-[Ru(acac)$_2$-(η^2-C$_8$H$_{14}$)$_2$]: a synthetic precursor to *trans*- and *cis*-bis(acetylacetonato)ruthenium(II) complexes †

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Reduction of [Ru(acac)$_3$] with zinc amalgam or zinc dust in hot THF containing some water in the presence of an excess of cyclooctene generated in solution *cis*-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)$_2$], which cannot be isolated in solid form but has been identified on the basis of its ^{1}H NMR spectrum. It is a useful synthetic precursor because the co-ordinated olefins are easily displaced by many ligands. Treatment with pyridine, *tert*-butyl isocyanide, tertiary phosphines, phosphites and triphenylarsine (L) at room temperature gave red-brown complexes *trans*-[Ru(acac)$_2$L$_2$], which isomerise in solution to the more stable *cis* compounds on heating. In contrast, the similarly prepared trimethylamine complex, *trans*-[Ru(acac)$_2$(NMe$_3$)$_2$], does not undergo *trans* to *cis* isomerisation. Reaction of *cis*-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)$_2$] with acetonitrile or triphenylstibine (L′) gave monosubstitution products *cis*-[Ru(acac)$_2$-(η^2-C$_8$H$_{14}$)L′], which react on heating with an excess of L′ to give *cis*-[Ru(acac)$_2$L′$_2$]. Treatment of *cis*-[Ru(acac)$_2$-(η^2-C$_8$H$_{14}$)$_2$] (1 mol) with Ph$_2$PCH$_2$PPh$_2$ (dppm) (2 mol) at room temperature gave *trans*-[Ru(acac)$_2$(η^1-dppm)$_2$], whereas the ligands Ph$_2$P(CH$_2$)$_m$PPh$_2$ (L–L, *m* = 2, dppe; m = 3, dppp) under the same conditions gave oligomers [{Ru(acac)$_2$(L–L)}$_n$], which probably contain mutually *trans*-phosphorus atoms. On heating all three compounds are converted into *cis*-[Ru(acac)$_2$(L–L)]. Treatment of *trans*-[Ru(acac)$_2$L$_2$] (L = NMe$_3$ or PPh$_3$) with CO at room temperature and pressure gave *trans*-[Ru(acac)$_2$(CO)L], which, in the case of L = PPh$_3$, isomerises to the *cis* compound on heating; reaction of *trans*-[Ru(acac)$_2$(AsPh$_3$)$_2$] with CO under the same conditions gave *cis*-[Ru(acac)$_2$(CO)(AsPh$_3$)] directly. The structures of *trans*-[Ru(acac)$_2$(CNBu^t)$_2$], *trans*-[Ru(acac)$_2$(PMePh$_2$)$_2$], *cis*-[Ru(acac)$_2$(CNBu^t)$_2$] (in the form of a molecular adduct with [Ru(acac)$_3$]), *cis*-[Ru(acac)$_2$(PMePh$_2$)$_2$] and *trans*-[Ru(acac)$_2$(η^1-dppm)$_2$] have been determined by X-ray crystallography, and trends in the metal–ligand distances are discussed. The formation of *trans*-[Ru(acac)$_2$L$_2$] from *cis*-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)$_2$] may proceed *via* a square-pyramidal intermediate [Ru(acac)$_2$L].

It has long been known that the chelating dienes cycloocta-1,5-diene (cod) and bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, nbd) react with solutions of ruthenium trichloride to give poorly soluble ruthenium(II) compounds [{RuCl$_2$(η^2,η^2-diene)}$_n$], which are believed to have a polymeric structure consisting of chains of metal atoms each co-ordinated octahedrally by the diene and bridging chlorine atoms.[1,2] These complexes are useful synthetic precursors because the bridges are readily cleaved and the diene is easily replaced by other ligands. However, potentially even more labile analogues containing two molecules of ethene or monoalkene in place of the diene are unknown. The blue solutions obtained by reduction of RuCl$_3$ in aqueous hydrochloric acid have been reported to absorb one mole of ethene per ruthenium.[3] The species formed may be the cation [Ru(H$_2$O)$_5$(η^2-C$_2$H$_4$)]$^{2+}$, the tosylate (toluene-*p*-sulfonate) salt of which has been isolated from the reaction of ethene (60 bar) with [Ru(H$_2$O)$_6$][OTs]$_2$.[4] Analogues containing 2,5-dihydrofuran and 5,6-bis(methoxymethyl)-7-oxanorbornene have been obtained similarly from [Ru(H$_2$O)$_6$][OTs]$_2$;[5,6] complexes of the type [Ru(H$_2$O)$_5$(η^2-alkene)]$^{2+}$ are intermediates in the [Ru(H$_2$O)$_6$]$^{2+}$-catalysed ring-opening metathesis polymerisation (ROMP) and isomerisation of olefins.[5–7] The closely related pentammines, [Ru(NH$_3$)$_5$(η^2-alkene)]$^{2+}$, are obtained by reduction of [RuCl(NH$_3$)$_5$]Cl$_2$ with zinc amalgam in the presence of the alkene.[8–10] Prolonged reaction of ethene (60 bar) with [Ru(H$_2$O)$_6$]$^{2+}$ gives the bis(ethene) salt, *cis*-[Ru(H$_2$O)$_4$(η^2-C$_2$H$_4$)$_2$][OTs]$_2$,[4] and analogous chelate compounds [Ru(H$_2$O)$_4$(η^2,η^2-diene)]$^{2+}$ (diene = cod[11] or diallyl ether[6]) and [Ru(NH$_3$)$_4$(η^2,η^2-diene)]$^{2+}$ (diene = *s*-*trans*-buta-1,3-diene, penta-1,4-diene or hexa-1,5-diene)[12] have been described. Chelate monoalkene compounds have also been isolated, *e.g.* [Ru(H$_2$O)$_4$(CH$_2$=CHCH$_2$CH$_2$OH)][OTs]$_2$ from but-3-en-1-ol and [Ru(H$_2$O)$_2$(MeCH=CHCH$_2$COO)$_2$] from pent-3-enoic acid.[6]

The existence of complexes containing only classical non-π-acceptor ligands such as H$_2$O and NH$_3$ in the co-ordination sphere as well as an alkene prompted us to search for neutral complexes of the type [Ru(acac)$_2$(η^2-alkene)$_2$] (acac = acetylacetonate, C$_5$H$_7$O$_2$) which, unlike the cationic species mentioned above, would be expected to be readily soluble in organic solvents. Here we describe the generation from [Ru(acac)$_3$] of the labile cyclooctene complex *cis*-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)$_2$] **1** and its subsequent reactions with ligands.

Results

Treatment of [Ru(acac)$_3$] in THF containing *ca.* 5% v/v water with an excess of cyclooctene and either *ca.* 2% zinc amalgam

† Dedicated to Professor Helmut Werner, University of Würzburg, with best wishes on the occasion of his 65th birthday.

Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3451/

Also available: NMR data for the complexes. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/3451/, otherwise available from BLDSC (No. SUP 57625, 10 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

or activated zinc dust at room temperature gives initially a deep brown solution, which changes to red-brown after heating for a few hours; filtration gives a very air-sensitive, orange-red solution. The brown-black oily residue obtained after evaporation to small volume shows in its ^{1}H NMR spectrum in d_6-benzene two sharp 3 H singlets at δ 1.78 and 1.96 due to acac methyl protons and a sharp 1 H singlet at δ 5.20 due to the γ-CH proton, consistent with the presence of a *cis*-Ru(acac)$_2$ group attached to two identical ligands. In addition to a symmetrical multiplet at δ 5.62 due to residual free cyclooctene, there is a 2 H multiplet of similar appearance at δ 3.80, which we assign to the olefinic protons of co-ordinated cyclooctene. The *ca*. 2 ppm shift to low frequency is similar to those observed for $[Ru(NH_3)_5(\eta^2\text{-}C_2H_4)]^{2+}$ (δ 3.57),[8] *cis*-$[Ru(H_2O)_4(\eta^2\text{-}C_2H_4)_2]^{2+}$ (δ 3.81),[4] and $[Ru(H_2O)_5(\eta^2\text{-}C_2H_4)]^{2+}$ (δ 5.04)[4] (*cf*. δ 5.46 for free C_2H_4). There are also well resolved multiplets at δ 1.6–1.8 and 2.4 assignable to the CH_2 protons of co-ordinated cyclooctene, which are distinguishable from broad singlets at δ 1.42 and 2.06 due to the corresponding resonances of free cyclooctene.

The ^{1}H NMR data are consistent with the presence in solution of *cis*-$[Ru(acac)_2(\eta^2\text{-}C_8H_{14})_2]$ **1**, the co-ordinated cyclooctene of which clearly does not exchange rapidly with free cyclooctene on the NMR timescale. Although on one occasion a yellow-brown crystalline solid of this formula was isolated by cooling the reaction residue to 0 °C overnight, the procedure was not reproducible. Attempts to remove the excess of cyclooctene *in vacuo* caused the appearance of additional peaks at δ 1.73 (s), 2.04 (s) due to acac CH_3, δ 5.09 (s), 5.12 (s) due to acac γ-CH, and δ 4.64 (symmetrical multiplet) due to co-ordinated cyclooctene. These signals disappeared when more cyclooctene was added and the original spectrum was reformed; hence the new peaks may be due to species such as $[Ru(acac)_2(\eta^2\text{-}C_8H_{14})(solv)]$ (solv = H_2O or THF). Experiments in progress indicate that the ethene analogue of compound **1** can be generated by a similar procedure and that it is stable enough to be isolated.[13] If the preparation is carried out with norbornadiene in place of cyclooctene the known complex $[Ru(acac)_2(\eta^4\text{-nbd})]$[14] can be isolated in *ca*. 50% yield.

Both cyclooctene ligands are displaced from solutions of complex **1** at room temperature by pyridine, *tert*-butyl isocyanide, various monodentate P-donors, and triphenylarsine to give red-brown complexes of the general type *trans*-$[Ru(acac)_2L_2]$, which isomerise to the more stable, more soluble, orange-brown *cis* compounds on heating in benzene, toluene or aromatic solvents of higher boiling point. The IR spectra of the complexes generally show four intense absorptions in the regions 1560–1570, 1500–1520, 1430–1450 and 1400–1410 cm^{-1}, which are characteristic of bidentate, O-bonded acac.[15] Although the IR spectra in these regions of corresponding *trans* and *cis* isomers do not differ significantly, the isomers are readily identified by their ^{1}H and ^{13}C NMR spectra, details of which are available as SUP 57625. As expected, the *trans* isomers show just one acac methyl singlet [δ(^{1}H) 1.3–1.7, δ(^{13}C) 27–28], whereas the *cis* show two [δ(^{1}H) 1.6–2.1, δ(^{13}C) 27–28]. In addition, the *trans* isomers show just one C=O resonance in their ^{13}C NMR spectra in the region of δ 184, whereas the *cis* show two. The spectra of both *trans*- and *cis*-$[Ru(acac)_2L_2]$ complexes show only one acac γ-CH resonance in the regions of δ 5.0(^{1}H) and 100 (^{13}C); for a given pair, this resonance is always more shielded in the ^{1}H NMR spectrum and less shielded in the ^{13}C NMR spectrum for the *trans* than for the *cis* isomer. The configurations of the *cis* and *trans* isomers of $[Ru(acac)_2L_2]$ (L = Bu^{t}NC or $PMePh_2$) have been confirmed by X-ray crystallographic analysis (see below).

The ^{31}P-{^{1}H} NMR spectra of the tertiary phosphine complexes $[Ru(acac)_2L_2]$ show the expected singlets; those of the *trans* isomers are always *ca*. 20 ppm more shielded than those of the corresonding *cis*, which is opposite to the trend observed in *cis*- and *trans*-$[PtCl_2L_2]$.[16–18] These data also are available as SUP 57625. Other features of the NMR spectra of the tertiary phosphine complexes are consistent with the assigned geometries. For the methylphosphine complexes *trans*-$[Ru(acac)_2L_2]$ (L = PMe_3, PMe_2Ph or $PMePh_2$), the PMe resonance appears as a 1 : 2 : 1 triplet in both the ^{1}H and ^{13}C NMR spectra as a consequence of the expected strong coupling between the equivalent, mutually *trans* ^{31}P nuclei[19–21] (for example, $^2J_{PP}$ values of 308 and 229 Hz have been reported for isomers of the type $[RuCl_2(CO)_2(Bu^t_2PH)_2]$ in which the secondary phosphine ligands are *trans*[22]). For the complexes *cis*-$[Ru(acac)_2L_2]$ (L = PMe_3 or $PMePh_2$) the PMe resonance in the ^{1}H NMR spectrum consists of a filled-in doublet as a consequence of the much smaller value of $^2J_{PP}$ (probably *ca*. 20–30 Hz); in *cis*-$[Ru(acac)_2(PMe_2Ph)_2]$ the PMe resonance appears as a pair of filled-in doublets because the PMe groups are diastereotopic. As in the cases of planar bis(tertiary phosphine) complexes of palladium(II) and platinum(II),[21,23] the corresponding ^{13}C resonances are less diagnostic, consisting of a triplet (L = PMe_3), a pair of triplets (L = PMe_2Ph), and a doublet of doublets with a pair of weak outer lines (L = $PMePh_2$). The CH_2 resonance in the ^{13}C NMR spectra of the complexes $[Ru(acac)_2(PEt_3)_2]$ is a 1 : 2 : 1 triplet for the *trans* isomer and a doublet of doublets with weak outer lines for the *cis*.

The *trans* to *cis* isomerisations of $[Ru(acac)_2L_2]$ (L = PMe_2Ph or PMe_3) require more forcing conditions (refluxing xylene and mesitylene, respectively) than those of other members of the series. The isolated products contain a small amount of a carbonyl complex, probably *cis*-$[Ru(acac)_2(CO)L]$, which can be detected in the mass spectra and by the ν(CO) band at *ca*. 1940 cm^{-1} in the IR spectra. The CO may be formed by degradation of the acac ligands, although this has not been proved.

Surprisingly, the cyclooctene ligands of complex **1** are also displaced at room temperature by an excess of trimethylamine to give *trans*-$[Ru(acac)_2(NMe_3)_2]$ as a brownish green solid. The same compound is obtained more conveniently by zinc amalgam reduction of $[Ru(acac)_3]$ in aqueous THF in the presence of an excess of trimethylamine. The EI-mass spectrum shows a very weak parent ion peak together with peaks arising from the successive loss of NMe_3. The *trans* configuration follows from the ^{1}H NMR spectrum, which shows singlets at δ 1.82 (12 H), 2.16 (18 H) and 5.37 (2 H) in d_6-benzene due to the acac methyl, NMe_3 and acac methine protons, respectively. The corresponding resonances in the ^{13}C NMR spectrum are at δ 28.11, 53.93 and 101.32, and there is also a singlet at δ 183.5 due to the equivalent C=O groups. The compound can be sublimed with some decomposition at 60 °C/10^{-4} mmHg to give a brown oil that slowly solidifies.

Unlike other members of the *trans*-$[Ru(acac)_2L_2]$ series, the NMe_3 complex does not undergo *trans* to *cis* isomerisation in refluxing aromatic solvents. It is apparently unreactive towards cyclooctene and phenylacetylene, and reacts only slowly with triphenylphosphine to give *trans*-$[Ru(acac)_2(PPh_3)_2]$. However, treatment with CO displaces one of the NMe_3 ligands to give *trans*-$[Ru(acac)_2(CO)(NMe_3)]$ as a dark brown solid that smells strongly of the amine. The presence of a terminal CO ligand is evident from a very strong ν(CO) band at 1920 cm^{-1} (KBr disc) [1953 cm^{-1} (C_6H_{12})] in the IR spectrum, a signal at δ 212.2 in the ^{13}C NMR spectrum, and a parent ion peak at *m*/*z* 387 in the FAB-mass spectrum. The EI-mass spectrum did not show this parent ion peak but did contain peaks at *m*/*z* 655, 627 and 599 apparently arising from $Ru_2(acac)_4$ fragments. The ^{1}H NMR spectrum of the compound in d_6-benzene shows singlets at δ 1.71 (12 H), 2.24 (9 H) and 5.08 (2 H) due to the acac methyl, NMe_3, and acac methine protons, respectively, and is therefore consistent with the formulation. The corresponding peaks in the ^{13}C NMR spectrum in CD_2Cl_2 are at δ 27.09, 49.64 and 100.48, and the acac C=O resonance is at δ 199.0.

Carbon monoxide also reacts readily at room temperature with *trans*-$[Ru(acac)_2(PPh_3)_2]$ to give *trans*-$[Ru(acac)_2(CO)(PPh_3)]$ as yellow microcrystals, which show a singlet at δ 16.1 in the ^{31}P NMR spectrum. The complex *cis*-$[Ru(acac)_2(PPh_3)_2]$

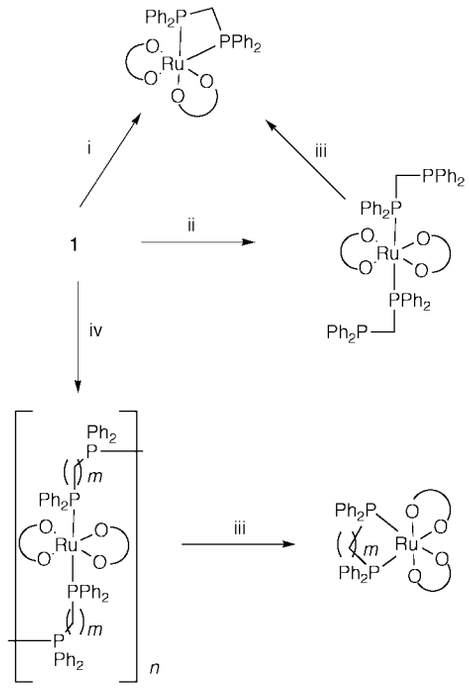
fails to react with CO under the same conditions. As expected for a *trans* isomer, the ^{1}H and ^{13}C NMR spectra show singlet acac methyl and methine resonances. In addition, the ^{13}C NMR spectrum contains a singlet at δ 188.9 due to the acac C=O groups and a doublet at δ 208.0 ($^2J_{PC}$ = 123 Hz) due to C=O. The latter peak was measured on the compound made from ^{13}CO and the coupling was reproduced in the ^{31}P NMR spectrum. Although the IR spectrum shows, as expected, one intense ν(CO) band [1940 (KBr), 1966 (C_6H_{12}), 1959 (toluene), 1956 (CH_2Cl_2), 1935 cm^{-1} (THF)], other, less intense absorptions are also observed in the region 1935–1955 cm^{-1} for which we have no adequate explanation; they appear to be due to ν(CO) modes because they exhibit the expected shifts to low frequency in the spectrum of the ^{13}CO-labelled compound. The EI-mass spectrum of *trans*-[Ru(acac)$_2$(CO)(PPh$_3$)] contains peaks at *m*/*z* 590 and 562 due to $[M]^+$ and $[M - CO]^+$ but occasionally we observed peaks in the FAB-mass spectrum at *m*/*z* 656, 628 and 600, apparently due to fragments containing $Ru_2(acac)_4$. These phenomena are being investigated further.

When *trans*-[Ru(acac)$_2$(CO)(PPh$_3$)] is heated under reflux in toluene it is converted into the yellow-brown *cis* isomer, whose ^{31}P chemical shift, δ 53.4, is fortuitously close to that of *cis*-[Ru(acac)$_2$(PPh$_3$)$_2$]. As expected for the formulation, the ^{1}H NMR spectrum shows four acac methyl and two acac methine singlet resonances. In the ^{13}C NMR spectrum only two of the expected four acac methyl singlets are observed, presumably because of accidental overlap, but there are two acac methine resonances in the region of δ 99–100 and four acac C=O resonances in the region of δ 185–189. In the ^{13}C NMR spectrum of the ^{13}CO complex there is a doublet due to C=O at δ 207.8 ($^2J_{PC}$ = 18.5 Hz), this coupling being reproduced in the ^{31}P NMR spectrum. The magnitude of $^2J_{PC}$ is consistent with a *cis* arrangement of the CO and PPh$_3$ ligands. The EI-mass spectrum shows the expected $[M]^+$ and $[M - CO]^+$ peaks and the IR spectrum contains just one strong ν(CO) band at *ca*. 1950 cm^{-1}.

The reactions of *trans*-[Ru(acac)$_2$L$_2$] (L = PPh$_3$ or PMePh$_2$) with PMe$_3$ at room temperature have also been investigated briefly by ^{31}P and ^{1}H NMR spectroscopy. In both cases L is displaced and some *trans*-[Ru(acac)$_2$(PMe$_3$)$_2$] is formed. The main species present in both cases is *trans*-[Ru(acac)$_2$(PMe$_3$)L], characterised by an AB quartet with a $^2J_{PP'}$ value of *ca*. 400 Hz. The ^{1}H NMR spectra of the solutions also contain a new singlet at δ *ca*. 4.8 that can be assigned to the acac methine protons of the mixed ligand complex.

The triphenylarsine complex *trans*-[Ru(acac)$_2$(AsPh$_3$)$_2$] also reacts readily with CO (3 bar) at room temperature to give, as the main product, *cis*-[Ru(acac)$_2$(CO)(AsPh$_3$)] as a bright yellow solid. Its IR spectrum shows one intense ν(CO) band at *ca*. 1940 cm^{-1} and the EI-mass spectrum contains peaks due to $[M]^+$ and $[M - CO]^+$. The *cis* configuration is assigned on the basis that there are four acac methyl and two acac methine resonances in the ^{1}H and ^{13}C NMR spectra. In addition, there are four acac C=O resonances between δ 186 and 189 and a singlet due to C=O at δ 208.2. There was no evidence in this case for the formation of the *trans* isomer as a intermediate.

The tendency to from *trans*-[Ru(acac)$_2$L$_2$] as a kinetic product from *cis*-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)$_2$] is evident even in the reactions with bidentate ditertiary phosphines (Scheme 1). The reaction with bis(diphenylphosphino)methane (dppm) in a 1:2 mol ratio at 0 °C precipitates almost quantitatively *trans*-[Ru(acac)$_2$(η^1-dppm)$_2$] as a red-brown solid whose structure has been determined by X-ray crystallographic analysis (see below). The ^{1}H and ^{13}C NMR spectra show the expected features due to the acac groups and the ^{31}P-{^{1}H} NMR spectrum consists of a pair of triplets at δ 36.6 and −28.3, each with a separation of 14 Hz between the outer arms, due to the bound and free phosphorus atoms. The compound tends to lose dppm in solution with formation of the chelate complex *cis*-[Ru(acac)$_2$(dppm)] (δ_P 17.7), which is formed directly in high yield by treatment of



Scheme 1 (i) dppm (1 equivalent); (ii) dppm (2 equivalents); (iii) heat; (iv) dppe (*m* = 2), dppp (*m* = 3).

1 with an equimolar amount of dppm. Treatment of *trans*-[Ru(acac)$_2$(η^1-dppm)$_2$] with CO also causes displacement of dppm, identified by its characteristic ^{31}P resonance at δ −22.4. The main complex present is believed to be *trans*-[Ru(acac)$_2$-(CO)(η^1-dppm)], which shows a ν(CO) band at 1957 cm^{-1} and a pair of doublets at δ 14.7 and −28.9 ($^2J_{PP}$ = 37.8 Hz) due to the co-ordinated and free phosphorus atoms. Attempts to isolate this compound caused reformation of *trans*-[Ru(acac)$_2$(η^1-dppm)$_2$]. The *cis* complex [Ru(acac)$_2$(dppm)] has been identified by microanalysis, mass spectrometry, and by its ^{1}H and ^{13}C NMR spectra.

Treatment of complex **1** with 1,2-bis(diphenylphosphino)-ethane (dppe) causes immediate precipitation of a yellow-brown solid of empirical formula [Ru(acac)$_2$(dppe)] whose EI-mass spectrum shows a parent-ion peak. The solid is insoluble in all common organic solvents and its IR spectrum contains strong bands typical of chelate O-bonded acac at 1560, 1510, 1435 and 1405 cm^{-1}. On heating in a mixture of xylene and di-*n*-butyl ether the solid slowly dissolves to give an orange solution from which *cis*-[Ru(acac)$_2$(dppe)] can be isolated as a bright yellow powder. The ^{1}H and ^{13}C NMR spectra of this compound show the expected two acac methyl and one acac methine resonance and the ^{13}C NMR spectrum also contains two C=O resonances in the region of δ 185. The initially formed brown solid is, therefore, the kinetic product, which presumably is an isomer or a mixture of isomers of oligomeric structure containing *trans*-[Ru(acac)$_2$] units connected by bridging dppe units.

The reaction of complex **1** with 1,3-bis(diphenylphosphino)-propane (dppp) in THF proceeds similarly to that with dppe except that the initially formed oligomer is more soluble. Its ^{1}H NMR spectrum contains many overlapping singlets due to acac methyl protons in the region δ 1.35–1.48, four singlets due to acac methine protons in the region δ 4.6–4.8, and broad multiplets in the regions of δ 2.5 and 7.0–7.65 due to the methylene and aromatic protons, respectively, of dppp. On prolonged heating in THF the compound is converted into *cis*-[Ru(acac)$_2$-(dppp)].

The reaction of complex **1** with 2,2′-bipyridyl (bipy) gives *cis*-[Ru(acac)$_2$(bipy)] as a dark green solid directly at room temperature. This compound has been made previously by a

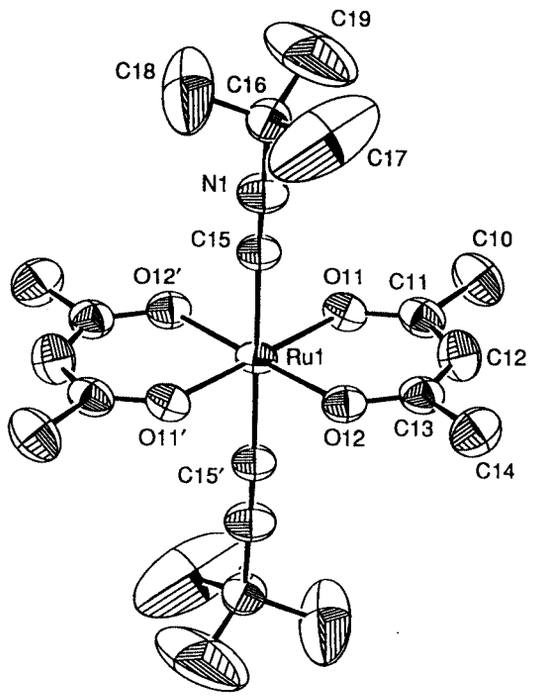


Fig. 1 Molecular structure of *trans*-[Ru(acac)$_2$(CNBu^t)$_2$]. Ellipsoids represent 50% probability levels.

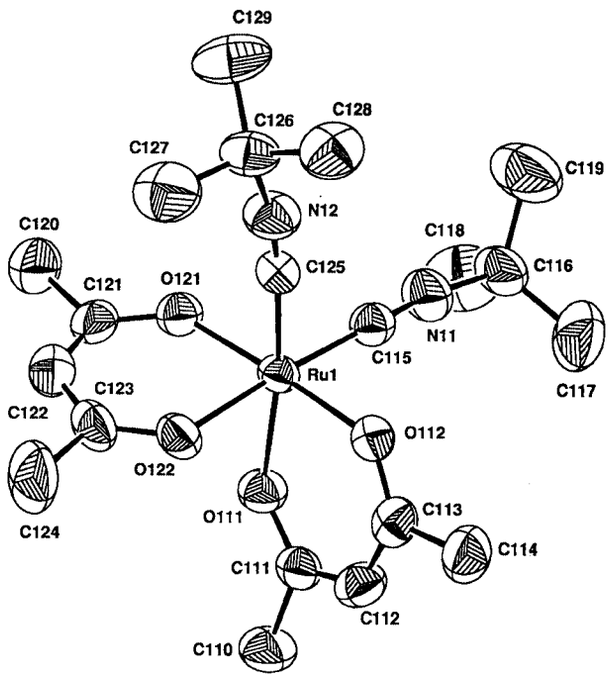


Fig. 2 Molecular structure of *cis*-[Ru(acac)$_2$(CNBu^t)$_2$]. Ellipsoids represent 50% probability levels.

multi-step procedure starting from $K_2[RuCl_5(H_2O)]$,[24] but the present method is probably more convenient.

So far we have been unable to isolate or detect intermediate monosubstitution products [Ru(acac)$_2$(η^2-C_8H_{14})L] with the monodentate P-donors discussed above. However, from the reaction of complex **1** with acetonitrile or triphenylstibine at room temperature we could isolate *cis*-[Ru(acac)$_2$(η^2-C_8H_{14})L′] (L′ = MeCN or $SbPh_3$) as stable, yellow-brown solids. The *cis* geometry is evident from the ^{1}H NMR spectra, which show four acac methyl and two acac methine singlets, and from the presence of four acac C=O resonances in the ^{13}C NMR spectra. The inequivalent olefinic protons appear as a pair of multiplets in the region δ 4.5–5.0 and the corresponding pair of carbon resonances is observed in the regions δ 83–86 (L′ = MeCN) and 73–79 (L′ = $SbPh_3$). The methyl resonance of co-ordinated acetonitrile in *cis*-[Ru(acac)$_2$(η^2-C_8H_{14})(NCMe)] displays a notable shielding in C_6D_6 [δ_H 2.37 ($CDCl_3$), 0.73 (C_6D_6); δ_C 4.61 ($CDCl_3$), 2.33 (C_6D_6)]; a similar effect is observed for the MeCN resonance of *cis*-[Ru(acac)$_2$(NCMe)$_2$] [δ_H 2.53 ($CDCl_3$), 1.06 (C_6D_6)]. Both monosubstitution products are converted into the corresponding *cis* complexes [Ru(acac)$_2$L′$_2$] (L = MeCN or $SbPh_3$) on heating with an excess of the appropriate ligand; the *trans* isomers could not be detected as intermediates under these conditions.

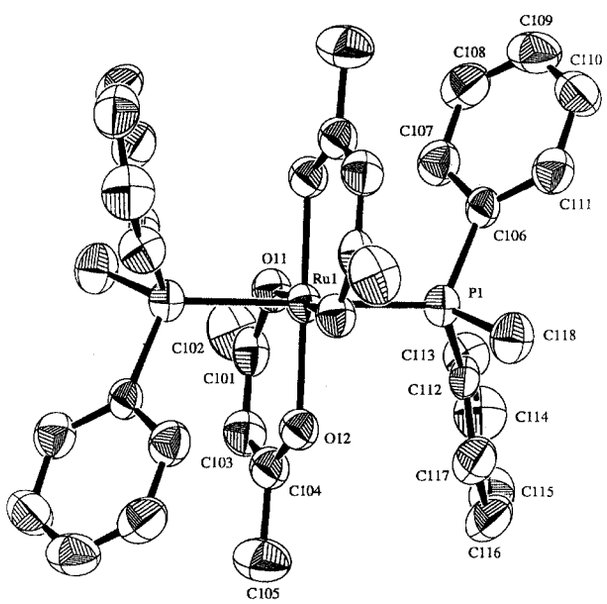


Fig. 3 Molecular structure of *trans*-[Ru(acac)$_2$(PMePh$_2$)$_2$]. Ellipsoids represent 50% probability levels.

Molecular structures

The molecular geometries of *trans*- and *cis*-[Ru(acac)$_2$(CNBu^t)$_2$], *trans*- and *cis*-[Ru(acac)$_2$(PMePh$_2$)$_2$], and *trans*-[Ru(acac)$_2$(dppm)$_2$] are shown in Figs. 1–5, respectively, together with atom numbering. Selected interatomic distances and angles are listed in Tables 1–5. The crystals of *cis*-[Ru(acac)$_2$(CNBu^t)$_2$] were obtained in the form of a 1 : 1 molecular adduct with [Ru(acac)$_3$] which had presumably been formed by partial oxidative degradation during the crystallisation; there is no obvious interaction between the two species in the crystal. In all cases, the ligand environment about the metal centre is close to octahedral and the configurations agree with those deduced on the basis of NMR data. In *trans*- and *cis*-[Ru(acac)$_2$(CNBu^t)$_2$] the isocyanide groups are almost linear, the deviations from linearity at the carbon and nitrogen atoms being at most 6 and 10°, respectively. The Ru–C distance in the *trans* isomer [2.006(5), 2.021(6) Å for two independent molecules] is significantly greater than that in the *cis* [1.920(5), 1.910(6) Å in one molecule]. These distances fall in the range of 1.90–2.04 Å that has been found in various octahedral and half-sandwich complexes of ruthenium(II) containing *tert*-butyl isocyanide, *e.g.* [RuCl(Ph)(CO)(CNBu^t)(PMe$_2$Ph)$_2$][25] and [RuI(η-C_5H_5)(CNBu^t)(PPh$_3$)].[26] A similar *trans*-bond weakening influence is evident from a comparison of the Ru–P distances in *trans*- and *cis*-[Ru(acac)$_2$(PMePh$_2$)$_2$] [2.343(1), 2.346(1) Å in independent molecules of the *trans* isomer; 2.2765(9) Å in the *cis*]. The distances in the *trans* isomer are significantly shorter than for the mutually *trans*-PMePh$_2$ ligands in both *cis*-[RuCl$_2$(CO)(PMePh$_2$)$_3$] [2.407(8), 2.433(8) Å] and *trans*-[RuCl$_2$(CO)(PMePh$_2$)$_3$] [2.403(4) Å].[27] Also, the Ru–P distance in *cis*-[Ru(acac)$_2$(PMePh$_2$)$_2$] is significantly less than for Ru–P *trans* to Cl in *cis*-[RuCl$_2$(CO)(PMePh$_2$)$_3$] [2.327(7) Å]. These trends can probably be traced to the relatively uncrowded co-ordin-

Table 1 Selected bond distances (Å) and angles (°) for *trans*-[Ru(acac)$_2$(CNBu^t)$_2$][a]

Ru(1)–O(11)	2.063(3)	Ru(2)–O(21)	2.072(3)
Ru(1)–O(12)	2.061(4)	Ru(2)–O(22)	2.066(3)
Ru(1)–C(15)	2.006(5)	Ru(2)–C(25)	2.021(6)
C(15)–N(1)	1.147(8)	C(25)–N(2)	1.145(7)
C(16)–N(1)	1.455(9)	C(26)–N(2)	1.461(8)
C(11)–O(11)	1.265(6)	C(21)–O(21)	1.259(5)
C(13)–O(12)	1.270(6)	C(23)–O(22)	1.266(6)
O(11)–Ru(1)–O(12)	93.1(1)	O(21)–Ru(2)–O(22)	93.4(1)
O(11)–Ru(1)–C(15)	90.4(2)	O(21)–Ru(2)–C(25)	91.8(2)
O(11)–Ru(1)–O(12′)	86.9(1)	O(21)–Ru(2)–O(22″)	86.6(1)
O(11)–Ru(1)–C(15′)	89.6(2)	O(21)–Ru(2)–C(25″)	88.2(2)
O(12)–Ru(1)–C(15)	88.4(2)	O(22)–Ru(2)–C(25)	94.2(2)
O(12)–Ru(1)–C(15′)	91.6(2)	O(22)–Ru(2)–C(25″)	85.8(2)
Ru(1)–C(15)–N(1)	177.6(5)	Ru(2)–C(25)–N(2)	173.6(4)
C(15)–N(1)–C(16)	175.8(5)	C(25)–N(2)–C(26)	171.1(5)

[a] Primes and double primes indicate atoms generated by the symmetry operations ($1 - x$, $1 - y$, $1 - z$) and ($1 - x$, $1 - y$, $-z$), respectively.

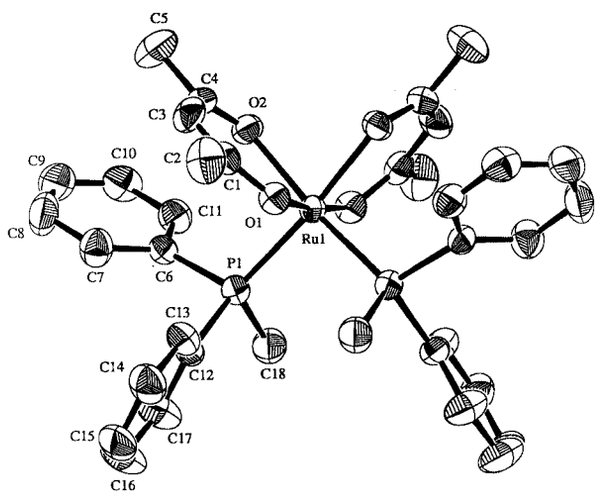


Fig. 4 Molecular structure of *cis*-[Ru(acac)$_2$(PMePh$_2$)$_2$]. Ellipsoids represent 50% probability levels.

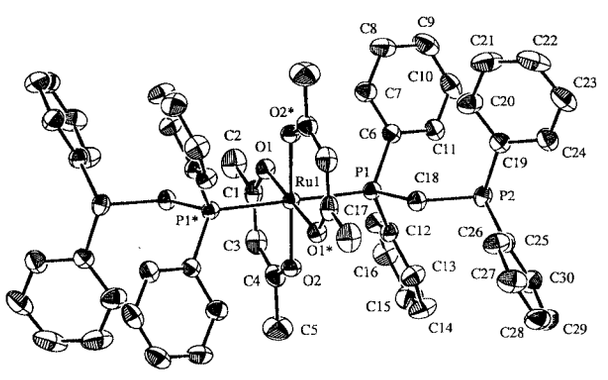


Fig. 5 Molecular structure of *trans*-[Ru(acac)$_2$(η^1-dppm)$_2$]. Ellipsoids represent 30% probability levels.

ation environment in the bis(acetylacetonato)ruthenium(II) complexes.

The Ru–O (acac) bond lengths are generally in the range 2.06–2.07 Å, similar to those in the Ru^{II}(acac)$_2$ chelate complexes of *o*-CH$_2$=CHC$_6$H$_4$NMe$_2$[28] and *o*-PhC≡CC$_6$H$_4$NMe$_2$[29] and, as expected, greater than those in [Ru(acac)$_3$][30] and the Ru^{III}(acac)$_2$ complexes of the unsaturated amines (*ca.* 2.00 Å). In *cis*-[Ru(acac)$_2$(PMePh$_2$)$_2$], however, the Ru–O distances opposite PMePh$_2$ [2.104(2) Å] are significantly greater than those *trans* to the acac oxygen atoms [2.072(2) Å], consistent with the higher *trans* influence of the tertiary phosphine. A similar though smaller effect is observed in *cis*-[Ru(acac)$_2$(CNBu^t)$_2$] [2.092 Å (av.) *trans* to CNBu^t *vs.* 2.060 Å (av.) *trans* to O (acac)].

Table 2 Selected bond distances (Å) and angles (°) for *cis*-[Ru(acac)$_2$(CNBu^t)$_2$] in its 1 : 1 adduct with [Ru(acac)$_3$]

Ru(1)–O(111)	2.093(4)	Ru(1)–O(112)	2.057(4)
Ru(1)–O(121)	2.064(4)	Ru(1)–O(122)	2.091(3)
Ru(1)–C(115)	1.920(5)	Ru(1)–C(125)	1.910(6)
C(115)–N(11)	1.155(7)	C(125)–N(12)	1.164(8)
C(116)–N(11)	1.462(8)	C(126)–N(12)	1.448(8)
C(111)–O(111)	1.268(7)	C(121)–O(121)	1.265(8)
C(113)–O(112)	1.270(6)	C(123)–O(122)	1.263(8)
O(111)–Ru(1)–O(112)	91.6(2)	O(111)–Ru(1)–O(121)	86.7(2)
O(111)–Ru(1)–O(122)	83.6(1)	O(111)–Ru(1)–C(115)	93.2(2)
O(111)–Ru(1)–C(125)	172.0(2)	O(112)–Ru(1)–O(121)	177.2(1)
O(112)–Ru(1)–O(122)	85.9(2)	O(112)–Ru(1)–C(115)	92.1(2)
O(112)–Ru(1)–C(125)	89.8(2)	O(121)–Ru(1)–O(122)	91.7(2)
O(121)–Ru(1)–C(115)	90.2(2)	O(121)–Ru(1)–C(125)	91.6(2)
O(112)–Ru(1)–C(115)	176.2(2)	O(122)–Ru(1)–C(125)	88.6(2)
C(115)–Ru(1)–C(125)	94.6(2)		

Table 3 Selected bond distances (Å) and angles (°) for *trans*-[Ru(acac)$_2$(PMePh$_2$)$_2$]

Ru(1)–P(1)	2.343(1)	Ru(2)–P(2)	2.346(1)
Ru(1)–O(11)	2.060(3)	Ru(2)–O(21)	2.064(2)
Ru(1)–O(12)	2.057(3)	Ru(2)–O(22)	2.060(3)
P(1)–C(106)	1.828(4)	P(2)–C(206)	1.832(4)
P(1)–C(112)	1.837(4)	P(2)–C(212)	1.816(4)
P(1)–C(118)	1.816(4)	P(2)–C(218)	1.816(4)
C(101)–O(11)	1.273(4)	C(201)–O(21)	1.271(4)
C(104)–O(12)	1.273(4)	C(204)–O(22)	1.266(4)
P(1)–Ru(1)–O(11)	88.72(1)	P(2)–Ru(2)–O(21)	89.49(7)
P(1)–Ru(1)–P(11′)	91.28(7)	P(2)–Ru(2)–O(21″)	90.51(7)
P(1)–Ru(1)–O(12)	90.22(7)	P(2)–Ru(2)–O(22)	93.79(7)
P(1)–Ru(1)–O(12′)	89.78(7)	P(2)–Ru(2)–O(22″)	86.21(7)
O(11)–Ru(1)–O(12)	94.00(10)	O(21)–Ru(2)–O(22)	93.48(10)
O(11)–Ru(1)–O(12′)	86.00(10)	O(21)–Ru(2)–O(22″)	86.53(10)

[a] Primes and double primes indicate atoms generated by the symmetry operations ($-x$, $-y$, $-z$) and ($\frac{1}{2} - x$), ($\frac{1}{2} - y$), ($\frac{1}{2} - z$), respectively.

Table 4 Selected bond distances (Å) and angles (°) for *cis*-[Ru(acac)$_2$(PMePh$_2$)$_2$][a]

Ru(1)–P(1)	2.2765(9)	Ru(1)–O(1)	2.072(2)
Ru(1)–O(2)	2.104(2)	P(1)–C(6)	1.835(3)
P(1)–C(12)	1.833(3)	P(1)–C(18)	1.828(3)
C(1)–O(1)	1.269(3)	C(4)–O(2)	1.260(4)
P(1)–Ru(1)–P(1′)	96.23(5)	P(1)–Ru(1)–O(1)	98.38(6)
P(1)–Ru(1)–O(1′)	86.03(6)	P(1)–Ru(1)–O(2)	90.63(6)
P(1)–Ru(1)–O(2′)	172.62(6)	O(1)–Ru(1)–O(1′)	173.4(1)
O(1)–Ru(1)–O(2)	90.30(8)	O(1)–Ru(1)–O(2′)	84.75(8)
O(2)–Ru(1)–O(2′)	82.7(1)		

[a] Primes indicate atoms generated by the symmetry operation ($-x$, y, $\frac{1}{2} - z$).

The molecular structure of *trans*-[Ru(acac)$_2$(dppm)$_2$]·2CH$_2$Cl$_2$ ‡ confirms the presence of two monodentate dppm ligands, the pendant CH$_2$PPh$_2$ groups being in an *anti* orientation. The Ru–P distance [2.377(1) Å] is slightly longer than those in *trans*-[Ru(acac)$_2$(PMePh$_2$)$_2$] and in [RuCl(η-C$_5$H$_5$)(PPh$_3$)(η^1-dppm)] [2.319(2) Å].[31] The metrical parameters for [Ru(acac)$_3$] in its adduct with *cis*-[Ru(acac)$_2$(CNBu^t)$_2$] are similar to those derived from various recent structural determinations of the pure compound.[30]

‡ We have also solved the structure of a second modification, *trans*-[Ru(acac)$_2$(dppm)$_2$]·CH$_2$Cl$_2$, which belongs to the same space group, $P\bar{1}$ (no. 2), with *a* 10.774(2), *b* 11.362(3), *c* 13.463(3) Å, *α* 66.78(2), *β* 74.20(1), *γ* 86.95(2)°. The Ru–P distance in this solvate is 2.3575(8) Å; the other metrical parameters do not differ significantly from those in *trans*-[Ru(acac)$_2$(dppm)$_2$]·2CH$_2$Cl$_2$.

Table 5 Selected bond distances (Å) and angles (°) for *trans*-[Ru(acac)$_2$(dppm)$_2$][a]

Ru(1)–P(1)	2.377(1)	Ru(1)–O(1)	2.067(2)
Ru(1)–O(2)	2.066(2)	P(1)···P(2)	3.198(1)
P(1)–C(6)	1.833(3)	P(1)–C(12)	1.832(4)
P(1)–C(18)	1.830(3)	P(2)–C(18)	1.866(4)
P(2)–C(19)	1.832(4)	P(2)–C(25)	1.835(4)
C(1)–O(1)	1.272(4)	C(4)–O(2)	1.282(4)
P(1)–Ru(1)–O(1)	89.91(7)	P(1)–Ru(1)–O(1′)	90.09(7)
P(1)–Ru(1)–O(2)	88.22(7)	P(1)–Ru(1)–O(2′)	91.78(7)
O(1)–Ru(1)–O(2)	92.45(9)	O(1)–Ru(1)–O(2′)	87.55(9)

[a] Primes indicate atoms generated by symmetry operation $(-x, -y, -z)$.

Discussion

The formation of *cis*-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)$_2$] **1** by zinc amalgam or zinc dust reduction of [Ru(acac)$_3$] in the presence of cyclooctene provides a further example of the ability of monomeric ruthenium(II) bearing saturated ligands to bind unsaturated molecules and reflects the π-donor ability of this metal ion.[32] The procedure can probably be extended to other alkenes and alkynes. We have used it previously to make the 1,2,5,6η-cyclooctatetraene complex [Ru(acac)$_2$(η^2,η^2-C$_8$H$_8$)][33] as well as chelate alkene and alkyne complexes such as [Ru(acac)$_2$(*o*-CH$_2$=CHC$_6$H$_4$NMe$_2$)][28] and [Ru(acac)$_2$(*o*-PhC≡CC$_6$H$_4$NMe$_2$)].[29] *trans*-η^2,η^2-Diene complexes [Ru(acac)$_2$(diene)] have been prepared from [Ru(acac)$_3$] by reduction with activated zinc dust in ethanol,[34,35] but this system is not suitable for the preparation of complex **1**, which is rapidly decomposed by ethanol. In the first step [Ru(acac)$_3$] is probably reduced to [Ru(acac)$_3$]$^-$,[36,37] which in turn reacts on heating with the alkene according to eqn. (1). The presence of a small amount of water

$$[Ru(acac)_3]^- + 2C_8H_{14} \longrightarrow [Ru(acac)_2(\eta^2\text{-}C_8H_{14})_2] + acac^- \quad (1)$$

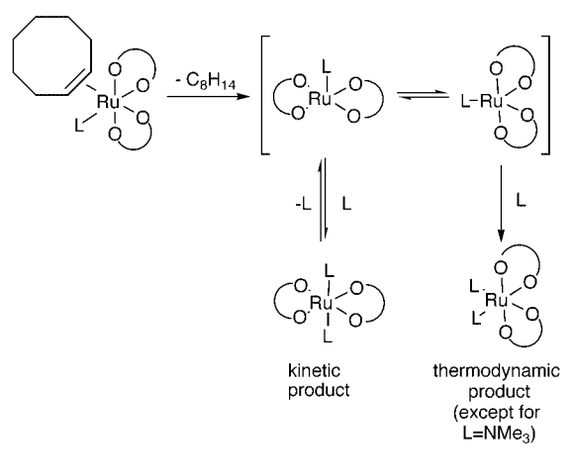
is necessary for the formation of the cyclooctene complex, possibly because it increases the reducing power of the zinc by solvation of Zn^{2+}.

The ready displacement of cyclooctene from *cis*-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)$_2$] by monodentate ligands (L) provides a range of complexes of the type *trans*-[Ru(acac)$_2$L$_2$], most of which isomerise on heating to their *cis* counterparts. While our work was in progress, Ernst *et al.*[34] reported the displacement of hexa-2,4-diene or 2,3-dimethylbutadiene from their Ru(acac)$_2$ complexes by PEt$_3$ or P(OMe)$_3$ to give mixtures of *cis*- and *trans*-[Ru(acac)$_2$L$_2$]. These authors suggested that the predominance of the *trans* isomer in the isolated product was due to its lower solubility and that this effect would be assisted by rapid *cis* to *trans* isomerisation in solution. However, ^{31}P-{^{1}H} NMR spectroscopy shows clearly that the *trans* isomer is the kinetic product of reaction of complex **1** with monodentate tertiary phosphines and phosphites and that isomerisation to the stable *cis* product is relatively slow at room temperature. Werner and co-workers[38] have reported recently that zinc amalgam reduction of [Ru(acac)$_3$] in hot aqueous THF in the presence of triisopropylstibine gives *cis*-[Ru(acac)$_2$(SbPr$^i_3$)$_2$], analogous to our SbPh$_3$ complex.

The only other examples of isolated *cis* and *trans* isomers of [Ru(acac)$_2$L$_2$] to our knowledge are those containing acetonitrile and pyrazine. The *cis* isomers were obtained by zinc amalgam reduction of [Ru(acac)$_3$] in aqueous ethanol in the presence of the ligands,[39,40] the *trans* isomers by reaction of the ligands with *trans*-[Ph$_4$As][RuCl$_2$(acac)$_2$].[40] The complexes *cis*-[Ru(acac)$_2$L$_2$] (L = CO[41] or PPh$_3$[42–44]) are well known. It has been claimed[43,44] that solid *cis*-[Ru(acac)$_2$(PPh$_3$)$_2$] exists in interconvertible orange and green forms that are identical in solution, but we found no evidence for this behaviour in the orange compound prepared by isomerisation of *trans*-[Ru(acac)$_2$(PPh$_3$)$_2$]. Clearly, the suggestion[43] that one of the forms contains *trans*-PPh$_3$ groups in the solid state must be dismissed on the basis of our results. Complexes of the type [Ru(acac)$_2$L$_2$] containing various allylic sulfides, sulfoxides, amines, imines and phosphines have been mentioned in a paper dealing with double bond isomerisation catalysed by tris(β-diketonato)ruthenium(III) complexes but they were not fully characterised.[45]

Reaction with complex **1** also allows the formation of metastable *trans*-[Ru(acac)$_2$] complexes containing potentially bidentate ditertiary phosphines (L–L). In [Ru(acac)$_2$(dppm)$_2$] the ligand is monodentate, whereas in oligomeric [Ru(acac)$_2$(dppe)] and [Ru(acac)$_2$(dppp)] the ligands are probably bridging. All three compounds are converted into the stable *cis*-[Ru(acac)$_2$(L–L)] complexes on heating. Complexes of this type containing chiral ditertiary phosphines such as (*S*)-BINAP [BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] have been made previously from [Ru(acac)$_3$] and the ligand under hydrogen (70 bar) or from [Ru(acac)$_2$(cod)] and the ligand at 145 °C.[46]

The formation of *trans*-[Ru(acac)$_2$L$_2$] from *cis*-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)$_2$] represents an unusual example of a well defined stereochemical course of ligand substitution at an octahedral metal centre.[47] Detailed kinetics studies have not yet been carried out, but the isolation in two cases of monosubstitution products *cis*-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)L′] (L′ = MeCN or SbPh$_3$) supports the idea that the olefins are replaced stepwise, most likely by a dissociative process. In the case of the Group 15 donors and Bu^{t}NC the second olefin must be replaced more rapidly than the first. The five-co-ordinate intermediate [Ru(acac)$_2$L] generated at this step is assumed to be square pyramidal; preferential attack by the entering ligand L at the vacant site will give *trans*-[Ru(acac)$_2$L$_2$] (Scheme 2). The square pyramidal geometry for a



Scheme 2 Suggested pathway for formation of *trans*- and *cis*-[Ru(acac)$_2$L$_2$] from *cis*-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)L].

five-co-ordinate d^6-metal complex is expected on the basis of theoretical considerations[48,49] and is observed in complexes such as [RuCl$_2$(PPh$_3$)$_3$].[50] At higher temperatures a trigonal bipyramidal geometry for [Ru(acac)$_2$L] may become accessible, hence reversible dissociation of L from *trans*-[Ru(acac)$_2$L$_2$] gives finally the *cis* isomer. It is not yet known whether the formation of *cis*-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)L] in the first substitution step proceeds through a similar sequence *via* an undetected intermediate *trans*-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)L]. This *trans* to *cis* isomerisation of [Ru(acac)$_2$L$_2$] occurs most readily for L = PPh$_3$, PMePh$_2$, P(OPh)$_3$, P(OMe)$_3$, AsPh$_3$ and Bu^{t}NC, presumably reflecting in part the *trans*-bond weakening influences of these ligands.[51,52] In the case of L = P(OPh)$_3$ this process occurs even on heating the solid compound. The corresponding isomerisations for L = PMe$_3$ or PMe$_2$Ph require higher temper-

atures and in these cases reversible one-ended dissociation of acac may play a role.

The lability of the ligands NMe_3, PPh_3 and $AsPh_3$ in their *trans*-$[Ru(acac)_2L_2]$ complexes is also evident from the ready displacement of L by CO to give either *trans*-$[Ru(acac)_2(CO)L]$ (L = NMe_3 or PPh_3) or *cis*-$[Ru(acac)_2(CO)(AsPh_3)]$. The only reported examples of this type of monocarbonyl complex are the derivatives *trans*-$[Ru(acac)_2(CO)(ROH)]$ (R = Me, Et or ^{i}Pr), which have been made by γ radiolysis of alcoholic solutions of $[Ru(acac)_3]$ under CO.[53]

The greater thermodynamic stability of the *cis* isomers presumably reflects the tendency of even the most weakly π-acceptor ligands to avoid competition for the same d orbital on ruthenium(II) and, in agreement, only the bis(trimethylamine) complex *trans*-$[Ru(acac)_2(NMe_3)_2]$ fails to undergo isomerisation; steric repulsion between adjacent NMe_3 groups may also destabilise the corresponding *cis* isomer. The compound *trans*-$[Ru(acac)_2(NMe_3)_2]$ is an unusual example of monodentate tertiary amine co-ordination to a later transition element, although low-valent metal carbonyl derivatives such as $[M(CO)_5(NMe_3)]$ (M = Cr, Mo or W)[54] and $[Fe(CO)_4(NMe_3)]$,[55] and compounds with early transition elements, such as $[MCl_3(NMe_3)_2]$ (M = Ti, V or Cr),[56] are well known. The surprising stability to air of *trans*-$[Ru(acac)_2(NMe_3)_2]$ can be attributed to the relatively unhindered nature of the $[Ru(acac)_2]$ acceptor and to the steric protection to oxidation at the metal centre by the methyl groups of the amine.

Conclusion

The cyclooctene complex $[Ru(acac)_2(\eta^2\text{-}C_8H_{14})_2]$ **1**, which is easily accessible from $[Ru(acac)_3]$, provides a convenient entry into a wide range of *trans*- and *cis*-$[Ru(acac)_2L_2]$ complexes. Since the acac ligands should also be readily removed by protonation, these compounds may also prove to be useful synthetic precursors in ruthenium chemistry.

Experimental

All operations were carried out under anaerobic conditions with use of standard Schlenk techniques. Cyclooctene and norbornadiene were filtered through a column of neutral, freshly degassed alumina to remove peroxides; solvents were freshly degassed by distillation under nitrogen before use. The following instruments were used: Varian XL-200 (^{1}H at 200 MHz, ^{31}P NMR at 80.9 MHz), Varian Gemini 300 BB or VXR 300 (^{1}H at 300 MHz, ^{13}C NMR at 75.4 MHz, ^{31}P NMR at 121.4 MHz), Perkin-Elmer 683 or 1800(FT) (IR spectra on solids as KBr discs or Nujol mulls between KBr windows, or on solutions in 0.1 mm KBr cells), VG Micromass 7070 or Fisons Instruments VG Autospec [electron-impact (EI) mass spectra at 70 eV (≈1.1215×10^{-17} J)], and VG ZAB2-SEQ [fast-atom bombardment (FAB) mass spectra on samples prepared in CH_2Cl_2 and added to a matrix of tetraglyme (2,5,8,11,14-pentaoxapentadecane) or 3-nitrobenzyl alcohol]. Microanalyses were performed in-house. Samples for analysis were usually dried *in vacuo* at 60–80 °C for 3 h to remove traces of solvent. In the case of *trans*-$[Ru(acac)_2\{P(OPh)_3\}_2]$ this procedure caused some decomposition and *trans* to *cis* isomerisation, so this sample was dried *in vacuo* at room temperature. Melting points were determined on a Kofler hot-stage. Elemental analyses and mass spectral data are listed in Table 6.

Liquid zinc amalgam (2–3% Zn)[57] and $[Ru(acac)_3]$[30,58] were prepared by the appropriate literature procedures. Zinc dust was treated immediately before use with dilute H_2SO_4, and washed successively with water, alcohol and diethyl ether.

Preparations

***cis*-$[Ru(acac)_2(\eta^2\text{-}C_8H_{14})_2]$ 1.** The following procedure is typical. To a solution of $[Ru(acac)_3]$ (500 mg, 1.26 mmol) in freshly distilled THF (100 cm^3) containing cyclooctene (15 cm^3) and water (2 cm^3) was added liquid zinc amalgam (50 cm^3) and the mixture heated under reflux with magnetic stirring in an argon atmosphere for 3 h. The initially dark solution turned orange within 30 min. The supernatant liquid was filtered through degassed Celite into a graduated Schlenk flask and the orange-red filtrate evaporated under reduced pressure to *ca*. 100 cm^3 to give a solution assumed to contain 0.0126 mmol cm^{-3} of *cis*-$[Ru(acac)_2(\eta^2\text{-}C_8H_{14})_2]$ **1**.

To obtain the ^{1}H NMR spectrum of complex **1**, solvents were removed under reduced pressure and the resulting yellow-brown oil was taken up in C_6D_6 containing a few drops of cyclooctene. If cyclooctene was not added the more complex spectrum described in the text was obtained. On one occasion yellow-brown crystals with a C,H microanalysis corresponding to $[Ru(acac)_2(C_8H_{14})_2]$ were obtained when the solution was evaporated to dryness and set aside at 0 °C. Found: C, 59.65; H, 8.24. $C_{26}H_{42}O_4Ru$ requires C, 60.11; H, 8.09%. EI-MS: *m*/*z* 399 $[Ru_2(acac)_2]$.

$[Ru(acac)_2(\eta^4\text{-nbd})]$. A mixture of $[Ru(acac)_3]$ (600 mg, 1.5 mmol), ethanol (100 cm^3), water (5 cm^3), norbornadiene (10 cm^3) and zinc amalgam (50 cm^3) was heated under reflux with magnetic stirring for 90 min. The solution turned brown then grey-green. It was siphoned off and evaporated to dryness under reduced pressure to give the crude product as a yellow-green solid. This was purified by passage of a solution in chloroform through a neutral alumina column (activity III), eluting with $CHCl_3$–hexane. The product, $[Ru(acac)_2(\eta^4\text{-nbd})]$, crystallised as a yellow solid on concentration of the eluate. The yield was 300 mg (51%). Found: C, 52.20; H, 5.84. $C_{17}H_{22}O_4Ru$ requires C, 52.17; H, 5.62%. The ^{1}H NMR spectrum agreed with that reported.[14]

$[Ru(acac)_2(py)_2]$. A solution of *cis*-$[Ru(acac)_2(\eta^2\text{-}C_8H_{14})_2]$ **1** (2.5 mmol) in THF (40 cm^3) was stirred with an excess of pyridine (1.0 cm^3) at room temperature for 6 h. A red-brown solid that had deposited from the dark red solution was separated by centrifugation and washed with hexane. The yield of *trans*-$[Ru(acac)_2(py)_2]$ was 650 mg (57%).

The *trans* isomer (450 mg, 0.98 mmol) was heated under argon in refluxing xylene for 15 h to give, after filtration through Celite, a deep red solution. The ^{1}H NMR spectrum of the solid obtained after removal of solvent showed the presence of *cis*- and *trans*-$[Ru(acac)_2(py)_2]$. The dark red crystals obtained in the first fraction by crystallisation from THF–hexane also contained a mixture of isomers. Chromatography of the supernatant on neutral alumina (activity III) gave a bright red band, which was evaporated to dryness. The sticky residue was washed with ether to give pure *cis*-$[Ru(acac)_2(py)_2]$ as a bright red solid, mp 188–190 °C (200 mg, 44%).

$[Ru(acac)_2(bipy)]$. A solution of complex **1** (1.0 mmol) in THF (10 cm^3) was stirred overnight with a solution of 2,2′-bipyridyl (bipy) (190 mg, 1.2 mmol) in THF (10 cm^3). The precipitated solid was separated from the dark green suspension by centrifugation and washed with hexane (3 × 10 cm^3). The yield of crude *cis*-$[Ru(acac)_2(bipy)]$ was 339 mg (75%). The compound was purified by filtration of a CH_2Cl_2 solution through a column of neutral alumina (Activity III), which removed some unidentified purple material. The green filtrate was evaporated to small volume and the product precipitated by addition of hexane.

$[Ru(acac)_2(CNBu^t)_2]$. A solution of complex **1** (1.25 mmol) in THF (30 cm^3) was treated with *tert*-butyl isocyanide (0.5 cm^3, 4.4 mmol) and the mixture stirred for 6 h. Some orange *trans*-$[Ru(acac)_2(CNBu^t)_2]$ precipitated. The solution was evaporated to dryness under reduced pressure and the residue dissolved in

Table 6 Elemental analyses and mass spectra of $[Ru(acac)_2L(L')]$ complexes

L,L′	Geometry	Analysis(%)[a] C	H	Other	*m/z*[b]
2py	*trans*	52.55(52.5)	5.5(5.25)	6.0(6.1)(N)	458
	cis	52.7(52.5)	5.3(5.25)	5.9(6.1)(N)	458
$2Bu^tNC$	*trans*	51.5(51.6)	7.2(6.9)	5.6(6.0)(N)	466
	cis	51.7(51.6)	7.0(6.9)	5.9(6.0)(N)	466
C_8H_{14}, MeCN	*cis*	53.0(53.3)	7.0(6.8)	2.9(3.1)(N)	451[c]
$2NMe_3$	*trans*	46.15(46.0)	7.7(7.7)	6.3(6.7)(N)	418
bipy	*cis*	53.6(52.7)	4.5(4.8)	6.15(6.15)(N)	456
$2PPh_3$	*trans*	67.7(67.1)	5.6(5.3)	7.4(7.5)(P)	824
	cis	67.0(67.1)	5.3(5.3)	7.65(7.5)(P)	824
$2P(C_6H_4Me\text{-}p)_3$	*trans*	69.0(68.7)	6.5(6.2)	6.5(6.8)(P)	908
	cis	68.5(68.7)	6.1(6.2)	6.5(6.8)(P)	908
$2PMePh_2$	*trans*	61.0(61.8)	6.0(5.7)	8.7(8.9)(P)	699
	cis	61.8(61.8)	5.9(5.7)	8.9(8.9)(P)	700
$2PMe_2Ph$	*trans*	54.0(54.3)	6.3(6.3)	10.5(10.8)(P)	576
	cis	54.1(54.3)	6.3(6.3)	10.9(10.8)(P)	576
$2PMe_3$	*trans*	41.7(42.6)	7.4(7.1)	14.8(13.7)(P)	376[d]
	cis	44.4(42.6)	7.3(7.1)	14.0(13.7)(P)	452
$2PEt_3$	*trans*	49.0(49.35)	8.3(8.2)	11.6(11.6)(P)	536
	cis	49.6(49.35)	7.9(8.2)	11.2(11.6)(P)	536
$2P(OMe)_3$	*trans*	35.2(35.1)	5.8(5.85)	11.0(11.3)(P)	548
	cis	35.3(35.1)	6.2(5.85)	12.1(11.3)(P)	548
$2P(OPh)_3$	*trans*	59.9(60.1)	4.9(4.8)	6.7(6.7)(P)	920
	cis	60.3(60.1)	4.7(4.8)	6.6(6.7)(P)	920
$2AsPh_3$	*trans*	60.6(60.6)	4.6(4.8)		912
	cis	60.3(60.6)	5.2(4.8)		912
C_8H_{14}, $SbPh_3$	*cis*	56.9(56.7)	5.8(5.6)		652[e]
$2SbPh_3$	*cis*	54.6(55.0)	4.4(4.4)		1006
2dppm $0.5CH_2Cl_2$	*trans*	65.9(65.4)	5.45(5.35)	10.6(11.2)(P) 3.8(3.2)(Cl)	968[f]
dppm	*cis*	61.6(61.5)	5.3(5.3)	9.1(9.1)(P)	684
dppe	*trans*	61.6(62.0)	5.6(5.45)	8.8(8.9)(P)	698
	cis	60.9(62.0)	5.6(5.45)	8.95(8.9)(Cl)	698
dppp	*cis*	62.4(62.4)	5.7(5.6)	8.8(8.7)(P)	712
CO, NMe_3	*trans*	44.0(43.5)	6.45(5.95)	3.75(3.6)(N)	387[c]
CO, PPh_3	*trans*	58.8(59.0)	5.2(4.9)	5.3(5.25)(P)	590
	cis	59.4(59.0)	4.9(4.9)	5.7(5.25)(P)	589
CO, $AsPh_3$	*cis*	55.35(55.0)	4.8(4.85)		634

[a] Calculated values given in parentheses. [b] Molecular ion peaks in electron-impact mass spectra, except where stated. [c] FAB-mass spectrum. [d] $[M - PMe_3]^+$. [e] $[M - C_8H_{14}]^+$. [f] $[M - acac]^+$.

warm toluene. Addition of hexane at 0 °C gave deep orange crystals of *trans*-$[Ru(acac)_2(CNBu^t)_2]$, mp 169–174 °C (385 mg, 66%).

A solution of the *trans* isomer (400 mg, 0.86 mmol) in toluene (30 cm^3) was heated under reflux for 3 h. The red-brown gum remaining after removal of solvent under reduced pressure solidified when hexane was added; the mixture was set aside at 0 °C. The yield of *cis*-$[Ru(acac)_2(CNBu^t)_2]$, mp 134–137 °C, was 250 mg (62%). Recrystallisation from toluene–hexane gave the complex as dark crystals, mp 137–141 °C.

$[Ru(acac)_2(\eta^2\text{-}C_8H_{14})(NCMe)]$. A solution of complex **1** (*ca.* 4 mmol) in THF (40 cm^3) was stirred with acetonitrile (0.5 cm^3, 9.6 mmol) at room temperature overnight and the mixture evaporated almost to dryness. The residue was dissolved in THF (*ca.* 10 cm^3) and the solution filtered through an ice-cooled column of degassed Celite, eluting with THF–hexane. Evaporation of the yellow-brown filtrate to dryness gave a light brown powder, which was recrystallised from toluene–hexane containing a few drops of cyclooctene at 0 °C. The rust-brown microcrystals were separated by filtration and washed with cold hexane to give *cis*-$[Ru(acac)_2(\eta^2\text{-}C_8H_{14})(NCMe)]$, mp 128–145 °C. The yield was 1.1 g (62%).

***cis*-$[Ru(acac)_2(NCMe)_2]$.** This was made following the procedure of Kobayashi *et al.*[39] A suspension of $[Ru(acac)_3]$ (4.5 g, 1.13 mmol) in a mixture of ethanol (300 cm^3), acetonitrile (20 cm^3) and water (20 cm^3) was stirred overnight with an excess of zinc amalgam (*ca.* 70 cm^3). The orange suspension was filtered through degassed Celite and the dark orange filtrate evaporated to dryness. The residue was extracted with dichloromethane–ether and again filtered through degassed Celite, an initial green-black fraction being discarded. The dark orange fraction was evaporated to dryness to give *cis*-$[Ru(acac)_2(NCMe)_2]$ as a brown powder (2.0 g, 46%).

$[Ru(acac)_2(NMe_3)_2]$. (i) A solution of complex **1** (*ca.* 1 mmol) in THF (10 cm^3) was treated with an excess of aqueous trimethylamine and the mixture stirred in a closed vessel at room temperature for 40 h. The rust-brown mixture was evaporated to dryness to give an orange solid that turned green on addition of THF–hexane. The solution was filtered through an ice-cooled column of Celite, leaving a brown residue. The filtrate was evaporated to dryness and the residue dissolved in toluene–hexane (*ca.* 10 cm^3). The green solution, kept at −78 °C for 4 d, deposited a green-brown solid, which was washed with ice-cold hexane. The yield of *trans*-$[Ru(acac)_2(NMe_3)_2]$ was *ca.* 50%. The compound could be sublimed as a brown oil at 60 °C/10^{-4} mmHg with some loss.

(ii) A solution of $[Ru(acac)_3]$ (600 mg, 1.5 mmol) in THF (80 cm^3) was heated with magnetic stirring at 110 °C for 4 h in a closed pressure vessel with zinc amalgam (1.7%, 50 cm^3) and trimethylamine (3 cm^3 of 17.8% aqueous solution, 9 mmol). The mixture was allowed to cool to room temperature and the organic phase filtered through Celite. The brown filtrate was evaporated to dryness to give a yellow-brown solid (800 mg), which was dissolved in THF (5 cm^3). Addition of hexane (*ca.* 10 cm^3) and cooling to −78 °C gave *trans*-$[Ru(acac)_2(NMe_3)_2]$ as a

green-black solid, which was washed with cold hexane and dried *in vacuo*. The yield was 370 mg (59%).

[Ru(acac)$_2$(PPh$_3$)$_2$]. A solution of complex **1** (2.5 mmol) in THF (40 cm^3) was added to a solution of triphenylphosphine (1.30 g, 4.96 mmol) in THF (20 cm^3) and the mixture stirred for 24 h at room temperature. A red-brown solid precipitated and more product was obtained by addition of hexane (20 cm^3). The solid was separated by filtration and washed with hexane to give *trans*-[Ru(acac)$_2$(PPh$_3$)$_2$] (1.4 g, 68%). The compound can be recrystallised from a large volume of CH_2Cl_2–hexane to which a small amount of PPh_3 has been added.

A solution of *trans*-[Ru(acac)$_2$(PPh$_3$)$_2$] (0.50 g, 0.61 mmol) in benzene (20 cm^3) was heated overnight under reflux in an argon atmosphere for 12 h. The pale yellow-brown solution was evaporated to dryness under reduced pressure and the residue recrystallised from ether–hexane to give *cis*-[Ru(acac)$_2$(PPh$_3$)$_2$] as bright yellow microcrystals, mp 194–198 °C (400 mg, 80%). The same compound was obtained by heating *trans*-[Ru(acac)$_2$(PPh$_3$)$_2$] under reflux in toluene for 4 h.

Similarly prepared were *trans*-[Ru(acac)$_2${P(*p*-MeC$_6$H$_4$)$_3$}$_2$] (red-brown solid, mp 177–180 °C, 69%), *cis*-[Ru(acac)$_2$-{P(*p*-MeC$_6$H$_4$)$_3$}$_2$] (yellow-brown solid, mp 198–205 °C, 70% after recrystallisation from THF–hexane), *trans*-[Ru(acac)$_2$-(PMePh$_2$)$_2$] (red-brown solid, 80%), *cis*-[Ru(acac)$_2$(PMePh$_2$)$_2$] (yellow-brown solid, mp 185–188 °C, 70%), *trans*-[Ru(acac)$_2$-(AsPh$_3$)$_2$] (orange-brown solid, mp 165–168 °C, 66%) and *cis*-[Ru(acac)$_2$(AsPh$_3$)$_2$] (yellow-brown solid, mp 195–198 °C, 75%).

***cis*-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)(SbPh$_3$)].** A solution of complex **1** (1.5 mmol) in THF (15 cm^3) was treated with a solution of $SbPh_3$ (550 mg, 1.55 mmol) in THF (15 cm^3) and the mixture stirred at room temperature overnight. A small sample of the solution was evaporated to dryness and the sticky brown residue dissolved in CD_2Cl_2; the ^{1}H NMR spectrum showed that the main species present was *cis*-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)(SbPh$_3$)]. The mixture was evaporated to dryness, the residue dissolved in THF, and the solution filtered through Celite. The solvent was removed from the filtrate to give a yellow-green foam, which was taken up in hexane to which a drop of cyclooctene had been added. On cooling in solid CO_2 a small amount of yellow-green solid separated, which was removed by filtration. Evaporation of the filtrate to dryness gave *cis*-[Ru(acac)$_2$-(η^2-C$_8$H$_{14}$)(SbPh$_3$)] as a yellow-brown solid, mp 123–130 °C (200 mg, 17%).

***cis*-[Ru(acac)$_2$(SbPh$_3$)$_2$].** A solution of complex **1** (1.5 mmol) in THF (15 cm^3) was combined with a solution of $SbPh_3$ (1.1 g, 3.1 mmol) in THF (15 cm^3) and the mixture stirred at room temperature overnight. At this stage the ^{1}H NMR spectrum of a test sample showed the presence of free cyclooctene and *cis*-[Ru(acac)$_2$(η^2-C$_8$H$_{14}$)(SbPh$_3$)]; there was no further reaction after 24 h. A grey precipitate was removed by centrifugation, the liquid evaporated to dryness, and the red-brown residue heated under reflux in toluene (20 cm^3) for 5 h. Solvent was removed under reduced pressure and the solid residue recrystallised from THF–hexane to give *cis*-[Ru(acac)$_2$(SbPh$_3$)$_2$] (800 mg, 53%) as an orange powder, mp 190–192 °C.

[Ru(acac)$_2$(PMe$_2$Ph)$_2$]. A solution containing complex **1** (1.07 mmol) in either 1,4-dioxane or THF (12 cm^3) was added to a solution of PMe_2Ph (306 mg, 2.2 mmol) in the same solvent and the mixture stirred at room temperature overnight. The solution was evaporated to dryness under reduced pressure and the residue taken up in THF (2 cm^3). Addition of hexane (3 cm^3) gave impure *trans*-[Ru(acac)$_2$(PMe$_2$Ph)$_2$] as a red-brown solid, which was filtered off and washed with ice-cold hexane. The compound was purified (though with considerable loss) by filtering its solution in THF through Celite. Addition of ether gave the *trans* isomer as a brown solid, mp 175–178 °C, which was washed with ether at −78 °C. The yield was 100 mg (16%).

A solution of crude *trans*-[Ru(acac)$_2$(PMe$_2$Ph)$_2$] (*ca.* 1.0 mmol) in xylene (10 cm^3) was heated under reflux for 3 h and then evaporated to dryness under reduced pressure. The residue was taken up in hexane and the solution filtered through alumina (activity III). The solid remaining after removal of solvent showed a broad *ν*(CO) band at 1938 cm^{-1}. Recrystallisation from ether–pentane at −78 °C gave *cis*-[Ru(acac)$_2$(PMe$_2$Ph)$_2$] as a bright, yellow-brown solid, which still showed a weak *ν*(CO) absorption in its IR spectrum at 1946 cm^{-1}. More product was obtained by again filtering the supernatant liquid through alumina and eluting with THF–hexane. The solid obtained by evaporating the yellow fraction to dryness was recrystallised from ether–pentane at −78 °C. The total yield of *cis*-[Ru(acac)$_2$-(PMe$_2$Ph)$_2$], mp 107–112 °C, was *ca*. 36%.

[Ru(acac)$_2$(PMe$_3$)$_2$]. To a solution of complex **1** (1.0 mmol) in THF (10 ml) was added *via* syringe trimethylphosphine (0.3 cm^3, 2.9 mmol). The mixture was stirred for 24 h and evaporated to dryness under reduced pressure to give a gummy, red-brown residue. At this stage monitoring by NMR (^{1}H, ^{31}P) spectroscopy showed the presence of *trans*-[Ru(acac)$_2$(PMe$_3$)$_2$] as the main product (δ_P 9.4), together with small amounts of Me_3PO and [Ru(acac)$_3$]. The residue was dissolved in a small volume of THF and the solution filtered through degassed silica gel 60, eluting with THF–hexane. Some red material remained on the column. Evaporation of the filtrate to dryness gave crude *trans*-[Ru(acac)$_2$(PMe$_3$)$_2$] as a red-brown solid in *ca.* 60% yield. This gave red-brown crystals, mp 170–175 °C (53 mg, 11%), from THF–hexane.

A sample of the crude *trans* isomer (*ca.* 900 mg, 2.5 mmol) was heated under reflux in mesitylene (8 cm^3) for 3 h to give a red-brown solution, which gave an oily residue after removal of solvent. The ^{31}P NMR spectrum showed one peak at δ 31.7 due to the *cis* isomer, together with a small peak at δ 27.2. Some, though not all, of the species responsible for the latter could be removed by filtering a THF–hexane solution several times through alumina (Grade III), although this procedure also caused some decomposition on the column. Evaporation to dryness gave *cis*-[Ru(acac)$_2$(PMe$_3$)$_2$] as a red-brown gum, which over a period of days turned into a yellow-brown solid, mp 58–64 °C. The yield was *ca.* 50%. The IR spectrum showed an impurity *ν*(CO) band at 1940 (KBr), 1946 cm^{-1} (cyclohexane).

[Ru(acac)$_2$(PEt$_3$)$_2$]. To a solution of complex **1** (*ca.* 0.75 mmol) in THF (5 cm^3) was added *via* syringe triethylphosphine (0.25 cm^3, 1.7 mmol). Some rust-brown solid precipitated almost immediately. The mixture was stirred for 12 h and hexane added to precipitate the product, which was separated by filtration. More solid was obtained by adding hexane to the filtrate and cooling in a solid CO_2 bath. The total yield of *trans*-[Ru(acac)$_2$(PEt$_3$)$_2$] was 310 mg (77%).

A sample of the *trans* isomer (240 mg, 0.45 mmol) was heated under reflux in xylene (20 cm^3) for 4 h (there was no change in refluxing benzene). The ^{31}P NMR spectrum showed a peak at δ 46.3 due to the *cis* isomer together with a small peak at δ 48.3 due to Et_3PO. The solvent was removed under reduced pressure and the residue taken up in hexane. The solution was filtered through an ice-cooled column of neutral alumina (grade III) and the yellow band that eluted with THF–hexane evaporated to dryness. The yellow gummy residue solidified after several days. The yield of *cis*-[Ru(acac)$_2$(PEt$_3$)$_2$] was 150 mg (62%).

[Ru(acac)$_2${P(OMe)$_3$}$_2$]. A solution of complex **1** (2.5 mmol) in THF (40 cm^3) was stirred with trimethyl phosphite (0.7 cm^3, 6.0 mmol) in THF (20 cm^3) overnight. The mixture was evaporated to about half its volume and filtered through degassed Celite to remove a small amount of insoluble matter. Evaporation to *ca.* 10 cm^3 volume and addition of hexane (10 cm^3)

gave small orange crystals of *trans*-[Ru(acac)$_2${P(OMe)$_3$}$_2$], mp 142–146 °C, which were separated by filtration and washed with hexane. The yield was 1.3 g (95%).

A sample of the *trans* isomer (550 g, 1 mmol) was heated under reflux in toluene (20 cm^3) for 2 h, changing from orange to yellow-brown. Solvent was removed *in vacuo* and the residue dissolved in hexane. The solution was filtered through degassed Celite and the product eluted with THF–hexane; some unidentified material remained on the column. The filtrate was evaporated to dryness and the residue dissolved in a small volume of hexane. Pale yellow needles of *cis*-[Ru(acac)$_2$-{P(OMe)$_3$}$_2$] (100 mg, 18%) crystallised at −78 °C. Although analytically and spectroscopically pure, the compound appeared to melt over a range, 85–104 °C. A second crop of less pure material was obtained by cooling the supernatant liquid in a solid CO_2 bath.

[Ru(acac)$_2${P(OPh)$_3$}$_2$]. A solution containing complex **1** (2.3 mmol) in THF (40 cm^3) was stirred with freshly distilled triphenyl phosphite (1.2 cm^3, 4.5 mmol) at room temperature for 3 d. The volume was reduced to *ca.* 10 cm^3 and hexane added. The resulting rust-brown precipitate was separated by centrifugation and washed with hexane (3 × 20 cm^3) to give *trans*-[Ru(acac)$_2${P(OPh)$_3$}$_2$] (1.25 g, 59%) as a rust-brown powder, mp 118–120 °C. More solid that precipitated from the filtrate was shown by NMR (^{1}H, ^{31}P) spectroscopy to be mainly the *cis* isomer containing *ca.* 20% *trans* isomer. Recrystallisation from hot toluene–hexane gave pale grey-green crystals of *cis*-[Ru(acac)$_2${P(OPh)$_3$}$_2$] (300 mg, 14%). When a sample of the *trans* isomer was heated *in vacuo* at 80 °C for 4 h some isomerisation to the *cis* compound occurred, accompanied by decomposition.

[Ru(acac)$_2$(dppm)$_2$]. A solution of dppm (384 mg, 1.0 mmol) in THF (10 cm^3) was added to an ice-cooled solution of complex **1** (0.5 mmol) in THF (3.5 cm^3) to give an immediate rust-brown precipitate. The mixture was stirred for 4 h; the solid was separated by centrifugation and washed with hexane (3 × 20 cm^3) to give *trans*-[Ru(acac)$_2$(dppm)$_2$] (520 mg, 97%). It could be recrystallised from THF–hexane or toluene–hexane, though some *cis*-[Ru(acac)$_2$(dppm)] was recovered from the filtrate. After recrystallisation the *trans* compound melted at 172–176 °C.

[Ru(acac)$_2$(dppm)]. A solution of dppm (384 mg, 1.0 mmol) in THF (10 cm^3) was added to a solution of complex **1** (1.0 mmol) in THF (7 cm^3). Evaporation under reduced pressure to *ca.* half-volume and addition of hexane gave a yellow precipitate of *cis*-[Ru(acac)$_2$(dppm)] (580 mg, 85%), mp 231–235 °C. The compound could be recrystallised from toluene–hexane and sublimed at *ca.* 200 °C/10^{-4} mmHg on to a cold-finger at −15 °C.

[Ru(acac)$_2$(dppe)]. Addition of a solution of dppe (850 mg, 2.13 mmol) in THF (20 cm^3) to a solution of complex **1** (2.0 mmol) in THF (50 cm^3) at room temperature gave immediately a yellow-brown suspension, which did not change after heating under reflux for 3 h. Solvent was removed under reduced pressure. The resulting brown solid was washed with THF (3 × 10 cm^3) and dried *in vacuo*. The yield of *trans*-[{Ru(acac)$_2$-(dppe)}$_n$], mp 210 °C, was quantitative. The compound is insoluble in common organic solvents. The same product was obtained by heating *cis*-[Ru(acac)$_2$(NCMe)$_2$] (1.14 g, 3.0 mmol) with dppe (1.2 g, 3.0 mmol) in benzene overnight. The yield of precipitated yellow-brown powder was 950 mg (45%); evaporation of the filtrate to dryness gave more of the same brown solid.

A sample of *trans*-[{Ru(acac)$_2$(dppe)}$_n$] (1.14 g, 1.64 mmol) was heated overnight under reflux in a mixture of xylene (50 cm^3) and di-*n*-butyl ether (10 cm^3). Suspended solid was separated from the orange-brown solution by filtration and identified as unchanged starting material by its mp and IR spectrum. The filtrate was evaporated to dryness under reduced pressure and the residue dissolved in CH_2Cl_2–ether (10 cm^3). The solution was filtered through silica gel 60 to remove some black solid. Addition of hexane gave *cis*-[Ru(acac)$_2$(dppe)] as a bright yellow powder (550 mg, 58%), mp 188–194 °C.

[Ru(acac)$_2$(dppp)]. A solution of complex **1** (1.25 mmol) in THF (25 cm^3) was stirred overnight with dppp (515 mg, 1.25 mmol) dissolved in THF (40 cm^3). In contrast with the behaviour of dppe there was no colour change or precipitate. On heating under reflux overnight a light orange solution was formed, which gave a gummy solid after removal of solvent. The solution in THF (10 cm^3) was filtered through a silica gel 60 column made up in hexane and an orange band eluted with ether. Solvent was evaporated and the residue recrystallised from ether–hexane to give *cis*-[Ru(acac)$_2$(dppe)] as a bright yellow powder, mp 208–211 °C. The yield was 400 mg (45%).

[Ru(acac)$_2$(CO)(NMe$_3$)]. A solution of *trans*-[Ru(acac)$_2$-(NMe$_3$)$_2$] (100 mg, 0.24 mmol) in hexane (14 cm^3) was stirred at room temperature under CO (2 bar) in a small pressure vessel for 2 d. The IR spectrum of the resulting brown solution showed a strong ν(CO) band due to *trans*-[Ru(acac)$_2$(CO)-(NMe$_3$)] at 1953 cm^{-1}, together with weak peaks due to unidentified products at 1935, 1908 and 1670 cm^{-1}. The solution was evaporated to dryness under reduced pressure and the residue recrystallised from a small volume of THF–hexane at −78 °C to give *trans*-[Ru(acac)$_2$(CO)(NMe$_3$)] as a dark brown solid that smelt strongly of the amine. The yield was *ca.* 60%. The C≡O stretching frequency (cm^{-1}) in the IR spectrum appeared at 1920vs (KBr), 1953vs (C_6H_{12}), 1942vs (Et_2O), and 1938vs (THF). Other bands (KBr) were as follows: 3000m, 2970m, 2900ms, 2850m, 2790w, 1550vs, 1515vs, 1480m, 1450–1425 (br), 1410m, 1380vs and 1360m cm^{-1}.

[Ru(acac)$_2$(CO)(PPh$_3$)]. Carbon monoxide was bubbled through an ice-cooled suspension of *trans*-[Ru(acac)$_2$(PPh$_3$)$_2$] (520 mg, 0.63 mmol) in THF (20 cm^3) for 3 h. After *ca.* 2 h, a bright yellow, almost clear solution had formed. The volume was reduced to *ca.* 5 cm^3 under reduced pressure and hexane (5 cm^3) was added to the warm solution. On cooling, *trans*-[Ru(acac)$_2$(CO)(PPh$_3$)] precipitated as yellow microcrystals, mp 135–138 °C (230 mg, 62%). Bands (cm^{-1}) due to ν(CO) appeared at 1940vs, 1905m (KBr), 1966vs, 1944w, 1935m (C_6H_{12}, 1 mm path length), 1959vs, 1929ms (toluene, 0.1 mm path length), 1935vs (THF, 0.1 mm path length) and 1956vs (br) (CH_2Cl_2, 0.1 mm path length).

For the preparation of *trans*-[Ru(acac)$_2$(^{13}CO)(PPh$_3$)] a suspension of *trans*-[Ru(acac)$_2$(PPh$_3$)$_2$] (687 mg, 0.83 mmol) in THF (6 cm^3) was treated with ^{13}CO (200 kPa) in a small pressure vessel. After 2 h the suspension had cleared and the IR spectrum, measured in toluene or cyclohexane, showed bands at 1912vs and 1865m cm^{-1}. Addition of hexane precipitated a brown solid which still contained starting material. The solid was redissolved in THF and the solution stirred again under ^{13}CO (100 kPa) for 2 d. The isolated solid, [Ru(acac)$_2$-(^{13}CO)(PPh$_3$)], still contained starting material, but was suitable for spectroscopic studies.

A suspension of *trans*-[Ru(acac)$_2$(CO)(PPh$_3$)] (280 mg, 0.47 mmol) in toluene (6 cm^3) was heated under reflux for 3 h in an atmosphere of CO to give a bright yellow solution. Evaporation to a few cm^3 volume and addition of hexane gave *cis*-[Ru(acac)$_2$(CO)(PPh$_3$)] (147 mg, 52%) as yellow-brown microcrystals, mp 164–168 °C. The ^{13}CO-labelled material was formed similarly by heating *trans*-[Ru(acac)$_2$(^{13}CO)(PPh$_3$)] in toluene under argon. The product was contaminated with orange *cis*-[Ru(acac)$_2$(PPh$_3$)$_2$], as shown by ^{31}P NMR spectroscopy.

Table 7 Crystal and structure refinement data for *trans*-[Ru(acac)$_2$(CNBu^t)$_2$], *cis*-[Ru(acac)$_2$(CNBu^t)$_2$]·[Ru(acac)$_3$], *trans*-[Ru(acac)$_2$(PMePh$_2$)$_2$], *cis*-[Ru(acac)$_2$(PMePh$_2$)$_2$] and *trans*-[Ru(acac)$_2$(η^1-dppm)$_2$]·2CH$_2$Cl$_2$

	trans-[Ru(acac)$_2$-(CNBu^t)$_2$]	*cis*-[Ru(acac)$_2$-(CNBu^t)$_2$]·[Ru(acac)$_3$]	*trans*-[Ru(acac)$_2$-(PMePh$_2$)$_2$]	*cis*-[Ru(acac)$_2$-(PMePh$_2$)$_2$]	*trans*-[Ru(acac)$_2$-(η^1-dppm)$_2$]
Chemical formula	$C_{20}H_{32}N_2O_4Ru$	$C_{35}H_{53}N_2O_{10}Ru_2$	$C_{36}H_{40}O_4P_2Ru$	$C_{36}H_{40}O_4P_2Ru$	$C_{60}H_{58}O_4P_4Ru\cdot 2CH_2Cl_2$
M	465.56	465.56 + 398.40	699.73	699.73	1068.08 + 169.87
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)
a/Å	8.875(1)	16.233(4)	40.162(3)	12.270(2)	10.571(3)
b/Å	9.099(1)	17.091(5)	9.466(4)	15.443(4)	13.108(4)
c/Å	16.081(1)	15.618(3)	19.354(3)	17.748(3)	13.278(4)
α/°	94.27(1)				61.84(2)
β/°	95.89(1)	109.04(1)	112.937(7)	90.46(1)	69.52(2)
γ/°	113.85(1)				85.32(3)
U/Å^3	1171.7(2)	4096(2)	6776(2)	3362(1)	1511.8(8)
Z	2	4	8	4	1
T/K	299(1)	295(1)	296(1)	296(1)	296(1)
μ/cm^{-1}	57.3	7.72	5.94	5.98	5.87
X-Radiation (graphite monochromated)	Cu-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
Total reflections	3693	7474	6598	3262	7361
Unique reflections	3470 (R_{int} = 0.012)	7186 (R_{int} = 0.014)	6395 (R_{int} = 0.017)	3103 (R_{int} = 0.011)	6985 (R_{int} = 0.016)
Used reflections	2615 [$I > 3\sigma(I)$]	4253 [$I > 3\sigma(I)$]	4070 [$I > 3\sigma(I)$]	2263 [$I > 3\sigma(I)$]	5317 [$I > 2\sigma(I)$]
No. parameters	283	442	391	196	340
R (used reflections)[a]	0.036	0.036	0.033	0.029	0.045
R' (used reflections)[a]	0.054	0.044	0.023	0.022	0.051
Goodness of fit	1.47	1.01	1.78	1.86	2.32
ρ_{max}, ρ_{min}/e Å^{-3}	1.0, −0.4	0.3, −0.3	0.4, −0.4	0.35, −0.41	0.71, −0.74

[Ru(acac)$_2$(CO)(AsPh$_3$)]. A suspension of *trans*-[Ru(acac)$_2$-(AsPh$_3$)$_2$] (140 mg, 0.19 mmol) in toluene (3 cm^3) was treated with CO (3 bar) at room temperature for 30 h to give a clear brown solution. The IR spectrum showed strong bands at 2057, 1983 and 1943 cm^{-1}, the first two probably being due to [Ru(CO)$_2$(acac)$_2$].[41] The solution was filtered through silica gel 60 with THF–hexane (1:9). The filtrate was evaporated to dryness and the resulting bright yellow solid washed with hexane. The yield of *cis*-[Ru(acac)$_2$(CO)(AsPh$_3$)], mp 158–162 °C, was *ca.* 50%.

X-Ray crystallography

Selected crystal data and details of data collection and structure refinement are in Table 7. All non-hydrogen atoms were refined anisotropically by full-matrix least squares except for the terminal methyl carbon atoms of the *tert*-butyl group of one of the two independent molecules of *trans*-[Ru(acac)$_2$-(CNBu^t)$_2$]. These were disordered over two orientations and refined with isotropic displacement factors as two populations with occupancies of p and $(1 - p)$ with restraints on their bond lengths and angles. The final refined value of p was 0.56(2). *tert*-Butyl hydrogen atoms were placed at calculated positions (C–H 0.95 Å with staggered conformations) and not refined but were recalculated periodically. The acac hydrogen atoms were placed at calculated positions with torsion angles selected so as best to fit the peaks observed in a difference map (C–H 0.95 Å, tetrahedral or trigonal at the appropriate carbon atom).

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See http://www.rsc.org/suppdata/dt/1999/3451/ for crystallographic files in .cif format.

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