Reactivity of Co-ordinated Ligands. Part XVIII.† Cationic Ruthenium(II) and Osmium(II) Complexes by Electrophilic Attack on a π-Allyl Ligand

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Monocationic ruthenium(II) and osmium(II) complexes containing labile acetonitrile ligands have been prepared by electrophilic attack on a π-allyl ligand in M(diene)(π-allyl)$_2$ species (M = Ru or Os, diene = norbornadiene or cyclo-octa-1,5-diene). The acetonitrile ligands may be replaced by Group V$_A$ chelating ligands. The allyl ligand in the monocationic species is also attacked by electrophiles to yield dicationic complexes. The stereospecific exchange of acetonitrile ligands in the cationic species is described. N.m.r. data, including a reinterpretation of those for the Ru(diene)(π-allyl)$_2$ species, are presented and discussed.

It is well known that ' pure ' π-allyl transition metal complexes,[1] as well as several complexes outside this classification,[2] react with strong protonic acids to liberate the corresponding olefin. However, electrophilic attack on a π-allyl ligand has not been explored as a preparative route to cationic transition metal complexes, a route similar in principle to electrophilic attack on co-ordinated acetylacetonate,[3] acetate,[4] or trifluoroacetate[5] ion. A valuable application of this technique involves the preparation of some cationic ruthenium(II) and osmium(II) complexes from species of the type M(diene)(π-allyl)$_2$ (M = Ru or Os), *e.g.* equation (1) where nbd = norbornadiene. This and analogous cationic species

$$\mathrm{Ru(nbd)(\pi\text{-}C_3H_5)_2} \xrightarrow[\mathrm{CH_3CN}]{\mathrm{Ph_3C^+BF_4^-}} \textit{cis}\text{-}[\mathrm{Ru(nbd)(\pi\text{-}C_3H_5)(CH_3CN)_2}]^+\mathrm{BF_4^-} \quad (1)$$

serve as starting materials for a range of cationic species as a result of the following properties: (i) the acetonitrile ligands are readily displaced by Group V$_A$ donor ligands; (ii) the allyl group in monocationic species is slowly attacked by a second mole of electrophile to yield dicationic species; and (iii) the diene may be displaced from the dicationic species. The primary objective is therefore to describe this preparative scheme.

† Part XVII, J. A. S. Howell, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 293.

[1] See, for example, G. Wilke, *Angew. Chem. Internat. Edn.*, 1966, **5**, 151.

[2] J. Powell and B. L. Shaw, *Chem. Comm.*, 1966, 236, 323; *J. Chem. Soc.* (*A*), 1968, 583 and 780; R. Hüttel, J. Kratzer, and M. Bechter, *Chem. Ber.*, 1961, **94**, 766; A. D. Ketler and J. Braatz, *Chem. Comm.*, 1968, 169.

DISCUSSION

The preparative scheme is presented in the form of a flow chart in the Scheme. The discussion is subdivided into four parts. The M(diene)(π-allyl)$_2$ complexes, the monocationic, and the dicationic species are each discussed in turn then the phenomenon of acetonitrile exchange. Analytical and spectroscopic data and definition of notation can be found in the Experimental section.

The M(diene)(π-allyl)$_2$ *Species.*—Powell and Shaw[6] first described the preparation of Ru(cod)(π-C_3H_5)$_2$, Ru(cod){π-$CH_2C(CH_3)CH_2$}$_2$, and Ru(nbd)(π-C_3H_5)$_2$ by the reaction of [Ru(diene)Cl$_2$]$_x$ with the appropriate Grignard reagent. We have found analogous Ru^{II} or Os^{II} species to be available by an identical route. High yield isolation of these species was best effected simply by solvent removal after passage of a pentane solution through alumina. Preparation of the complexes reported here was dictated primarily by their value in subsequent reactions and is not meant to be comprehensive.

A short discussion of a previously unrecognized aspect of the n.m.r. spectra of these species is of interest since it is closely related to a phenomenon which occurs in several of the cationic diene complexes prepared here. The Ru(cot)(π-C_3H_5)$_2$, Ru(nbd)(π-allyl)$_2$, Ru(cod)(π-allyl)$_2$, and Os(cod)(π-allyl)$_2$ [allyl = C_3H_5 or $CH_2C(CH_3)CH_2$] complexes are found to be primarily or

[3] B. F. G. Johnson, J. Lewis, and D. A. White, *J. Amer. Chem. Soc.*, 1969, **91**, 5186.

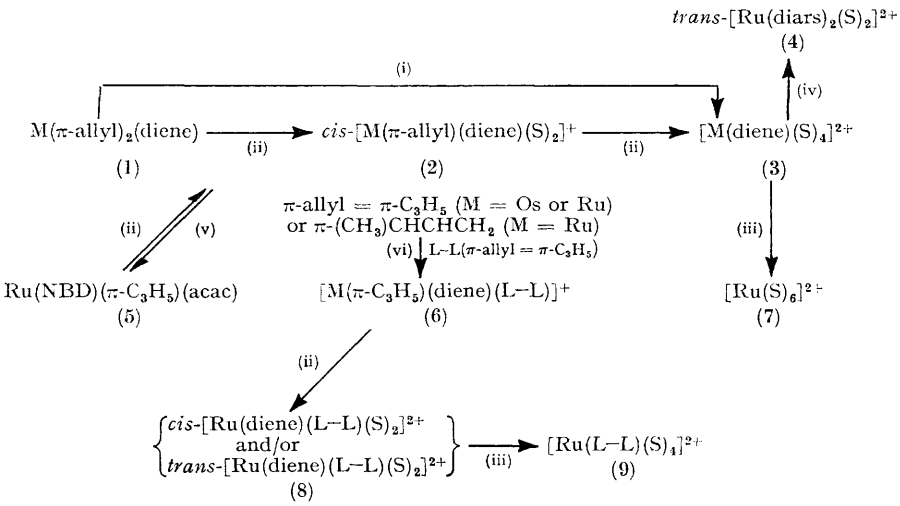
[4] P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 3322.

[5] C. White and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1971, 3322.

[6] J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 159.

exclusively one of the two possible isomers having C_2 symmetry.* This is evidenced by the observation (as reported for previous examples [6]) that the π-allyl groups are equivalent and therefore give rise to only one series of resonances for, for example, the five protons attached to a three-carbon moiety. The location and appearance of these resonances varies little with the identity of the metal or the diene and their assignment is consistent with decoupling experiments. We now find that the diene portions of the spectra are also consistent with the low symmetry of these species as shown by the following: (i) irradiation of the methine resonance in the spectrum of Ru(nbd)(π-allyl)$_2$ [allyl = C_3H_5 or $(CH_3)CHCHCH_2$] causes collapse of the resonances in the τ 5·70—5·90 and τ 8·65—8·75 regions to doublets and the methylene resonance to a singlet, demonstrating that the resonances in the τ 5·8 and 8·7 regions must be ascribed to two non-equivalent olefin proton sets; (ii) the spectrum of Ru(cot)(π-C_3H_5)$_2$ contains four distinct and well separated signals due to the cot protons; † and (iii) decoupling experiments for the M(cod)(π-allyl)$_2$ complexes [allyl = C_3H_5 or $CH_2C(CH_3)CH_2$, M = Ru or Os] also clearly suggest that the extreme cod resonances are due to the non-equivalent olefin proton sets (see Experimental section). In all cases the chemical shift difference of the olefin proton sets is of the order of 260—300 Hz. As will be shown later, olefin proton chemical shift differences of up to 160 Hz are found in complexes (with no symmetry) which do not contain a π-allyl group. Therefore the cause of this phenomenon must be more closely associated with the low symmetry (or asymmetry) of the six-co-ordinate complexes as a whole rather than the presence of any one particular ligand.

The cis-[M(diene)(π-allyl)$(CH_3CN)_2$]$^+$ *Species and their Derivatives.*—One π-allyl group in the M(diene)(π-allyl)$_2$ species is readily attacked by one mole of trityl or a proton to yield Ph_3C-allyl or the corresponding olefin respectively and (2) (see Scheme). The presence of two acetonitrile n.m.r. resonances (in CH_2Cl_2 at −30 °C) shifted downfield from the position where an uncoordinated acetonitrile resonance would occur and two ν(C≡N) bands in the i.r. spectrum together suggest the configuration of (2) to be *cis*. These species are soluble in polar organic solvents (*e.g.*, acetone, dichloromethane, nitromethane, or acetonitrile) although decomposition (Ru > Os) is evident in the absence of free acetonitrile under ambient conditions. The organic product of trityl attack in the case where allyl = $(CH_3)CHCHCH_2$ was found to be $Ph_3CCH_2CH{=}CHCH_3$; the stereochemistry about the double bond could not be determined unambiguously.



SCHEME (i) π-Allyl = π-$CH_2C(CH_3)CH_2$, in CH_3CN with an excess of H^+; (ii) Ph_3C^+, CH_3CN; (iii) heat in CH_3CN; (iv) diars; (v) Tlacac; (vi) L–L (π-allyl = π-C_3H_5); diene = nbd (norbornadiene, M = Ru) or cod (cyclo-octa-1,5-diene, M = Ru or Os); L–L = 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), or *o*-phenylenebisdimethylarsine (diars); S = acetonitrile.

An analogue of (2) with allyl = $CH_2C(CH_3)CH_2$ could not be prepared although its existence was indicated by the low-yield preparation of derivatives analogous to (6). It is likely, therefore, that the rate of electrophilic attack varies significantly from one allyl group to another. The rates observed qualitatively for (1) ⟶ (3) are $CH_2C(CH_3)CH_2 > C_3H_5 \sim (CH_3)CHCHCH_2$.

The acetonitrile ligands in (2) can be readily displaced by a neutral chelating ligand to yield (6) or by acac to yield (5). The reaction is believed to be facilitated by the ready dissociation of acetonitrile (*vide infra*) and it is this fact upon which the success of the scheme depends. Attempts to perform reactions similar to (2) ⟶ (6) with 1,2-bis(diphenylphosphino)ethane or with mono-

* Complexes containing the π-$(CH_3)CHCHCH_2$ ligand give rise to considerably more complex n.m.r. spectra, which have not been interpreted in detail. Some aspects of the spectra may be taken as evidence that an isomer or isomers not having C_2 symmetry are present. The fact that the allyl ligand itself is not symmetric increases the number of possible isomers to ten, six of which have no symmetry.

† The n.m.r. spectrum is inconsistent with C_8H_8 bonded as a 1,3-diene since this situation would destroy the C_2 symmetry of the complex. Cyclo-octatetraene must therefore be bonded in its tub form as a 1,5-diene.

dentate donors [*e.g.* PPh_3, $PPhMe_2$, $P(OMe)_3$, or pyridine] failed. N.m.r. spectra of these reaction mixtures indicated that extensive replacement of the diene had occurred.

The n.m.r. spectra of (2), (5), and (6) are complicated by the fact that the complexes are asymmetric. Nevertheless, in many cases it is possible to identify all resonances. Several interesting points should be noted. The chemical shift difference of the acetonitrile resonances is surprisingly large; *e.g.*, τ 7·49 and 7·90 in *cis*-$[Ru(nbd)(\pi\text{-}C_3H_5)(CH_3CN)_2]^+$. Secondly, the degree of variation in chemical shifts for the four non-equivalent olefin protons is also considerable and comparable to chemical shift differences for non-equivalent olefin proton *sets* in the Ru(diene)(π-allyl)$_2$ species (*vide supra*); *e.g.*, the difference between the extreme olefin proton resonances in $Ru(nbd)(\pi\text{-}C_3H_5)(acac)$ is 246 Hz. Thirdly, there is evidence of isomeric species in the spectra of $Ru(nbd)(\pi\text{-}C_3H_5)(CH_3CN)_2]^+$ and its derivatives. In the parent complex weak resonances (*ca.* 20% of major intensities) may be identified at τ 5·34 (t, J *ca.* 4, olefin), τ 7·42 (d, J 10—12, anti allyl), and τ 8·87 (AB quartet, nbd methylene) consistent with a second isomer of *cis*-$[Ru(nbd)(\pi\text{-}C_3H_5)(CH_3CN)_2]^+$ in which the allyl ligand is 'flipped' with respect to the plane passing through the metal and the first and third carbons of the allyl ligand (not a molecular plane). If this interpretation is correct then it may be said that the isomers are not interconverted at a rate which is rapid on the n.m.r. time scale at 80 °C in CD_3CN and their ratio remains unchanged upon returning to room temperature. Whether the minor isomer is formed from an undetected isomer of $Ru(nbd)(\pi\text{-}C_3H_5)_2$ or during the preparation of the cationic species remains in doubt at this time. Finally, the n.m.r. spectrum of $Ru(nbd)(\pi\text{-}C_3H_5)(acac)$ is temperature dependent in [$^2H_8$]toluene. By 110 °C all resonances have collapsed to yield a series of broad, non-descript peaks. The rearrangement process shows several stages including one in which the major and minor isomers of this species {analogous to those of $[Ru(nbd)(C_3H_5)(CH_3CN)_2]^+$, *vide supra*} are interconverting at a rapid rate on the n.m.r. time scale, *i.e.*, only one double triplet pattern is observed for the central allyl proton resonance. However, it is clear that other, possibly independent, rearrangement processes are taking place concurrently; *e.g.*, only one acac-methyl resonance is observed. Although an identical spectrum, complete with an unchanged isomer ratio, is regenerated upon cooling to room temperature, there is not enough information available at this time to elucidate the rearrangement process(es).

The Dicationic Species.—Dicationic Ru^{II} complexes are formed by electrophilic attack on an allyl group in a monocationic complex. Thus (3) may be prepared by the slow reaction of (2; π-allyl = π-C_3H_5) with trityl tetrafluoroborate but is more readily and rapidly prepared from Ru(diene){π-$CH_2C(CH_3)CH_2$}$_2$ employing H^+ as the electrophile. Likewise, the reaction of (6) with trityl tetrafluoroborate yields (8). The formation of dicationic species suggests that the presence of a formal positive charge does not significantly alter the nature of the allyl group with respect to electrophilic attack.

The stereochemistry of (8) depends upon the identity of L–L and/or the diene. Where diene = nbd and L–L = bipy or phen a mixture of *cis* and *trans* isomers results. However, only *trans*-$[Ru(cod)(bipy)(CH_3CN)_2]^{2+}$ and only *cis*-$[Ru(nbd)(diars)(CH_3CN)_2]^{2+}$ could be isolated; the other isomer in each case could not be detected (by n.m.r.) in the crude product or *in situ* in CD_3CN. An attempt to prepare *trans*-$[Ru(nbd)(diars)(CH_3CN)_2]^{2+}$ by the room temperature reaction of a stoicheiometric quantity of diars with $[Ru(nbd)(CH_3CN)_4]^{2+}$ gave only a 50% yield of *trans*-$[Ru(diars)_2(CH_3CN)_2]^{2+}$. In contrast, the reaction of $[Ru(nbd)(CH_3CN)_4]^{2+}$ with 2,2′-bipyridyl gave *trans*-$[Ru(nbd)(bipy)(CH_3CN)_2]^{2+}$. The possibility that isomerisation of *cis*- (8) to *trans*- (8) takes place after *cis*- (8) is formed seems unlikely since *cis*- and *trans*-forms could not be interconverted by heating in nitromethane or in acetonitrile. [In acetonitrile alternative reactions took precedence (*vide infra*).] It is likely, therefore, that the isomers of (8) are formed during the reaction (6) ⟶ (8) and the outcome could conceivably be determined by whether electrophilic attack is directed at the first or the third carbon atom of the allyl ligand. Nevertheless, the generation of a *trans*- (8) species must still involve a rearrangement of L–L and diene with respect to one another during the course of the reaction.

The diene in (3) and (8) is liberated upon heating in acetonitrile to generate (7) and (9) respectively. The rate of displacement is not first order.* Reactions in which diene = cod occur to the extent of only *ca.* 20% in the time during which the comparable reactions where diene = nbd are complete. Norbornadiene therefore appears to be a much more 'labile' ligand than cyclo-octadiene in Ru^{II} complexes of this nature. *cis*- (8) Isomers also react noticeably faster (*ca.* five times) than the corresponding *trans*- (8) isomers. Differences in the rates of reaction for a series of *trans*- (8) complexes (L–L = bipy, phen, or diars) appear to be smaller in magnitude.

The n.m.r. spectra of the *cis*- (8) complexes show two singlets due to the non-equivalent acetonitrile ligands and diene portions of the spectra similar to those of other asymmetric diene complexes, (1), (2), (5), and (6). An extreme of the latter is illustrated in the n.m.r. spectrum of *cis*-$[Ru(nbd)(bipy)(CH_3CN)_2]^{2+}$ in which each proton on the nbd ligand exhibits a separate resonance. This finding confirms that the presence of a π-allyl ligand is not solely responsible for the large effect upon the chemical shift of protons on the diene ligand.

The n.m.r. spectra of *trans*- (8), (3), (4), (7), and (9) are simplified due to the C_{2v} or higher symmetry. All olefin protons are equivalent in each case. There is one resonance due to the acetonitrile ligands in *trans*- (8), (4), and (7), and two in (3) and (9).

In the n.m.r. spectra of (3) and (9) it is not known

* The half-life of the reaction of *cis*-$[Ru(nbd)(bipy)(MeCN)_2]^{2+}$ with MeCN in $MeNO_2$ to yield $[Ru(bipy)(MeCN)_4]^{2+}$ was shown qualitatively to be very dependent upon MeCN concentration.

which acetonitrile ligand set is responsible for a given resonance. [A similar problem arises in the case of (2) and *cis*- (8)]. In connection with studies of acetonitrile ligand exchange (*vide infra*) it was desirable, and possible, to obtain this information for (3) and (9). The assignments were made by examination of a complex of each type, $[Ru(7\text{-phenylnorbornadiene})(CH_3CN)_4]^{2+}$ (3c) and $[Ru(5\text{-methyl-1,10-phenanthroline})(CH_3CN)_4]^{2+}$ (9d). In each case the acetonitrile ligands *trans* to the chelating ligand are, in theory, non-equivalent and could therefore exhibit separate resonances. The spectrum of (3c) showed CH_3CN resonances at τ 7·29 (6), 7·59 (3), and 7·63 (3) at 100 MHz while that of (9d) showed CH_3CN resonances at τ 7·310 (3), 7·315 (3), and 7·97 (6) at 220 MHz. Therefore by analogy it is the resonance to higher field in (3a) [$\tau(CH_3CN)$ 7·30 and 7·60] but that to lower field in (9b) [$\tau(CH_3CN)$ 7·32 and 7·99] which is due to the acetonitrile ligands *trans* to nbd and phen respectively. Results obtained from exchange studies suggest that an analogous situation exists for (3b) and for (9a) and (9c) respectively. These findings suggest that a correlation of chemical shift with stereochemical position may be possible only in very closely similar species and no general relationships should therefore be expected.

The Stereospecific Exchange of Acetonitrile.—The Table is a collection of semi-quantitative data concerning the rate of exchange of CH_3CN ligands with CD_3CN solvent. Exchange was most conveniently studied in neat CD_3CN or in CH_2Cl_2 or CH_3NO_2 in the presence of at least a ten-fold excess of CD_3CN. The half-life was determined by integration of the resonances due to co-ordinated acetonitrile *versus* free acetonitrile or other resonances in the spectrum.

The resonances attributable to the acetonitrile ligands (S_1) which are *trans* to the chelating ligand in (3) or (9) (*vide supra*) are those which disappear most rapidly as co-ordinated CH_3CN is replaced by CD_3CN. The

	Compound	τ CH_3CN [a]	$t_{\frac{1}{2}}$ of exchange	Temp.[b]
(9a)	$[Ru(bipy)(CH_3CN)_4]^{2+}$	*7·38* [c]	3·5 ± 0·5 h	81·6
		7·88 [c]	37 ± 2 h	81·6
(9b)	$[Ru(phen)(CH_3CN)_4]^{2+}$	*7·32* [c]	13 ± 1 h	81·6
		7·99 [c]	55 ± 5 h	81·6
(9c)	$[Ru(diars)(CH_3CN)_4]^{2+}$	*7·52* [c]	19 ± 3 min	29
		7·78	*ca.* 11 days	81·6
(9d)	$[Ru(5\text{-Mephen})(CH_3CN)_4]^{2+}$	*7·310*(3)		
		7·315(3)		
		7·97(6)		
(3a)	$[Ru(nbd)(CH_3CN)_4]^{2+}$	*7·57* [c]	7 ± 0·5 h	22
		7·28 [d]	25 days [e]	22
			25 ± 5 min [e]	81·6
(3b)	$[Ru(cod)(CH_3CN)_4]^{2+}$	*7·57* [e]	11 days	22
			3·5 ± 0·5 h	50
			7 ± 1 min	81·6
		7·34 [d]	20 ± 1 h [e]	81·6
(3c)	$[Ru(7\text{-Phnbd})(CH_3CN)_4]^{2+}$	*7·59*(3)	6·5 ± 0·5 h	22
		7·63(3)	7·5 ± 0·5 h	22
		7·29(6)	25 ± 5 min	81·6
(8a)	*cis*-$[Ru(nbd)(bipy)(CH_3CN)_2]^{2+}$	7·14 [f]	*ca.* 12 h	0
		7·91 [f]	*ca.* 12 h	0
(8b)	*cis*-$[Ru(nbd)(phen)(CH_3CN)_2]^{2+}$	*7·11*		
		7·93		
(8c)	*cis*-$[Ru(nbd)(diars)(CH_3CN)_2]^{2+}$	*7·24* [g]	3·5 ± 0·5 h	22
		7·80	*ca.* 80 h	22
(8d)	*trans*-$[Ru(nbd)(bipy)(CH_3CN)_2]^{2+}$	7·76	→(9a) w/o exchange	81·6
(8e)	*trans*-$[Ru(nbd)(phen)(CH_3CN)_2]^{2+}$	7·89	→(9b) w/o exchange	81·6
(8f)	*trans*-$[Ru(cod)(bipy)(CH_3CN)_2]^{2+}$	7·78 [c]	11 ± 1 h [e]	81·6
(2a)	*cis*-$[Ru(nbd)(\pi\text{-}C_3H_5)(CH_3CN)_2]^{+}$	*7·49* [g]	*ca.* 12 min	−30
		7·90 [g]	*ca.* 1 h	−30
(2b)	*cis*-$[Os(cod)(\pi\text{-}C_3H_5)(CH_3CN)_2]^{+}$	*7·39*	*ca.* 10 min	29
		7·63	> $t_{\frac{1}{2}}$ of 7·39 peak	29

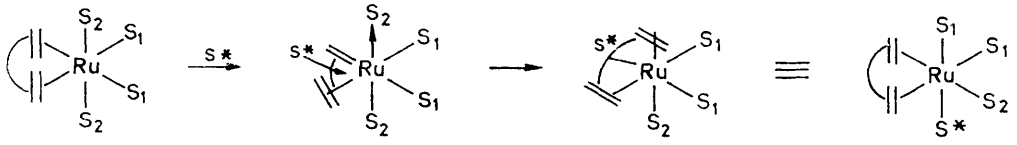
[a] τ Value in italic indicates the most the labile acetonitrile ligand or ligand set. The experiment was performed in neat CD_3CN unless otherwise noted. See Experimental section for an explanation of abbreviations. [b] 81·6 °C Is the temperature of the vapour above boiling acetonitrile. An oil well in contact with the vapour constituted a constant 81·6 °C temperature bath. Other temperatures are accurate to *ca.* ±3 °C. [c] First order with respect to CD_3CN concentration in nitromethane as solvent using at least a ten-fold molar excess of CD_3CN. [d] Greater than first order dependence was observed under the conditions in *c*. [e] Free diene was detected to the extent of *ca.* 5%. [f] There was some indication that the τ 7·14 resonance disappeared slightly faster than the τ 7·91 resonance though this difference was, in general, within experimental error. [g] In dichloromethane as a solvent. Greater than a ten-fold molar excess of CD_3CN was added to the solution after cooling to −30 °C. The half-life of the τ 7·49 resonance was found to be invariant upon increasing the amount of added CD_3CN by a factor of ten.

specificity of the exchange process is most dramatically illustrated in the case of (9c) where the difference in the rate of exchange of the S_1 set is faster than the mutually *trans* CH_3CN set (S_2) by a factor which may approach 10^5.* The less dramatic rate differences found in the case of (9a) and (9b) are no less significant in demonstrating that it is possible to exchange essentially all S_1 (two molecules per complex) before any exchange of S_2 takes place, *i.e.*, the stereochemical identity of S_1 is maintained throughout the exchange process. Significantly, the half-life for exchange of S_1 in (9a—c) in CH_3NO_2 is independent of CD_3CN concentration indicating the rate of

* An estimate of the rate of exchange of S_1 at 81·6 °C may be obtained by using values of E_a and log A calculated from the data for (3b) (E_a = 28 ± 3 kcal, log A = 13·26).

exchange to be first order with respect to acetonitrile (see Table). Therefore S_1 must exchange *via* a rate determining dissociative step. Although the rate of exchange of S_2 in (9a) and (9b) is also first order with respect to acetonitrile it cannot be determined at this time if S_2 exchanges independently of S_1.†

Stereospecific exchange of acetonitrile in (3a) and (3b) is superficially identical to that in (9), *i.e.*, it is the S_1 set (that *trans* to the diene) which exchanges most rapidly with a half-life which is independent of the CD_3CN concentration in nitromethane. One significant difference, however, is that the half-life for exchange of S_2 is not independent of CD_3CN concentration (in CH_3NO_2 as a solvent). Therefore a bimolecular exchange mechanism may prevail. Since free diene may be formed under the conditions of S_2 exchange and nbd may in all cases be displaced completely from dicationic species, the mechanism of exchange of S_2, at least in part, could conceivably involve dissociation of one-half of the diene concurrent with approach of an acetonitrile ligand followed by loss of a *cis*-acetonitrile ligand and reco-ordination of the diene, *viz.*



On the other hand, the mechanism of exchange of S_1 in (3) must be closely similar to that for S_1 in (3) (9).

Based on the exchange rate data in the Table it is possible to construct a short kinetic *trans*-effect series for exchange of S_1 *trans* to L–L in the complexes, $[Ru(L–L)(S_2)_2(S_1)_2]^{2+}$: L–L = diars > nbd > cod > bipy > phen > 2-CH_3CN. ‡ This series applies strictly to CH_3CN exchange though there may be broader implications, *i.e.*, the reaction of $[Ru(nbd)(CH_3CN)_4]^{2+}$ with 2,2′-bipyridyl yielded *trans*-$[Ru(nbd)(bipy)(CH_3CN)_2]^{2+}$ while the reaction with diars yielded only *trans*-$[Ru(diars)_2(CH_3CN)_2]^{2+}$. Norbornadiene in the unknown *trans*-$[Ru(nbd)(diars)(CH_3CN)_2]^{2+}$ must be extremely labile.

Interpretation of exchange in (8a—c) is more difficult for two reasons: (i) an exchange mechanism involving the diene is viable; and (ii) the stereochemical identity of the most labile CH_3CN ligand is unknown. On the other hand, (8d—f) are comparatively simple since (i) the exchanging ligands are known to be mutually *trans* and (ii) exchange *via* a diene arm-off mechanism (*vide supra*) is forbidden § in agreement with the finding that exchange in (8f) is first order with respect to acetonitrile. It should also be noted in this context that nbd displacement from (8d) and (8e) by CD_3CN to form (9a) and (9b) respectively occurs without significant exchange of the mutually *trans* acetonitrile ligands.

Interpretation of exchange in (2) is further complicated by the possibility of π-allyl ⇄ σ-allyl behaviour. However, the exchange process and any possible dynamic allyl behaviour appear to be distinct as shown by heating an n.m.r. sample of (2a) in CH_3NO_2 in the presence of two moles of CH_3CN. At room temperature the co-ordinated acetonitrile resonances occur at τ 7·49 and 7·87, the free acetonitrile resonance at τ 8·07. The τ 7·49 and 8·07 peaks are significantly broadened even at 30 °C. They are near the coalescence point at 80 °C. The 7·87 peak is also significantly broadened at 80 °C. During this interval the *syn* and two *anti* allyl proton resonances at τ 6·85, 7·01, and 8·27 respectively remain unchanged. The factors contributing to the extremely rapid rate of ligand exchange in (2a) (and in its cod analogue ¶) are presently unknown.

The significantly less ready exchange in (2b) is in keeping with the general tendency of Os^{II} complexes to be kinetically more inert than the Ru^{II} analogues.

It would of course be desirable to know in detail the mechanism of the exchange process described here, especially in those instances where possible formation of a five-co-ordinate intermediate is indicated. Five-co-ordinate d^6 species have been postulated many times in CO exchange [7] or ligand substitution [8] reactions. However, it cannot be stated *a priori* that such a species will adopt a geometry which is best described as a trigonal bipyramid or a tetragonal pyramid, rather than one which could better be described as a distorted octahedron with a ' vacant ' co-ordination site.[9] ‖ Although

† It is possible stereospecifically to label a $[Ru(L–L)(S_2)_2(Si^*)_2]^{2+}$ species (* implies CD_3CN) to the extent of about 85% for L–L = bipy. If no significant S_1/S_2 scrambling were to occur upon heating this species in an inert solvent for a time equal to or greater than that for the half-life of S_2 exchange, then S_1 and S_2 would exchange independently by dissociative steps to yield different intermediates. Unfortunately, the only available solvent (nitromethane) is not co-ordinatively inert, a fact which undoubtedly contributed to decomposition of the labelled complex in the above experiment. Concomitant S_1/S_2 exchange was observed but no conclusions could be drawn.

‡ The exchange of acetonitrile in $[Ru(CH_3CN)_6]^{3+}$ is extremely slow ($t_{\frac{1}{2}}$ = 5 to 6 days at 81·6 °C).

§ The S entering at one of the diene's two co-ordination positions (thereby creating a monodentate diene) can never be equivalent to either of the two initially mutually *trans*-co-ordinated acetonitrile ligands in the absence of intramolecular rearrangement.

¶ Essentially complete exchange takes place in $[Ru(cod)(\pi\text{-}C_3H_5)(CH_3CN_2)]^+$ within the time needed to prepare the sample and run the spectrum (*ca.* 1 min).

‖ Structural determinations of several isolable five-co-ordinate ruthenium(II) species have been done: $RuI_2(CH_3)(PPh_3)_2$ (ref. 9a), $RuCl_2(PPh_3)_3$ (ref. 9c), $RuH(CO)(PPh_3)_3$ (ref. 9d), and $RuHCl(PPh_3)_3$ (ref. 9b). It is clear that under some circumstances the geometry is reasonably well defined, *e.g.* a square pyramid for $RhI_2(CH_3)(PPh_3)_2$ (ref. 9a). Steric considerations associated with the bulky PPh_3 molecule probably play a significant role in most, if not all, of these cases.

[7] R. K. Pomeroy, R. S. Gay, G. O. Evans, and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1972, **94**, 272 and references therein.

[8] M. L. Tobe, *Stud. Chem. Struc. Reactiv.*, 1966, 215.

[9] (*a*) P. G. H. Troughton and A. C. Skapski, *Chem. Comm.*, 1968, 575, and (*b*) 1230; (*c*) S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778; (*d*) *J. Amer. Chem. Soc.*, 1963, **85**, 3501.

the stereospecific exchange process observed here is unusual, the difficulties encountered in attempting to relate the mechanism and the steric course of exchange (or substitution) in other octahedral systems do not appear to have been overcome. We therefore feel that further elaboration is not justified at this time.

EXPERIMENTAL

The preparations of $[Ru(7\text{-Phnbd})Cl_2]_x$ and $[Ru(cot)Cl_2]_x$ were analogous to the published procedures for $[Ru(nbd)Cl_2]_x$[10] and $[Ru(cod)Cl_2]_x$.[11] $[Os(cod)Cl_2]_x$[12] was prepared by an improved procedure (*vide infra*). 7-Phenylnorbornadiene was prepared as described in the literature.[13] 5-Methyl-1,10-phenanthroline was purchased from K & K.

Microanalyses were performed at the University Chemical Laboratory, Cambridge. I.r. spectra were measured on a Perkin-Elmer 327 spectrometer calibrated with carbon monoxide. N.m.r. spectra were obtained with a Varian HA 100 instrument operating at 29 °C unless otherwise specified.

In the procedures below nbd = bicyclo[2.2.1]hepta-2,5-diene (norbornadiene), cod = cyclo-octa-1,5-diene, cot = cyclo-octa-1,3,5,7-tetraene, acac = pentane-2,4-dionato-anion (acetylacetonate), diars = *o*-phenylenebisdimethylarsine, bipy = 2,2′-bipyridyl, phen = *o*-phenanthroline. The allyl group is understood to be bonded in a π-fashion without being so stated in the formulae. ^{1}H N.m.r. shifts are given in units of τ *versus* an internal tetramethylsilane reference and i.r. frequencies in units of reciprocal centimeters (±2 cm^{-1}).

(a) *Preparation of* $Ru(nbd)(C_3H_5)_2$.—$[Ru(nbd)Cl_2]_x$ (1·0 g) in dry diethyl ether (50 ml) was treated with allyl magnesium chloride (25 ml, *ca.* 0·5M in diethyl ether) and stirred for 12 h. The suspension was filtered, cooled to 0 °C, and hydrolysed with water (40 ml cooled to 0 °C). The ether layer was separated and combined with further washings, dried ($CaCl_2$), and reduced on a rotary evaporator to a syrup, then at 0·05 mmHg for 10 min to a gum. The dark gum was dissolved in *ca.* 3 ml pentane and passed through a 1 × 6 cm neutral alumina column (6% water) with n-pentane (15 ml) as eluant to yield a faintly yellow solution. The solvent was removed *in vacuo* (0·05 mmHg) to yield a waxy ivory solid; yield 790 mg (76%) (Found: C, 57·5; H, 6·55. Calc. for $C_{13}H_{18}Ru$: C, 56·7; H, 6·6%). The parent peak in the mass spectrum occurred at 276 (^{102}Ru most intense). ^{1}H N.m.r. (τ) (C_6D_6): nbd, 5·90 (m, 2, olefin), 6·53 (m, 2, methine), 8·66 (m, 2, olefin), 8·80 (t, 2, *J ca.* 2, methylene); C_3H_5, 6·7—7·2 (overlap, 2, central), 6·30 (m, 2, syn), 6·92 (overlap, 2, anti), 8·35 (m, 2, syn′), 10·10 (m, 2, anti′). In the classification of n.m.r. data, syn refers to the C_1 proton *cis* to the central (C_2) proton or methyl group and syn′ similarly to the C_3 proton.

(b) *Preparation of* $Ru(nbd)\{CH_2C(CH_3)CH_2\}_2$.—Procedure analogous to (a). ^{1}H N.m.r. (τ) (C_6D_6): nbd, 5·73 (m, 2, olefin), 6·51 (overlap, 2, methine), 8·75 (m, 2, olefin), 8·86 (t, 2, *J ca.* 2, methylene); $CH_2C(CH_3)CH_2$, 6·28 (br s, 2, syn), 6·56 (br s, 2, anti), 8·34 (s, 6, CH_3), 8·45 (br s, 2, syn′), 9·82 (br s, 2, anti′).

(c) *Preparation of* $Ru(nbd)\{(CH_3)CHCHCH_2\}_2$.—The procedure analogous to (a) gave a colourless oil (Found: C, 60·3; H, 7·3. Calc. for $C_{15}H_{22}Ru$: C, 59·35; H, 7·3%) mass spec.: *m/e* 304 (^{102}Ru most intense). The ^{1}H n.m.r. spectrum was not readily interpretable.

(d) *Preparation of* $Ru(cod)(C_3H_5)_2$.—Procedure analogous to (a). ^{1}H N.m.r. (τ) (C_6D_6): cod, 5·99 (m, 2, olefin), 7·14 (m, 4, methylene), 7·8—8·5 (m, 4, methylene), 8·65 (m, 2, olefin); C_3H_5, 6·73 (m, 2, central), 6·30 (dd, 2, *J ca.* 7 and 2, syn), 7·38 (d, 2, *J ca.* 12, anti), *ca.* 8·2 (overlap, 2, syn′), **10·02** (d, 2, *J ca.* 11, anti′).

(e) *Preparation of* $Ru(cod)\{CH_2C(CH_3)CH_2\}_2$.—The procedure is analogous to (a) except benzene is used in place of n-pentane. ^{1}H N.m.r. (τ) (C_6D_6): cod, 6·05 (m, 2, olefin), 6·9—7·5 (m, 4, methylene), 7·9—8·6 (m, 4, methylene), 8·85 (m, 2, olefin); $CH_2C(CH_3)CH_2$, 6·51 (slight d, 2, *J* 1—2, syn), 7·16 (br s, 2, anti), 8·31 (s, 6, CH_3), 8·45 (br s, 2 syn′), 9·82 (br s, 2, anti′).

(f) *Preparation of* $Ru(7\text{-Phnbd})\{CH_2C(CH_3)CH_2\}_2$.—Procedure analogous to (a). ^{1}H N.m.r. (τ) (C_6D_6): 7-Phnbd (except Ph), 5·68, 5·96, 8·70, and 8·95 (each m, 1, olefin), *ca.* 6·3 (overlap, 2, methine), 7·12 (s, 1, bridging methine); $CH_2C(CH_3)CH_2$, *ca.* 6·3 [overlap, 2, syn(1) and syn(2)], 6·52 [s, 1, anti(1)], 6·58 [s, 1, anti(2)], 8·34 [s, 6, CH_3(1) and CH_3(2) coincident], *ca.* 8·4 [overlap, 1, syn′(1)], 8·46 [s, 1, syn′(2)], 9·80 [s, 1, anti′(1)], 9·85 [s, 1, anti′(2)]. The labels (1) and (2) refer to protons which are equivalent in the $Ru(nbd)(C_3H_5)_2$ species but are non-equivalent in the corresponding 7-Phnbd complex due to the presence of the phenyl group.

(g) *Preparation of* $Ru(cot)(C_3H_5)_2$.—Procedure analogous to (a). ^{1}H N.m.r. (τ) (C_6D_6): cot, 3·70 (dd, 2, *J ca.* 7·5 and 3), 4·17 (dd, 2, *J ca.* 7·5 and 3), 5·62 (dd, 2, *J ca.* 8 and 3), 8·53 (dd, 2, *J ca.* 8 and 3) with coupling sequence 3·70—(7·5)—4·17—(3)—8·53—(8)—5·62—(3)—3·70 and uncertain assignment; C_3H_5, 6·6—7·3 (m, 2, central), *ca.* 5·7 (overlap, 2, syn), *ca.* 6·9 (overlap, 2, anti), 8·13 (br d, 2, *J ca.* 6, syn′), 10·02 (d, 2, *J ca.* 11, anti′).

(h) *Preparation of* $[Os(cod)Cl_2]_x$.—OsO_4 (2·37 g) was warmed in a mixture of concentrated HCl (10 ml) and isoamyl alcohol (50 ml) for 10 min on a steam bath. Cycloocta-1,5-diene (5 ml) was added and the mixture was then distilled at 1 atm. until the temperature above the solution reached *ca.* 120 °C. At this point product formation was rapid and complete in *ca.* 15 min. The yellow-brown polymer was filtered off, washed with ethanol and diethyl ether, and vacuum dried; yield 3·1 g (90%).

(i) *Preparation of* $Os(cod)(C_3H_5)_2$.—The procedure is analogous to (a) except reaction times of 24 h are needed (Found: C, 44·65; H, 5·45. Calc. for $C_{14}H_{22}Os$: C, 44·2; H, 5·85%). ^{1}H N.m.r. (τ) (C_6D_6): cod, 6·19 (m, 2, olefin), 6·6—8·6 (series of overlapping multiplets, 8, methylene), 8·80 (m, 2, olefin); C_3H_5, *ca.* 7·0 (overlap, 2, central), 6·37 (dd, 2, *J ca.* 7 and 2, syn), 7·25 (overlap, 2, anti), 8·02 (br d, 2, *J ca.* 5, syn′), 9·81 (d, 2, *J ca.* 10, anti′).

(j) *Preparation of* $Os(cod)\{CH_2C(CH_3)CH_2\}_2$.—Procedure analogous to (i). ^{1}H N.m.r. (τ) (C_6D_6): cod, 6·29 (m, 2, olefin), 8·97 (m, 2, olefin), 6·7—8·8 (series of overlapping multiplets, 8, methylene); $CH_2C(CH_3)CH_2$, 6·53 (br s, 2, syn), 7·06 (br s, 2, anti), 8·10 (br s, 2, syn′), 8·18 (s, 6, CH_3), 9·70 (br s, 2, anti′).

(k) *Preparation of* cis-$[Ru(nbd)(C_3H_5)(CH_3CN)_2]^+BF_4^-$.—$Ru(nbd)(C_3H_5)_2$ (700 mg) in acetonitrile (320 mg) and di-

[10] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3178.
[11] M. A. Bennett and G. Wilkinson, *Chem. and Ind.*, 1959, 1516.
[12] G. Winkhaus, H. Singer, and M. Kricke, *Z. Naturforsch.*, 1966, **21b**, 1109.
[13] P. R. Story and S. R. Fahrenholtz, *J. Org. Chem.*, 1963, **28**, 1716.

chloromethane (4 ml) was treated slowly with trityl tetrafluoroborate (840 mg) to yield a yellow solution. Stepwise addition of a large excess of diethyl ether yielded yellow crystals of the product which were filtered off, washed with diethyl ether, and air dried; yield 930 mg (91%). An analytical sample was obtained as pale yellow needles by recrystallization from acetonitrile with diethyl ether (Found: C, 41·65; H, 4·55; N, 7·30. Calc. for $C_{14}H_{19}BF_4N_2Ru$: C, 41·7; H, 4·75; N, 6·95%). I.r. spectrum (Nujol): 2325w, 2300w cm^{-1} [ν(C≡N)]. ^1H N.m.r. (τ) (CD_3CN): nbd, 5·82 (m, 2, olefin), 6·12 (overlap, 1, olefin), 6·40 (br m, 2, methine), 7·70 (t, 1, *J ca.* 4, olefin), 8·66 (AB quartet, 2, methylene); C_3H_5, 4·90 (m, 1, central), 6·25 (dd, 1, *J ca.* 8 and 2, syn), 6·82 (dt 1, *J ca.* 8 and 2, syn'), 6·99 (dd, 1, *J ca.* 10 and 2, anti), 8·26 (d, 1, *J ca.* 12, anti'); CH_3CN (s, 3) at 7·49 and 7·90 (−30 °C), 7·40 and 7·76 at 29 °C in CD_2Cl_2.

The filtrate was reduced *in vacuo* to an oil (773 mg) which was dissolved in ethanol (3 ml). Crystals of $Ph_3CCH_2CH{=}CH_2$ formed rapidly and were filtered off and dried *in vacuo*; yield 440 mg (61%) (Found: C, 93·2; H, 7·15. Calc. for $C_{22}H_{20}$: C, 92·95; H, 7·1%). ^1H N.m.r. (τ) (except Ph in $CDCl_3$) 6·80 (dt, 2, *J ca.* 6 and 1, CH_2), 4·0—4·6 (m, 1, =CH−), 4·8—5·2 (m, 2, $=CH_2$).

(l) *Preparation of* cis-$[Ru(cod)(C_3H_5)(CH_3CN)_2]^+BF_4^-$.—The procedure is analogous to (k) employing 890 mg $Ru(cod)(C_3H_5)_2$, 736 mg acetonitrile, 4 ml dichloromethane, and 1·00 g trityl tetrafluoroborate; yield 900 mg (Found: C, 43·15; H, 4·95; N, 5·05. Calc. for $C_{15}H_{23}BF_4N_2Ru$: C, 43·0; H, 5·55; N, 6·7%). I.r. spectrum (Nujol): 2317w, 2289w cm^{-1} [ν(C≡N)].

(m) *Preparation of* cis-$[Ru(nbd)\{(CH_3)CHCHCH_2\}(CH_3CN)_2]^+BF_4^-$.—The procedure is analogous to (k) employing 87 mg $Ru(nbd)\{(CH_3)CHCHCH_2\}_2$, 33 mg acetonitrile, 1 ml dichloromethane, and 95 mg trityl tetrafluoroborate; yield 101 mg (85%) (Found: C, 43·3; H, 5·1; N, 7·55. Calc. for $C_{15}H_{21}BF_4N_2Ru$: C, 43·2; H, 5·8; N, 6·7%).

The filtrate was taken to dryness. An n.m.r. spectrum of the residue ($CDCl_3$) was consistent with the production of $Ph_3CCH_2CH{=}CH(CH_3)$ (isomer unknown). No evidence for $Ph_3CCH(CH_3)CH{=}CH_2$ could be found.

(n) *Preparation of* cis-$[Os(cod)(C_3H_5)(CH_3CN)_2]^+BF_4^-$.—$Os(cod)(C_3H_5)_2$ (191 mg) in dichloromethane (2 ml) and acetonitrile (0·5 ml) was treated with trityl tetrafluoroborate (166 mg) and allowed to stand for 5 min. Diethyl ether was added slowly to yield a dirty yellow microcrystalline product which was filtered off immediately, washed with diethyl ether, and vacuum dried; yield 135 mg. The initial filtrate produced additional white product (75 mg) upon standing for 1 h (Found: C, 35·4; H, 4·4; N, 5·55. Calc. for $C_{15}H_{23}BF_4N_2Os$: C, 35·45; H, 4·55; N, 5·5%). ^1H N.m.r. (τ) (CD_3CN); only the central allyl proton at 4·7—5·1 and the CH_3CN resonances at 7·39 and 7·63 could be positively identified.

(o) *Preparation of* $[Ru(nbd)(C_3H_5)(bipy)]^+BF_4^-,CH_2Cl_2$.—2,2′-Bipyridyl (77 mg) was slowly added to $[Ru(nbd)(C_3H_5)(CH_3CN)_2]^+$ (200 mg) in ethanol (20 ml) to yield a yellow solution and a pale yellow precipitate. Sufficient dichloromethane was added to dissolve the precipitate. The solution was filtered and reduced in volume on a rotary evaporator to *ca.* 10 ml. Slow stepwise addition of diethyl ether (8 ml) induced crystallization of yellow plates which were filtered off, washed with diethyl ether, and dried *in vacuo*; yield 190 mg (80%). Approximately one mole of dichloromethane is present as solvent of crystallization as shown by n.m.r. (Found: C, 45·25; H, 4·4; N, 5·4. Calc. for $RuC_{21}H_{23}BCl_2F_4N_2Ru$: C, 44·85; H, 4·1; N, 5·0%). ^1H N.m.r. (τ) (CD_2Cl_2): nbd, 5·96 (m, 2, olefin protons on different C=C), 6·14 (m, 2, methine), 7·19 and 7·30 (each a t, 1, *J ca.* 4, olefin), 8·50 (poor t, 2, methylene); C_3H_5, 5·55 (m, 1, central), 6·4—6·9 (m, 3, two syn and one anti), 8·17 (d, 1, *J ca.* 12, anti′); bipy, 0·33 (d, 1, *J ca.* 6), 1·3—1·9 (m, 4), 1·98 (t, 1, *J ca.* 8), 2·18 (t, 1, *J ca.* 6), 2·51 (t, 1, *J ca.* 6).

(p) *Preparation of* $[Ru(cod)(C_3H_5)(bipy)]^+BF_4^-,\frac{1}{2}CH_2Cl_2$.—$[Ru(cod)(C_3H_5)(CH_3CN)_2]^+BF_4^-$ (895 mg) in ethanol (10 ml) was treated (with vigorous stirring) with bipy (487 mg) to yield first partial dissolution, then precipitation of a flocculent golden solid. Dichloromethane was added till all the solid dissolved. The orange solution was reduced in volume on a rotary evaporator with steam heat till crystallization just began. The solution was set aside for 1 h when canary-yellow crystals (824 mg, 79%) were filtered off, and vacuum dried. Approximately one-half mole of dichloromethane is present as solvent of crystallization as shown by n.m.r. (Found: C, 48·8; H, 5·05; N, 5·45. Calc. for $C_{21.5}H_{26}BClF_4N_2Ru$: C, 48·2; H, 5·0; N, 5·25%). ^1H N.m.r. (τ) (CD_2Cl_2): cod, 5·91 (br m, 1, olefin), *ca.* 6·3 (overlap, 1, olefin), 7·0—8·2 (2 olefin and 8 methylene); C_3H_5, 5·05—5·60 (m, 1, central), *ca.* 6·3 (overlap, 1, syn), 6·72 (dd, 1, *J ca.* 8 and 1, syn′), 7·05 (dd, 1, *J ca.* 11 and 4, anti), *ca.* 7·8 (overlap, 1, anti′); bipy, 0·38 (d, 1, *J ca.* 6), 1·3—2·6 (7).

(q) *Preparation of* $[Ru(nbd)(C_3H_5)(phen)]^+BF_4^-$.—$[Ru(nbd)(C_3H_5)(CH_3CN)_2]^+BF_4^-$ (403 mg) in acetone (30 ml) was treated with *o*-phenanthroline hydrate (198 mg). The volume was reduced to *ca.* 10 ml and tetrahydrofuran (*ca.* 10 ml) added. Yellow-green crystals formed upon slow removal of acetone *in vacuo*; yield 400 mg. The product could not be obtained in a pure state. Its formulation is indicated by analogy with the corresponding 2,2′-bipyridyl complex and by its conversion to *cis* and *trans*-$[Ru(nbd)(phen)(CH_3CN)_2]^{2+}(BF_4^-)_2$ (*vide infra*).

(r) *Preparation of* $[Ru(nbd)(C_3H_5)(diars)]^+BF_4^-$.—$[Ru(nbd)(C_3H_5)(CH_3CN)_2]^+BF_4^-$ (264 mg) in dichloromethane (4 ml) was treated with diars (187 mg) in tetrahydrofuran (4 ml) under nitrogen. The dichloromethane was removed on a rotary evaporator. Diethyl ether was added in small amounts periodically over a period of 5 h. Cream-coloured microcrystals slowly formed during this time. The product was isolated by filtration, washed liberally with diethyl ether, and air and vacuum dried; yield 345 mg (87%). The last traces of free diars were removed by recrystallization in a similar manner (Found: C, 39·6; H, 5·35. Calc. for $C_{20}H_{29}As_2BF_4Ru$: C, 39·55; H, 4·8%). ^1H N.m.r. (τ) (CD_2Cl_2): nbd, 5·51, 5·90, 7·13, and 7·59 (each a t, 1, *J ca.* 4, olefin), 6·18 and 6·35 (each a br s, 1, methine), 8·67 (br, s, 2, methylene), coupling 5·90 ◄► 6·18 ◄► 7·13, 5·51 ◄► 7·13, 5·90 ◄► 7·59; C_3H_5, 5·5—5·9 (m, 1, central), 7·25 [dd, 1, *J ca.* 7 and 2, syn(?)]; the location of other allyl protons is uncertain; diars 7·78, 8·03, 8·53, and 9·04 (each a s, 3, CH_3), 1·8—2·6 (4, phenyl).

(s) *Preparation of* $[Os(cod)(C_3H_5)(bipy)]^+BF_4^-$.—$[Os(cod)(C_3H_5)(CH_3CN)_2]^+BF_4^-$ (35 mg) in dichloromethane (1 ml) was treated with 2,2′-bipyridyl (11 mg). Examination by n.m.r. indicated the reaction to be complete only after standing for 1 day. Ethanol (2 ml) was added and the volume reduced by bubbling nitrogen through the solution. Golden crystals formed which were filtered off, washed with

diethyl ether, and vacuum dried; yield 15 mg (Found: C, 42·9; H, 4·3; N, 4·5. Calc. for $C_{21}H_{25}BF_4N_2Os$: C, 43·3; H, 4·35; N, 4·8%).

(t) *Preparation of* cis- *and* trans-$[Ru(nbd)(bipy)(CH_3CN)_2]^{2+}(BF_4^-)_2$.—A mixture of $[Ru(nbd)(C_3H_5)(bipy)]^+BF_4^-$ (553 mg), acetonitrile (200 mg), trityl tetrafluoroborate (500 mg, *ca.* 1·3 mol), and dichloromethane (2 ml) was allowed to stand for 3 days. The yellow crystalline solid was filtered off and washed with methanol and diethyl ether; yield 400 mg. Addition of diethyl ether (10 ml) to the filtrate and allowing to stand for 10 min gave additional product (120 mg). The 400 mg sample is primarily the *trans*-form, the 120 mg sample *ca.* 50% *cis* (Found: C, 41·4; H, 3·4; N, 9·4. Calc. for $C_{21}H_{22}B_2F_8N_4Ru$ (mixture of isomers): C, 41·7; H, 3·65; N, 9·25%). Recrystallization of the former from acetonitrile (1·5 ml) with methanol (2 ml) and diethyl ether (2 ml) yielded the pure *trans* isomer (150 mg) as pale yellow plates. I.r. spectrum (Nujol): 2327w, 2303w cm^{-1} [ν(C≡N)]. ^1H N.m.r. (τ) (CD_3CN); 1·4—2·4 (8, bipy), 4·38 (t, 4, *J ca.* 3, olefin), 5·91 (br s, 2, methine), 7·76 (s, 6, CH_3CN), 8·28 (t, 2, *J ca.* 2, methylene).

An alternative preparation of the *trans*-form involves the stoicheiometric reaction of 2,2′-bipyridyl (30 mg) with $[Ru(nbd)(CH_3CN)_4]^{2+}(ClO_4^-)_2$ [see (z)] (100 mg) in nitromethane for 24 h at room temperature. Pure *trans*-$[Ru(nbd)(bipy)(CH_3CN)_2]^{2+}(ClO_4^-)_2$ (47 mg) crystallized upon addition of diethyl ether.

Preparation of small quantities of the pure *cis*-form was sometimes successful by very slow fractional crystallization from dichloromethane–acetonitrile mixtures. ^1H N.m.r. (τ) (CD_3CN): nbd, 4·25, 4·39, 4·92, and 5·82 (each a t, 1, *J ca.* 4, olefin), 5·91 and 6·00 (each a br s, 1, methine), 8·34 (AB quartet, 2, methylene); 7·14 and 7·91 (each a s, 3, CH_3CN); bipy, 0·37 (d, 1, *J ca.* 6), 0·92 (d, 1, *J ca.* 6), 1·3—2·4 (6). Decoupling experiments indicated the relative positions of the nbd methine and olefin protons to be the following (moving round the six membered ring using the chemical shift as a label): 5·91, 4·92, 5·82, 6·00, 4·39, 4·25.

(u) *Preparation of* trans-$[Ru(cod)(bipy)(CH_3CN)_2]^{2+}(BF_4^-)_2$.—$[Ru(cod)(C_3H_5)(bipy)]^+BF_4^-$ (400 mg) in dichloromethane (3 ml) containing acetonitrile (150 mg) was treated with trityl tetrafluoroborate (300 mg, 1·1 mol). After being set aside for 1 day yellow plates were filtered off, washed with dichloromethane, and air and vacuum dried; yield 366 mg (73%) (Found: C, 42·2; H, 4·15; N, 9·35. Calc. for $C_{22}H_{26}B_2F_8N_4Ru$: C, 42·55; H, 4·2; N, 9·0%). ^1H N.m.r. (τ) (CD_3CN), 1·3—2·4 (8, bipy), 4·89 (br, 4, olefin), 7·1—8·0 (m, 8, methylene), 7·78 (s, 6, CH_3CN).

(v) *Preparation of* cis *and* trans-$[Ru(nbd)(phen)(CH_3CN)_2]^{2+}(BF_4^-)_2$.—$[Ru(nbd)(C_3H_5)(phen)]^+BF_4^-$ (250 mg) plus acetonitrile (130 mg) in dichloromethane (2 ml) was treated with trityl tetrafluoroborate (300 mg) and set aside under nitrogen for 3 days. Methanol (1 ml) and diethyl ether (5 ml) were added and the sample set aside for 10 min to yield the product as fluffy yellow crystals (250 mg), approximately a 3 : 2 mixture of *cis*- and *trans*-forms. The *trans*-form may be isolated as for the bipyridyl analogue [see (t)] (Found: C, 44·1; H, 3·75; N, 9·05. Calc. for $C_{23}H_{22}B_2F_8N_4Ru$: C, 43·9; H, 3·55; N, 8·9%). I.r. spectrum (Nujol): 2331w, 2305w cm^{-1} [ν(C≡N)]. ^1H N.m.r. (τ) (CD_3CN); phenyl proton resonances (8), 4·19 (t, 4, *J ca.* 3, olefin), 5·81 (br s, 2, methine), 7·89 (s, 6, CH_3CN), 8·22 (t, 2, $J < 2$, methylene).

Isolation of the pure *cis*-isomer was not successful. However, its CH_3CN resonances at τ 7·11 and 7·93 could readily be distinguished from those of the *trans*-isomer in mixtures of *cis*- and *trans*-isomers.

(w) *Preparation of* cis-$[Ru(nbd)(diars)(CH_3CN)_2]^{2+}(BF_4^-)_2,CH_3CN$.—$[Ru(nbd)(C_3H_5)(diars)]^+BF_4^-$ (610 mg) plus acetonitrile (130 mg) in dichloromethane (2 ml) was treated with trityl tetrafluoroborate (500 mg) and set aside for 5 days under nitrogen. Methanol (2 ml) was added and the very pale yellow crystals filtered off, washed with methanol and diethyl ether, and vacuum dried; yield 575 mg (74%) (Found: C, 35·7; H, 4·0; N, 5·55. Calc. for $C_{23}H_{33}As_2B_2F_8N_3Ru$: C, 35·6; H, 4·3; N, 5·4%). I.r. spectrum (Nujol): 2321w, 2294w cm^{-1} [ν(C≡N)], 2252w cm^{-1} (free CH_3CN). ^1H N.m.r. (τ) (CD_3CN); 1·8—2·3 (4, diars), 4·47 (m, 2, olefin), 5·32 (t, 1, *J ca.* 4, olefin), 5·80 (br s, 1, methine), 5·99 (t, 1, *J ca.* 4, olefin), 6·26 (br s, 1, methine), 7·24 and 7·80 (each a s, 3, CH_3CN), 8·51 (narrow m, 2, methylene).

(x) *Preparation of* trans-$[Ru(diars)_2(CH_3CN)_2]^{2+}(ClO_4^-)_2$.—The attempted synthesis of *trans*-$[Ru(nbd)(diars)(CH_3CN)_2]^{2+}(ClO_4^-)_2$ *via* the stoicheiometric reaction of $[Ru(nbd)(CH_3CN)_4]^{2+}(ClO_4^-)_2$ (161 mg) with one mole of diars (83 mg) in nitromethane (2 ml) led to a 50 : 50 mixture of starting material and the title compound (by n.m.r.) after 1 day at room temperature. The addition of a second mole of diars took the reaction to completion after a second day. The product (177 mg, white needles) was isolated by addition of diethyl ether (Found: C, 30·4; H, 3·95; N, 3·2. Calc. for $C_{24}H_{38}As_4Cl_2N_2O_8Ru$: C, 30·35; H, 4·0; N, 2·95%). ^1H N.m.r. (τ) (CD_3CN); 1·8—2·0 and 2·2—2·3 (each a m, 4, diars), 8·00 (s, 6, CH_3CN), 8·16 (s, 24, diars CH_3).

(y) *Preparation of* $Ru(nbd)(C_3H_5)(acac)$.—Thallium acetylacetonate (181 mg) and $[Ru(nbd)(C_3H_5)(CH_3CN)_2]^+BF_4^-$ (240 mg) were stirred in acetone (10 ml) for 0·5 h. The greenish yellow solution was reduced to dryness, extracted with light petroleum (15 ml, 30—40 °C), filtered through kieselguhr, and reduced again *in vacuo* to a gold oil which solidified with vigorous scratching. Sublimation at 100 °C and 0·5 mmHg onto a cold finger cooled to −78 °C yielded a golden oil which again solidified when scratched; yield 166 mg (84%) (Found: C, 54·5; H, 6·2. Calc. for $C_{15}H_{20}O_2Ru$: C, 54·0; H, 6·05%). Mass spectrum: major (^{102}Ru) parent peak at 334. ^1H N.m.r. (τ) (C_6D_6): nbd, 5·87 (t, 1, *J ca.* 4, olefin), 6·05 (overlap, 1, olefin), 6·28 (overlap, 1, olefin), *ca.* 6·2 (br s, 1, methine), 6·62 (br s, 1, methine); 8·33 (t, 1, *J ca.* 4, olefin), 8·64 (AB quartet, 2, methylene); C_3H_5, 5·0—5·4 (m, 1, central), 6·38 (br d, 1, *J ca.* 8, syn), 6·79 (br d, 1, *J ca.* 8, syn′), 7·32 (br d, 1, *J ca.* 10, anti), 8·14 (d, 1, *J ca.* 12, anti′); acac, 4·94 (s, 1, CH), 8·00 (s, 3, CH_3), 8·44 (s, 3, CH_3).

(z) *Preparation of* $[Ru(nbd)(CH_3CN)_4]^{2+}(ClO_4^-)_2$.—A mixture of $Ru(nbd)\{CH_2C(CH_3)CH_2\}_2$ (380 mg), dichloromethane (2 ml), acetonitrile (1 ml), and $HClO_4$ (60%, 460 mg, 2·2 mol) (combined in that order) was warmed on a steam bath for 5 min and then cooled to room temperature. Stepwise addition of diethyl ether yielded yellow needles which were filtered off, washed with dichloromethane and diethyl ether, and dried *in vacuo*; yield 460 mg (66%) (Found: C, 32·4; H, 3·35; N, 10·0. Calc. for $C_{15}H_{20}Cl_2N_4O_8Ru$: C, 32·4; H, 3·65; N, 10·05%). I.r. spectrum (Nujol): 2328w, 2302w cm^{-1} [ν(C≡N)]. ^1H N.m.r. (τ) (CD_3CN); 4·60 (t, 4, *J ca.* 2·5, olefin), 6·02 (m, 2, methine), 7·28 and 7·57 (each a s, 6, CH_3CN), 8·42 (t, 2, *J* 1—2, methylene).

The corresponding tetrafluoroborate salt may be prepared employing tetrafluoroboric acid.

(aa) *Preparation of* $[Ru(7\text{-Phnbd})(CH_3CN)_4]^{2+}(ClO_4^-)_2$.—This species (55 mg, yellow needles) was prepared by a procedure analogous to (z) from $Ru(7\text{-Phnbd})\{CH_2C(CH_3)CH_2\}_2$ (50 mg) (Found: C, 39·95; H, 3·85; N, 9·05. Calc. for $C_{21}H_{24}Cl_2N_4O_8Ru$: C, 39·9; H, 3·85; N, 8·85%). ^1H N.m.r. (τ) (CD_3CN); 2·6—3·0 (5, phenyl), 4·55 and 4·80 (each a t, 2, *J ca.* 3, olefin), 5·62 (m, 2, bridgehead methine), 6·57 (br s, 1, bridging methine), 7·29 (s, 6, CH_3CN), 7·59 and 7·63 (each a s, 3, CH_3CN).

(bb) *Preparation of* $[Ru(cod)(CH_3CN)_4]^{2+}(ClO_4^-)_2$.—This preparation is analogous to (z) (Found: C, 33·25; H, 4·3; N, 10·05. Calc. for $C_{16}H_{24}Cl_2N_4O_8Ru$: C, 33·6; H, 4·25; N, 9·8%). I.r. spectrum (Nujol): 2330w, 2300w cm^{-1} [ν(C≡N)]. ^1H N.m.r. (τ) (CD_3CN); 5·28 (br s, 4, olefin), 7·2—8·0 (m, 8, methylene), 7·34 and 7·57 (each a s, 6, CH_3CN).

(cc) *Preparation of* $[Os(cod)(CH_3CN)_4]^{2+}(ClO_4^-)_2$.—$Os(cod)\{CH_2C(CH_3)CH_2\}_2$ (100 mg) in acetonitrile (1 ml) was treated with $HClO_4$ (60%, 100 mg, 2·4—2·5 mol). The initial reaction was not rapid and a wine-red solution was produced after standing overnight. Addition of diethyl ether yielded wine-coloured oils. The yellow solution above the oil was decanted and stood to yield colourless needles (*ca.* 10 mg). ^1H N.m.r. (τ) (CD_3CN); 5·33 (br s, 4, olefin), 7·2—8·0 (m, 8, methylene), 7·22 and 7·39 (each a s, 6, CH_3CN).

(dd) *Preparation of* $[Ru(bipy)(CH_3CN)_4]^{2+}(BF_4^-)_2$.—$[Ru(nbd)(bipy)(CH_3CN)_2]^{2+}(BF_4^-)_2$ (175 mg, a mixture of *cis*- and *trans*-forms) was heated in acetonitrile at *ca.* 80 °C for 48 h. The solution was filtered and diethyl ether added to yield the compound (150 mg) (Found: C, 36·1; H, 3·55; N, 14·0. Calc. for $C_{18}H_{20}B_2F_8N_6Ru$: C, 36·35; H, 3·4; N, 14·1%). I.r. spectrum (Nujol): 2327w, 2303w cm^{-1} [ν(C≡N)]. ^1H N.m.r. (τ) (CD_3CN); 0·90 (d, 2), 1·58 (d, 2), 1·86 (t, 2), 2·32 (t, 2), all with *J* 6—8 (bipy), 7·38 and 7·88 (each a s, 6, CH_3CN).

(ee) *Preparation of* $[Ru(phen)(CH_3CN)_4]^{2+}(BF_4^-)_2$.—$[Ru(nbd)(phen)(CH_3CN)_2]^{2+}(BF_4^-)_2$ (100 mg, a mixture of *cis* and *trans*) was heated in acetonitrile at *ca.* 80 °C for 24 h to yield free nbd (by n.m.r.) and the compound, isolated as fine yellow needles by addition of diethyl ether; yield 87 mg (89%) (Found: C, 38·35; H, 3·05; N, 13·15. Calc. for $C_{20}H_{20}B_2F_8N_6Ru$: C, 38·8; H, 3·25; N, 13·55%). ^1H N.m.r. (τ) (CD_3CN); 0·60 (dd, 2, *J ca.* 5 and 2), 1·30 (dd, 2, *J ca.* 8 and 2), and 1·7—2·1(4) due to phen, 7·32 and 7·99 (each a s, 6, CH_3CN).

(ff) *Preparation of* $[Ru(5\text{-Me-phen})(CH_3CN)_4]^{2+}(BF_4^-)_2$.—The route to this complex is identical to that for $[Ru(phen)(CH_3CN)_4]^{2+}$; yield 52% from $[Ru(nbd)(\pi\text{-}C_3H_5)(CH_3CN)_2]^+BF_4^-$ as canary-yellow crystals. ^1H N.m.r. (τ) (CD_3CN, 220 MHz); 0·58 (d, 1, *J* 5·4), 0·67 (d, 1, *J* 4·6), 1·21 (d, 1, *J* 8·5), 1·41 (d, 1, *J* 8·0), 1·99 (m, 3), and 7·12 (d, 3, *J* 1·0, methyl) due to phen, 7·310 (s, 3, CH_3CN), 7·315 (s, 3, CH_3CN), 7·97 (s, 6, CH_3CN).

(gg) *Preparation of* $[Ru(diars)(CH_3CN)_4]^{2+}(BF_4^-)_2$.—A solution of *cis*-$[Ru(nbd)(diars)(CH_3CN)_2]^{2+}$ (530 mg) in acetonitrile (5 ml) was refluxed for 48 h and taken to dryness at 0·05 mmHg. Sequential addition of dichloromethane (1 ml), methanol (1 ml), tetrahydrofuran (1 ml), and diethyl ether (4 ml) yielded the compound (460 mg) (Found: C, 29·5; H, 3·7; N, 7·9. Calc. for $C_{18}H_{26}As_2B_2F_8N_4Ru$: C, 29·9; H, 3·65; N, 7·75%). I.r. spectrum (Nujol): 2320w, 2290w cm^{-1} [ν(C≡N)]. ^1H N.m.r. (τ) (CD_3CN): 7·52 (s, 6, CH_3CN), 7·78 (s, 6, CH_3CN), 8·30 (s, 12, diars CH_3 groups); phenyl protons omitted.

(hh) *Preparation of* $[Ru(CH_3CN)_6]^{2+}(BF_4^-)_2$.—A solution of $[Ru(nbd)(CH_3CN)_4]^{2+}(BF_4^-)_2$ (70 mg) in acetonitrile (1 ml) was heated at *ca.* 80 °C for 24 h. An n.m.r. showed no starting material remaining. Slow, stepwise addition of diethyl ether caused formation of white flocculent microcrystals which were filtered off and air and vacuum dried; yield 55 mg (Found: C, 27·4; H, 3·5; N, 16·3. Calc. for $C_{12}H_{18}B_2F_8N_6Ru$: C, 27·65; H, 3·45; N, 16·1%). I.r. spectrum (Nujol): 2326w, 2300w cm^{-1} [ν(C≡N)]. ^1H N.m.r. (τ) (CD_3CN); 7·52(s).

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