Some Reactions of Co-ordinated Cycloheptatriene and Cyclo-octa-1,5-diene in Ruthenium (d^6) Complexes

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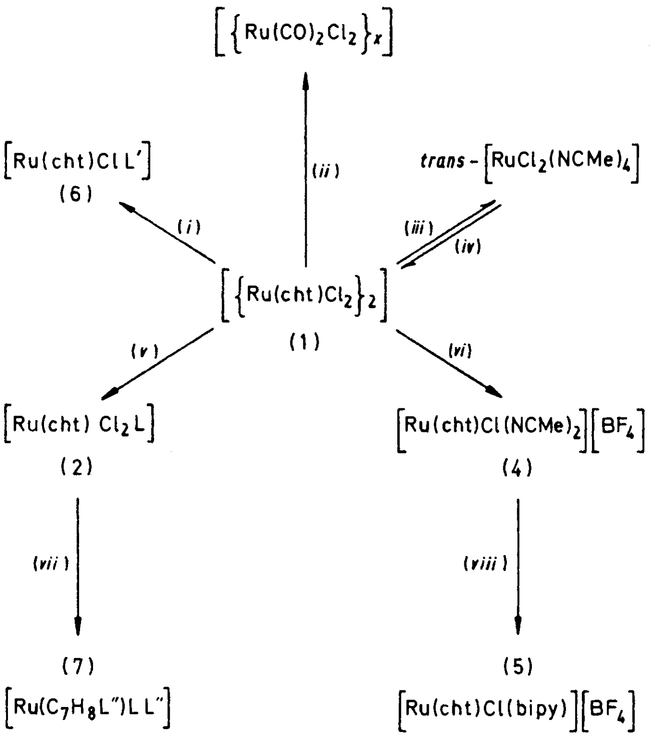
The complex of empirical formula Ru(cht)Cl_2 has been shown to be dimeric with the cycloheptatriene (cht) bonding as a tridentate ligand. This complex reacts with Group 5B Lewis bases (L) to give monomers [Ru(cht)Cl_2L]. Reaction of the dimer with halide-abstracting thallium salts gives the complexes [Ru(cht)ClL_2]$^+$ [L_2 = (MeCN)$_2$ or 2,2'-bipyridyl(bipy)]. The complexes [Ru(cht)Cl_2L] [L = PPh_3 or $AsPh_3$] react with thallium β-diketonates (L'') to give the complexes [Ru(C_7H_8L'')L''L], in which the olefin is bonded as a dienyl. The temperature-dependent n.m.r. spectrum of the 4-phenylbutane-2,4-dione derivative is discussed. The polymer [{Ru(cod)Cl_2}$_n$] (cod = cyclo-octa-1,5-diene) undergoes bridge-cleavage reactions with acetonitrile giving the monomer [Ru(cod)Cl_2($NCMe)_2$] which reacts with bipy to give [Ru(cod)Cl_2(bipy)].

ALTHOUGH olefin complexes of the zero-valent d^8 transition metals have been the subject of a great deal of interest, the chemistry of complexes of the bivalent d^6 metals has received relatively little attention. Most work has been directed towards the reactions of the polymeric complexes of norbornadiene and cyclo-octa-1,5-diene with various bridge-cleaving and halogen-abstracting reagents.[1,2] Recently, Zelonka and Baird [3] showed that, contrary to a previous report, the ruthenium dichloride complex of benzene is dimeric with the benzene acting as a tridentate ligand. Nucleophilic attack on the benzene complex was also shown to give rise to a cyclohexadienyl complex in solution. We now report a study of the structure and reactivity of the ruthenium dichloride complex of cycloheptatriene which had also been postulated as having halogen bridges, with cycloheptatriene bonding as a 1,5-diene.[4]

RESULTS AND DISCUSSION

The reaction of cycloheptatriene with ruthenium trichloride in ethanol was sensitive to the water concentration. Only in 95% ethanol was dichloro(cycloheptatriene)ruthenium, [{Ru(cht)Cl_2}$_2$] (1), obtained in good yield. The ^{1}H n.m.r. spectrum of complex (1) in trifluoroacetic acid showed five resonances in the intensity ratio 2 : 2 : 2 : 1 : 1. This is consistent with the cycloheptatriene co-ordinating as a 1,5-diene or triene but not as a 1,3-diene.[5,6] No evidence was found in trifluoroacetic acid, or in the deuteriated solvent, for proton addition to the organic ligand, and attempts to isolate any trifluoroacetic acid adduct of (1) were unsuccessful. Reaction of (1) with Group 5B Lewis bases gave neutral complexes of empirical formula [Ru(cht)Cl_2L] (2) [L = $AsPh_3$, PPh_3, P(OPh)$_3$, or PBu_3]. These were shown by osmometric molecular-weight measurements to be monomeric in chloroform.

Since Ru^{II} may be assumed to adopt a co-ordination number of six, the above observations are consistent with cycloheptatriene bonding as a tridentate ligand.[7] Thus, it is probable that complex (1) is a dimer and not a polymer as first thought. The ^{1}H n.m.r. spectrum, in chlorinated solvents, of complexes (2), except for the H^1 protons, showed a marked similarity in chemical shift. The H^1 resonances varied in position by up to τ 0.75, and this may be associated with the degree of bending of the ring from planarity.[8] Assignment of the spectrum was made by analogy with the [Mo(cht)(CO)$_3$] complex, and also on the basis of selective proton-decoupling studies.[9]



SCHEME Reactions of complex (1). (*i*) Thallium fluoro-β-diketonate (TlL'); (*ii*) CO; (*iii*) MeCN; (*iv*) cht–EtOH; (*v*) L = PR_3, P(OR)$_3$, or AsR_3; (*vi*) Tl[BF_4]–MeCN; (*vii*) thallium β-diketonate (TlL'); (*viii*) bipy

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[1] M. A. Bennett and G. Wilkinson, *Chem. and Ind.*, 1959, 1516.

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[3] R. Zelonka and M. C. Baird, *Canad. J. Chem.*, 1972, **50**, 3063.

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[8] M. A. Bennett, G. B. Robertson, and A. K. Smith, *J. Organometallic Chem.*, 1972, **43**, 141.

[9] G. Harald, *Z. Naturforsch.*, 1969, **29**, 680.

(A)

(B)

Complexes of the type (2) can potentially exist in two isomeric forms (A) and (B). On the basis of the ^1H n.m.r. alone, it is difficult to differentiate between these isomers. However, the ^{13}C n.m.r. spectrum of the $AsPh_3$ complex is similar to that of $[Mo(cht)(CO)_3]$, showing only four cycloheptatriene resonances. This argues strongly for the presence of the symmetric structure (A) in these complexes.[10] Complex (1) dissolves rapidly when heated under reflux in acetonitrile to give the complex $[RuCl_2(NCMe)_4]$ (3). The i.r. CN stretching frequency and ^1H n.m.r. spectrum of (3) exhibited only sharp singlets at 2 281 cm^{-1} and τ 7.50 respectively. These measurements are consistent only with a *trans*-dichloro stereochemistry for the complex. Heating complex (3) under reflux in 95% ethanol in the presence of cycloheptatriene reversed the reaction and gave (1).

In the presence of 1 mol of thallium tetrafluoroborate, complex (1) dissolved rapidly in acetonitrile to give the product $[Ru(cht)Cl(NCMe)_2][BF_4]$ (4) which was precipitated on addition of diethyl ether. The ^1H n.m.r. spectrum of (4) in trifluoroacetic acid or nitromethane showed the characteristic 2 : 2 : 2 : 1 : 1 ratio of resonances expected for tridentate cycloheptatriene, together with those associated with two-co-ordinate acetonitriles. However, these resonances were either broad or consisted of two distinct sets of signals and, significantly, the methyl resonances showed two signals in the ratio 1 : 3. This could arise from either co-existence of the two isomeric forms (A) and (B) of $[Ru(cht)Cl(NCMe)_2]^+$ or the formation of new complexes through interaction of the above complex with the solvent. It is clear that a condition on the latter would be the retention of both co-ordinated acetonitriles. Although a pure product was not isolated from (4), the mixture reacted with 2,2′-bipyridyl (bipy) to give the isolable product $[Ru(cht)Cl(bipy)][BF_4]$ (5).

Thallium fluoro-β-diketonates, TlL′, reacted with complex (1) to give neutral complexes [Ru(cht)ClL′] (6). Mass spectroscopy and osmometric molecular-weight determinations support their formulation as monomers. Although isomers of the type (A) and (B) are possible for these complexes, only one series of cycloheptatriene resonances was observed in the ^1H n.m.r. spectrum. However, the ^{19}F n.m.r. of the 1,1,1,5,5,5-hexafluoropentane-2,4-dionate derivative showed two CF_3 resonances separated by 0.5 Hz. This result argues strongly for the existence of isomer (B) in the complex. The 1,1,1-trifluoropentane-2,4-dionate derivative showed singlets for the CH_3 and CF_3 species in the proton and fluorine n.m.r. The i.r. spectra of both these complexes support an oxygen-bonded arrangement for the β-diketones.[11] The pentane-2,4-dionate derivative could not be prepared under similar conditions.

Complex (1) reacted with CO in refluxing chloroform with the displacement of cycloheptatriene to give a pale yellow solution, whose i.r. spectrum showed two bands at 2 076 and 2 007 cm^{-1}, consistent with $[\{Ru(CO)_2Cl_2\}_n]$.[12]

Complexes (2; L = PPh_3 or $AsPh_3$) reacted with thallium β-diketonates, TlL″, with the precipitation of 2 mol of thallium chloride and the formation of neutral hexane-soluble complexes of empirical formula $[Ru(cht)LL''_2]$ (7). The i.r. spectra of these complexes showed β-diketonate carbonyl-stretching frequencies in the 1650—1700 and 1500—1600 cm^{-1} regions characteristic of bonding *via* the central carbon and oxygen atoms, respectively.[13] Electrophilic attack by a β-diketonate on an organometallic complex can give rise to two distinct carbon-bonded forms: direct attack on the metal gives a M–C bond; attack on the co-ordinated ligand gives a C–C bond.[13,14]

The central methylene proton of a metal–carbon bonded β-diketonate is expected to give only a singlet in the ^1H n.m.r. spectrum, as ruthenium–proton coupling is not normally observed. However, as all the carbons in a cycloheptatriene ring possess hydrogen, these would be expected to couple with the central methylene proton of any carbon–carbon bonded β-diketonate to form a doublet. The ^1H n.m.r. spectrum of all the complexes showed resonances assignable to oxygen- and carbon-bonded central methylene protons. These gave rise to a sharp singlet and a higher-field doublet for the oxygen- and carbon-bonded β-diketonates respectively. Thus, complexes (7) contain a carbon–carbon bonded β-diketonate and are better described by the formula $[Ru(C_7H_8L'')LL'']$.

Three possible olefinic isomers may be envisaged for nucleophilic attack on co-ordinated cycloheptatriene, (7a), (7b), and (7c). The ^1H n.m.r. spectrum of the 1,3-diphenylpropane-1,3-dionate complex (L = PPh_3) in the range τ 3.5—10 consisted of a series of multiplets at τ 4.78 (1 H), 5.40 (1 H), 6.20 (1 H), 6.4—7.0 (3 H), 8.27 (1 H), and 9.73 (1 H) assignable to the co-ordinated olefin. Selective decoupling studies showed the resonances at τ 8.27 and 9.73 to be coupled to each other and to the common external resonance at τ 6.20. Irradiation of the resonance at τ 6.20 decoupled those at τ 8.27 and 9.73 and collapsed the carbon-bonded central methylene

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[10] B. E. Mann, *Chem. Comm.*, 1971, 776.

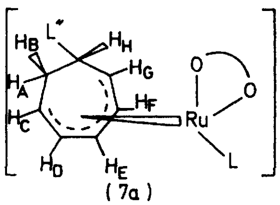
[11] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' Interscience, New York, p. 225.

[12] B. F. G. Johnson, R. D. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1969, 792.

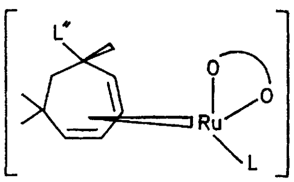
[13] B. F. G. Johnson, J. Lewis, and M. S. Subramanian, *J. Chem. Soc.* (*A*), 1968, 1993.

[14] D. Gibson, J. Lewis, and C. Oldham, *J. Chem. Soc.* (*A*), 1967, 72.

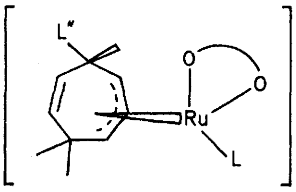
doublet of the diketonate to a singlet. The only isomer to allow two protons to be coupled to each other and to a common external proton (which in turn is coupled to the diketonate) is (7a), *viz.* the cycloheptadienyl. Further assignment of resonances in this complex was not possible due to the great multiplicity and overlapping of the resonances. However, the spectrum of the corresponding complex with L = $AsPh_3$ showed resonances which were much sharper and better separated, allowing a complete assignment of the spectrum by use of selective decoupling studies (Table 1). The resonances at τ 9.79 and 8.21 can be assigned to the methylene protons H_A and H_B in structure (7a). It is possible to further assign the highfield resonance at τ 9.79 to the *exo* position H_A by analogy with the relative *exo–endo* positions in the complex $[Mn(C_7H_8L'')(CO)_3]$.[15] The proton at τ 6.78, although coupled to protons H_A and H_B, is not coupled to the diketonate proton, whereas one of the protons in the τ 6.0—6.4 multiplet is, so these resonances may be assigned to protons H_C and H_H respectively. Proton H_C was coupled to the proton at τ 5.39, which is coupled to that at τ 4.40 and which in turn is coupled to a proton in the 6.0—6.4 multiplet. These resonances can be assigned to protons H_D, H_E, and H_F respectively. Finally the proton at τ 6.56 must be H_G.



(7a)



(7b)



(7c)

TABLE 1

Selective decoupling of complex $[Ru(C_7H_8L'')LL'']$ (L = $AsPh_3$ and L'' = PhCOCHCOPh)

Irradiation of resonance at τ	Effect
9.79	Decoupled 8.21 and collapsed 6.78 to t
8.21	Decoupled 9.79 and collapsed 6.78 to d of d
6.78	Collapse of 9.79 and 8.21 to d of d, 5.39 to d
6.0—6.4	Collapsed 9.79 and 8.21 to d of d, 4.40 to d, 5.08 to s
5.39	Collapsed 6.78 to d of d, 4.40 to d
4.40	Collapsed 6.0—6.4 (part of m) to d, 5.39 to d

It should be noted that although the final product (7) contains a dienyl structure (7a), it is possible that (7b) or (7c) are formed initially but rearrange rapidly *via* a metal hydrogen-transfer process to give the observed product.

At least six isomers of the 4-phenylbutane-2,4-dionate complex (7; L = PPh_3) are possible, excluding any due to the intrinsic asymmetry of the molecules. The ^1H n.m.r. spectrum of this complex exhibited considerable temperature dependence. At low temperatures (−68 °C) in dichloromethane six methyl resonances were observed. All the other resonances were broad except the central methylene proton of the oxygen-bonded diketonate which exhibited four resonances. Warming to 38 °C resulted in a general sharpening of the spectrum. The methyl resonances contracted to four (three sharp, one broad), the oxygen-bonded methylene to a sharp doublet, and the carbon-bonded methylene showed three sets of sharp doublets. At higher temperatures in toluene a limit of 104 °C was reached due to decomposition. At this point four sharp methyl resonances were observed, whose intensities were still varying with temperature. The oxygen- and carbon-bonded methylene resonances showed a sharp singlet and doublet respectively, and had remained unchanged for 30 °C. The remainder of the spectrum, excluding a sharp triplet at τ 4.9, consisted of multiplets but much sharpened. In support of the ^1H n.m.r., the ^{31}P n.m.r. spectrum of the complex in dichloromethane at −80 and 30 °C exhibited five resonances centred at −37.1 p.p.m. and one at −35.0 p.p.m. respectively. The conversion of the oxygen-bonded methylene resonances from four to one and the phosphorus resonances from five to one with increasing temperature indicates an equilibrium between the possible isomers. This could be envisaged as taking place through a labile five-co-ordinate intermediate, formed by the cleavage of a ruthenium–oxygen bond; the oxygen may then recombine to form an axial or equatorial octahedral bond. As either oxygen of the asymmetric diketonate could cleave, a complete scrambling and equilibration between the possible isomers would be expected for this process.

The dichloromethane solution and KBr disc i.r. spectra of the complexes in the carbonyl region are very similar. Although the 4-phenylbutane-2,4-dionate and 1,2-diphenylpropane-1,3-dionate derivatives exhibited the two carbonyl carbon-bonded stretching frequencies expected for these intrinsically asymmetric molecules, the pentane-2,4-dione complex showed only one stretching frequency. The triphenylarsine derivatives usually gave a better resolved ^1H n.m.r. spectrum at room temperature than the corresponding triphenylphosphine complex. This is in agreement with the generally greater stability, and hence expected higher activation energy towards isomer rearrangement, of phosphine relative to arsine complexes.[16]

Attempts to cause complexes (2) to react with thallium hexafluoro- and trifluoro-pentane-2,4-dionate resulted only in displacement of free cycloheptatriene. This is probably due to the lower electron density at the central

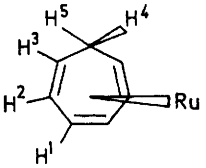
[15] M. I. Foreman and F. Hague, *J. Chem. Soc.* (*B*), 1971, 418.

[16] G. Booth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 1.

methylene carbon in the fluoro-derivatives, preventing nucleophilic attack on the co-ordinated cycloheptatriene. Complexes (7) are inherently unstable in solution, decomposing to paramagnetic species even *in vacuo*. This instability increases with increasing polarity and temperature of the solvent. Attempts to cause complex (5) to react with nucleophiles such as $[CN]^-$, $[OMe]^-$, and $[CH(CO_2Et)_2]^-$ appeared to result only in attack at the metal and displacement of free cycloheptatriene.

Heating the polymeric complex $[\{Ru(cod)Cl_2\}_n]$ (cod = cyclo-octa-1,5-diene) in boiling acetonitrile resulted in cleavage of the chloride bridges and formation of $[Ru(cod)Cl_2(NCMe)_2]$ (8). The ^1H n.m.r. spectrum of the complex in trifluoroacetic acid exhibited resonances characteristic of co-ordinated cod, and a single methyl resonance from the acetonitrile. Of the three isomers which could be expected for the complex, only two would give a single methyl resonance, *viz.* the *trans*-dichloro and *trans*-acetonitrile. However, the CN stretching region in the i.r. spectrum of complex (8) exhibited two sharp bands indicative of a *cis* arrangement of the acetonitriles. This was confirmed by comparison of the far-i.r. spectra of the chloride and bromide derivatives of (8) in the 250—600 cm^{-1} region. A single Ru–Cl band was observed at 313 cm^{-1}, which is absent in the bromide. This is consistent only with a *trans*-dichloro arrangement.[17] Complex (8) is a non-electrolyte in acetonitrile, but dissolves in water to form conducting solutions. Addition of the large anion tetraphenylborate to an aqueous solution of the complex precipitated a white solid which was too unstable to purify.

TABLE 2



Hydrogen-1 n.m.r. spectra(τ) of cycloheptatriene–ruthenium(II) complexes

Complex	Solvent	H^1	H^2	H^3	H^4	H^5	Me	Ph	Other
$[\{Ru(cht)Cl_2\}_2]$ (1)	CF_3CO_2H	3.96(m)	5.29(m)	6.21 (t of d)	7.39 (d of t)	9.59 (d of t)			
$[Ru(cht)Cl_2(PPh_3)]$ (2)	$CDCl_3$	4.24(m)	5.03(m)	6.20(m)	6.90(m)	8.30(m)		2.2—2.6	
$[Ru(AsPh_3)(cht)Cl_2]$ (2)	CD_2Cl_2	4.18(m)	5.08(m)	6.21(m)	6.92(m)	8.30(m)		2.0—2.8	
$[Ru(cht)Cl_2\{P(OPh)_3\}]$ (2)	CF_3CO_2H	4.04(m)	4.70(m)	5.82(m)	6.80	8.20(m)		2.73	
$[Ru(cht)Cl_2(PBu_3)]$ (2)	$CDCl_3$	3.49(m)	5.02(m)	6.23(m)	6.80(m)				Bu 7.6—9.6 (m)
$[Ru(cht)ClL']$ [a] (6)	$CDCl_3$	4.44 (d of d)	4.82(m)	5.69 (t of d)	6.68 (d of t)	8.85 (d of t)			$CF_3COCHCOCF_3$ 4.08 (s)
$[Ru(cht)ClL']$ [b] (6)	$CDCl_3$	3.54(m)	4.88(m)	5.76 (t of d)	6.69 (d of t)	8.83 (d of t)	7.85(s)		$CF_3COCHCOMe$ 4.40 (s)
$[Ru(cht)Cl(NCMe)_2]^+$ (4)	CF_3CO_2H	3.15 3.35 (m)	4.1—4.9 (m)	5.0—5.9 (overlapping t of d)	6.3—7.0 (m)	8.50 9.05 (d of t)	7.42 (s) 7.50 (s)		
$[Ru(cht)Cl(bipy)]^+$ (5)	CF_3CO_2H	3.00(m)	4.70(m)	5.74(m)	6.67(m)	8.40(m)			bipy 0.25—2.12

[a] L′ = 1,1,1,5,5,5-Hexafluoropentane-2,4-dionate. [b] L′ = 1,1,1-Trifluoropentane-2,4-dionate.

Heating complex (8) under reflux in acetonitrile with 2 mol of thallium tetrafluoroborate overnight gave a mixture whose ^1H n.m.r. spectrum showed it to be predominantly $[Ru(cod)(NCMe)_4]^{2+}$, with a small amount of $[Ru(NCMe)_6]^{2+}$.[2] Complex (8) underwent rapid ligand exchange with deuterioacetonitrile in the boiling solvent. Ligand exchange also occurred with 2,2′-bipyridyl (bipy) to give neutral $[Ru(cod)Cl_2(bipy)]$ (9), a species unobtainable by direct reaction of the polymer.[18] Comparison of the far-i.r. spectrum of this product and the dibromo-derivative showed it to have a *trans*-dichloro stereochemistry.

The polymer $[\{Ru(cod)Cl_2\}_n]$ reacted with benzonitrile at 110 °C to give $[RuCl_2(NCPh)_4]$ (10). The CN stretching frequency of this complex exhibited a single sharp absorption indicative of a *trans*-dichloro arrangement. The polymer $[\{Ru(cot)Cl_2\}_n]$ dissolved in acetonitrile at 45 °C, but as yet it has not been possible to isolate a product from the solution. However, the ^1H n.m.r. spectrum of the residue left after evaporation of the solvent showed two resonances at τ 3.94 and 5.51, indicative of cot bonding as a 1,5-diene.[2,19]

Conclusion.—This work clearly demonstrates that olefin complexes of Ru^{II} are reactive towards nucleophilic reagents. This behaviour is not unexpected and parallels the reactivity shown by Pd^{II}, but is in contrast to that of Ru^0 for which electrophilic reactions are known to occur.

EXPERIMENTAL

Di-μ-chloro-bis[chloro(cycloheptatriene)ruthenium(II)], (1).—Cycloheptatriene (1 cm^3) was refluxed with ruthenium trichloride (1.0 g) in 95% ethanol (15 cm^3) overnight. The cooled solution was filtered and washed with methanol and diethyl ether to give the brown dimeric product (84%)

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[17] J. A. Gilbert, M. C. Baird, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2198.

[18] E. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3178.

[19] A. Davidson, W. McFarlane, C. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4821.

[Found: C, 32.5; H, 2.75. $(C_7H_8Cl_2Ru)_2$ requires C, 31.8; H, 3.05%; coupling constants $J(H^4H^5)$ 14, $J(H^3H^5)$ 4, and $J(H^3H^4)$ 8 Hz.

Dichloro(cycloheptatriene)(triphenylphosphine)ruthenium(II), (2; L = PPh_3).—The dimer (1) (800 mg) was shaken in dichloromethane (30 cm^3) with triphenylphosphine (800 mg) until all the dimer had dissolved (1 h). The solution was filtered through Celite and then diethyl ether was added dropwise to precipitate an orange solid, which was recrystallised from acetone to give (2) (1.32 g, 83%) (Found: C, 57.35; H, 4.25; Cl, 13.35%; *M* 558. $C_{25}H_{23}Cl_2PRu$ requires C, 57.05; H, 4.35; Cl, 13.5%; *M* 526). Phosphorus-31 n.m.r. in CD_2Cl_2: δ −27.7 (s) p.p.m. relative to H_3PO_4. Carbon-13 n.m.r. in CD_2Cl_2 relative to $SiMe_4$: δ 24.7 (CH_2), 59.7(br.), 98.6, 100.6 (C–H), 127.9, 128.3, 130.4, 133.8, and 134.2 p.p.m. (Ph).

Dichloro(cycloheptatriene)(triphenylarsine)ruthenium(II), (2; L = $AsPh_3$).—Using the above procedure, the dimer (1) (400 mg) was treated with triphenylarsine (460 mg) to give an orange-red solid (660 mg, 76%) (Found: C, 52.65; H, 4.05; C, 12.45%; *M* 570. $C_{25}H_{23}Cl_2AsRu$ requires C, 53.05; H, 4.15; Cl, 12.71%; *M* 574). Carbon-13 n.m.r. in CD_2Cl_2 relative to $SiMe_4$: δ 24.4 (CH_2), 49.8, 98.0, 99.8 (CH), 128.7, 130.1, and 133.7 p.p.m. (Ph).

Dichloro(cycloheptatriene)(triphenyl phosphite)ruthenium(II), [2; L = $P(OPh)_3$].—Using the above procedure, the dimer (1) (400 mg) was treated with triphenyl phosphite (480 mg) to give an orange solid (750 mg, 85%) (Found: C, 52.25; H, 4.05; Cl, 12.1%; *M* 581. $C_{25}H_{23}Cl_2O_3PRu$ requires C, 52.30; H, 4.00; Cl, 12.3%; *M* 574).

Dichloro(cycloheptatriene)(tri-n-butylphosphine)ruthenium(II), (2; L = $PBu^n{}_3$).—The dimer (1) (200 mg) was heated under reflux in nitrogen-purged dichloromethane with tri-n-butylphosphine (0.3 cm^3). The solution was filtered through Celite and a pale orange solid precipitated by addition of diethyl ether; this was recrystallised from acetone (140 mg, 40%) (Found: C, 49.1; H, 7.40; Cl, 15.25%; *M* 462. $C_{19}H_{35}Cl_2PRu$ requires C, 48.95; H, 7.50; Cl, 15.2%; *M* 466).

Chloro(cycloheptatriene)(1,1,1,5,5,5-*hexafluoropentane*-2,4-*dionato)ruthenium*(II), (6).—The dimer (1) (500 mg) was shaken at room temperature in chloroform with thallium 1,1,1,5,5,5-hexafluoropentane-2,4-dionate (800 mg) until all the dimer had dissolved. After centrifuging to remove the thallium chloride, the solution was taken to dryness and an orange solid was obtained by recrystallisation from diethyl ether (367 mg, 45%) (Found: C, 33.15; H, 2.05; Cl, 7.95%; *M* 448. $C_{12}H_9ClF_6O_2Ru$ requires C, 33.1; H, 2.05; Cl, 8.15%; *M* 435), M^+ (Ru = 102, Cl = 35) 436, ν(CO)(Nujol) at 1 630 and 1 596 cm^{-1}. Coupling constants $J(H^4H^5)$ 13, $J(H^3H^5)$ 5, and $J(H^3H^4)$ 9 Hz. Fluorine-19 n.m.r. spectrum in CD_3COCD_3: two signals of slightly unequal intensity separated by 0.5 Hz at 74.88 p.p.m. relative to CCl_3F.

Chloro(cycloheptatriene)(1,1,1-*trifluoropentane*-2,4-*dionato)-ruthenium*(II), (6). Using the above procedure the dimer (1) (200 mg) was treated with thallium 1,1,1-trifluoropentane-2,4-dionate (270 mg) to give a yellow solid (32 mg, 11%) (Found: C, 37.55; H, 3.25; Cl, 10.2%; *M* 388. $C_{12}H_{12}ClF_3O_2Ru$ requires C, 37.75; H, 2.90; Cl, 9.30%; *M* 382), M^+ (Ru = 102, Cl = 35) 382, ν(CO) (Nujol) at 1 615 and 1 523 cm^{-1}. Coupling constants $J(H^4H^5)$ 13, $J(H^3H^5)$ 4.5, and $J(H^3H^4)$ 8.5 Hz. The fluorine-19 spectrum in CD_3COCD_3 showed a sharp singlet at 73.92 p.p.m. relative to CCl_3F.

Bis(acetonitrile)chloro(cycloheptatriene)ruthenium(II) *Tetrafluoroborate*, (4).—The dimer (1) (250 mg) was shaken in dry acetonitrile with thallium tetrafluoroborate (270 mg) until all the dimer had dissolved. After centrifuging to remove the thallium chloride, diethyl ether was added dropwise to the solution precipitating a pale yellow solid. All attempts at purification failed to give an analytically pure sample of the complex. The ^1H n.m.r. spectrum of the complex showed the expected resonances for the complex plus excess of solvent (Table 2).

(2,2′-*Bipyridyl)chloro(cycloheptatriene)ruthenium*(II) *Tetrafluoroborate*, (5).—Complex (3) was prepared as described above and dissolved in dry dichloromethane (20 cm^3). The solution was heated under reflux and 2,2′-bipyridyl (167 mg) dissolved in dichloromethane (10 cm^3) added slowly over a period of 30 min, a yellow solid precipitating from the solution as the bipy was added. After precipitation was complete (another 15 min), the solution bulk was reduced to 5 cm^3, filtered, and the solid washed with a small quantity of dichloromethane followed by diethyl ether. The product was recrystallised from methanol (181 mg, 41%) (Found: C, 42.75; H, 3.40; Cl, 6.95; N, 5.75. $C_{17}H_{16}BClF_4N_2Ru$ requires C, 43.25; H, 3.40; Cl, 7.55; N, 5.95%).

cis-*Bis(acetonitrile)dichloro(cyclo-octa*-1,5-*diene)ruthenium*(II), (8).—The polymer $[\{Ru(cod)Cl_2\}_n]$ (400 mg) was heated under reflux in nitrogen-purged acetonitrile (10 cm^3) overnight. The solution was filtered hot under nitrogen and set aside to cool, first to room temperature and then to −30 °C. The resulting golden-yellow plates were separated by filtration (230 mg, 45%) (Found: C, 39.15; H, 4.80; Cl, 19.0; N, 7.45. $C_{12}H_{18}Cl_2N_2Ru$ requires C, 39.8; H, 4.95; Cl, 19.6; N, 7.75%). Far-i.r. spectrum in Nujol: Ru-Cl at 313 cm^{-1} absent in bromide derivative; ν(CN) (Nujol) at 2 414 and 2 305 cm^{-1}. Molar conductivity (Λ): in water, 170; in MeCN, 0.7 S cm^2 mol^{-1}. Hydrogen-1 n.m.r. spectrum in CF_3CO_2H: τ 5.45 (m, 4 H, olefins), 7.32 (s, 6 H, MeCN), and 7.4—8.0 (m, 8 H, methylene).

trans-(2,2-*Bipyridyl)dichloro(cyclo-octa*-1,5-*diene)ruthenium*(II), (9).—Complex (8) (500 mg) was dissolved in dichloromethane (25 cm^3) and the solution heated under reflux. 2,2′-Bipyridyl (200 mg) was dissolved in dichloromethane (5 cm^3) and added to the refluxing solution over a period of 1 h. The solution was heated under reflux for another 20 min, cooled, and the solvent bulk reduced to 5 cm^3. The precipitated product was filtered off, washed with a small quantity of dichloromethane, then diethyl ether, to give an orange solid, which was recrystallised from dichloromethane (310 mg, 52%) (Found: C, 49.4; H, 4.55; Cl, 16.1; N, 6.45. $C_{18}H_{20}Cl_2N_2Ru$ requires C, 49,5; H, 4.60; Cl, 16.3; N, 6.45%). Hydrogen-1 n.m.r. (spectrum in CF_3CO_2H): τ 1.68 (m, 4 H, bipy), 1 94 (t, 2 H, bipy), 2.45 (t, 2 H, bipy), 4.93 (m, 4 H, olefinic). and 7.0—7.8 (m, 8 H, methylene). Far-i.r. spectrum (Nujol): Ru-Cl at 319 cm^{-1} absent in bromide derivative.

trans-*Tetrakis(acetonitrile)dichlororuthenium*(II), (3).—Dimer (1) (200 mg) was heated under reflux in acetonitrile until all the dimer had reacted. The product was filtered off and washed with diethyl ether to give the yellow solid (230 mg, 90%) (Found: C, 28.6; H, 3.60; Cl, 20.85; N, 16.8. $C_8H_{12}Cl_2N_4Ru$ requires C, 28.6; H, 3.55; Cl, 21.15; N, 16.65%). ν(CN) (Nujol) at 2 281 cm^{-1}, τ 7.50 in CF_3CO_2H.

trans-*Tetrakis(benzonitrile)dichlororuthenium*(II), (10).—The polymer $[\{Ru(cod)Cl_2\}_n]$ (400 mg) was stirred at 110 °C in benzonitrile (10 cm^3) for 24 h. The product was filtered off, then washed with acetone and diethyl ether to give the orange solid (710 mg, 85%) (Found: C, 57 7; H, 3.60; N, 9.60. $C_{28}H_{20}Cl_2N_4Ru$ requires C, 57.6; H, 3.45; N, 9.60%), ν(CN) (Nujol) at 2 240 cm^{-1}, τ 1.9—2.65 (br m) in CF_3CO_2H.

[6-(2,4-*Dioxopentyl*)*cycloheptadienyl*](*pentane*-2,4-*dionato*)(*triphenylphosphine*)*ruthenium*(II), (7).—Complex (2; L = PPh_3) (200 mg) was heated under reflux in dry nitrogen-purged hexane (15 cm^3) with thallium pentane-2,4-dionate (240 mg) for 1 h. The solution was filtered under nitrogen and the filtrate cooled to −78 °C to precipitate an orange-yellow solid (151 mg, 61%) (Found: C, 64.45; H, 5.85. $C_{35}H_{37}O_4PRu$ requires C, 64.35; H, 5.65%), M^+ (Ru = 102) 654, ν(CO) (KBr disc) at 1 690, 1 588, and 1 508 cm^{-1}. Hydrogen-1 n.m.r. spectrum in C_6D_6: τ 2.34 and 2.88 (m, 15 H, PPh_3), 4.78 (m, 1 H, H_E), 4.98 (s, 1 H, *O*-bonded diketone), 5.50 (br m, 1 H), 6.20 (br m, 1 H) 6.65 (br m, 3 H), 6.87 (d, 1 H, *C*-bonded diketone), 8.02 (s, 3 H, Me), 8.28 (s, 10 H, 3 Me + H_B), and 9.86 (m, 1 H, H_A).

[6-(2,4-*Dioxo*-4-*phenylbutyl*)*cycloheptadienyl*](4-*phenylbutane*-2,4-*dionate*)(*triphenylphosphine*)*ruthenium*(II), (7).—Using the above procedure complex (2; L = PPh_3) (100 mg) was treated with thallium 4-phenylbutane-2,4-dionate (140 mg) to give a yellow-brown solid (118 mg, 80%) (Found: C, 69.4; H, 5.80. $C_{45}H_{41}O_4PRu$ requires C, 69.55; H, 5.30%). ν(CO) (KBr disc) at 1 703 and 1 671 cm^{-1} (*C*-bonded diketone), 1 592, 1 565, or 1 512 cm^{-1} (*O*-bonded diketone plus phenyl). Hydrogen-1 n.m.r. spectrum in C_6D_6: τ 2.30 and 3.0 (m, 25 H, Ph), 4.30 (d, 1 H, *O*-bonded diketone), 4.88 (m, 1 H, H_E), 5.5 (m, 1 H), 5.96 (d, 1 H, *C*-bonded diketone), 6.0—7.2 (m, 4 H), 7.9(s), 7.95(s) and 8.23(s) (7 H, 2 Me + H_B), and 9.95 (m, 1 H, H_A).

[6-(*Dibenzoylmethyl*)*cycloheptadienyl*](1,3-*diphenylpropane*-1,3-*dionato*)(*triphenylphosphine*)*ruthenium*(II), (7).—Complex (2; L = PPh_3) (100 mg) was heated under reflux in nitrogen-purged heptane with thallium 1,3-diphenylpropane-1,3-dionate (190 mg) for 1 h. The solution was filtered under nitrogen and the filtrate cooled to −78 °C to precipitate an orange-brown solid (140 mg, 82%) (Found: C, 72.95; H, 5.35; $C_{55}H_{45}O_4PRu$ requires C, 73.25; H, 5.00%). ν(CO) (KBr disc) at 1 693 and 1 640 cm^{-1} (*C*-bonded diketone), 1590, 1545, and 1515 cm^{-1} (*O*-bonded diketone plus phenyl). Hydrogen-1 n.m.r. spectrum in CD_2Cl_2: τ 2.06 and 2.4—2.9 (m, 35 H, Ph), 3.66 (s, 1 H, *O*-bonded diketone), 4.78 (t, 1 H, H_E), 5.10 (d, 1 H, *C*-bonded diketone), 5.40 (m, 1 H), 6.20 (m, 1 H, H_H), 6.4—7.0 (m, 3 H), 8.27 (d of t, 1 H, H_B), and 9.73 (m, 1 H, H_A).

[6-(2,4-*Dioxopentyl*)*cycloheptadienyl*](*pentane*-2,4-*dionato*)(*triphenylarsine*)*ruthenium*(II), (7).—Complex (2; L = $AsPh_3$) (100 mg) was treated in nitrogen-purged dichloromethane (3 cm^3) with thallium pentane-2,4-dionate (120 mg). The solution was centrifuged to remove the thallium chloride and the dichloromethane was evaporated to dryness. After extracting the residue with nitrogen-purged pentane (30 cm^3), the solution was filtered under nitrogen and the filtrate cooled to −78 °C to precipitate a pale yellow solid (65 mg, 53%) (Found: C, 60.3; H, 5.80. $C_{35}H_{37}AsO_4Ru$ requires C, 60.3; H, 5.30%), ν(CO) (KBr disc) at 1 692, 1 580, and 1 510 cm^{-1}. Hydrogen-1 n.m.r. spectrum in $CDCl_3$; τ 2.68 (m, 15 H, Ph), 4.42 (m, 1 H, H_E), 5.16 (s, 1 H, *O*-bonded diketone), 5.67 (d of d, 1 H), 6.24 (d of d, 1 H), 6.94 (m, 3 H), 7.01 (d, 1 H, *C*-bonded diketone), 7.94, 8.10(s) and 8.37(s) (13 H, 4 Me + H_B), and 9.98 (m, 1 H, H_A).

[6-(*Dibenzoylmethyl*)*cycloheptadienyl*](1,3-*diphenylpropane*-1,3-*dionato*)(*triphenylarsine*)*ruthenium*(II), (7).—Complex (2; L = $AsPh_3$) (100 mg) was treated in nitrogen-purged dichloromethane (3 cm^3) with thallium 1,3-diphenylpropane-1,3-dionate (160 mg). The solution was centrifuged to remove the thallium chloride and decanted into nitrogen-purged hexane (100 cm^3). The resulting solution was filtered under nitrogen, reduced in volume to 40 cm^3, and cooled to −78 °C to precipitate a red-brown solid (53 mg, 32%) (Found: C, 68.85; H, 5.05. $C_{55}H_{45}AsO_4Ru$ requires C, 69,85; H, 4.75%). ν(CO) (KBr disc) at 1 690 and 1 654 cm^{-1} (*C*-bonded diketone), 1 588, 1 550, and 1 512 cm^{-1} (*O*-bonded diketone). Hydrogen-1 n.m.r. spectrum in CD_2Cl_2: τ 2.1 and 2.67 (m, 35 H, Ph), 3.66 (s, 1 H, *O*-bonded diketone), 4.40 (t, 1 H, H_E), 5.08 (d, 1 H, *C*-bonded diketone), 5.39 (d of d, 1 H, H_D), 6.0—6.4 (m, 2 H, H_H and H_F), 6.56 (m, 1 H, H_G), 6.78 (m, 1 H, H_C), 8.21 (m, 1 H, H_B), and 9.79 (m, 1 H, H_A).

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