Reactivity of Co-ordinated Ligands. Part XIV.[1] The Reactions of Some Cyclo-octa-1,3,5-triene Complexes of Cobalt(I), Rhodium(I), and Iridium(I)

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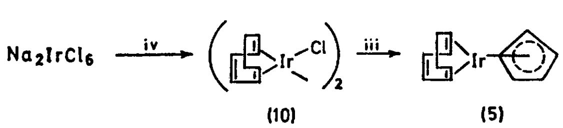
The cyclo-octa-1,3,5-triene (cotr) complexes [(cotr)MCl]$_2$, (cotr)M(π-cp) and (cotr)M(acac) (M = Rh^I or Ir^I) have been prepared and some of their reactions examined. Protonation of cotrM-(π-cp) (M = Co^I, Rh^I, or Ir^I) readily leads to cations of the type [(C$_8$H$_{11}$)M(π-cp)]$^+$. The C$_8$H$_{11}$$^+$ entity adopts a variety of bonding modes and interconversion between these various modes readily occurs. Kinetics of such interconversions for both the Rh^I and Ir^I cations have been followed by the change in their ^{1}H n.m.r. spectra with time. Possible mechanisms are discussed. Nucleophilic addition to these cations gives the expected neutral complexes of formula (C$_8$H$_{11}$Y)M(π-cp), the nature of these products depending on the reaction temperature employed. The rhodium complex, (C$_8$H$_{10}$)Rh(π-cp), does not react cleanly with any of the other electrophiles tried (AcCl–AlCl$_3$ or DMF–POCl$_3$).

CYCLIC DIENE COMPLEXES of palladium(II) and platinum(II) are susceptible to nucleophilic attack leading to σ-alkyl-π-olefin complexes.[2] In contrast, the corresponding complexes of iron(0) or ruthenium(0) favour electrophilic reactions. Thus, tricarbonyl(cyclo-octa-1,3,5-triene)iron(0) and tricarbonyl(cyclo-octatetraene)-M° (M = Fe, Ru, Os) are protonated in strong acid [3-5] whilst the iron complex undergoes Friedel–Crafts acetylation and Vilsmeir formylation.[6] The related π-cyclopentadiene complexes of cobalt(I), rhodium(I), and iridium(I) present an interesting intermediate case but have been studied less extensively. Hitherto the protonation of the corresponding cyclo-octa-1,3,5-triene-(π-cyclopentadiene)-cobalt(I) [3] and -rhodium(I) [4] complexes in concentrated sulphuric acid were thought to give unstable species. Recently, preliminary studies on the protonations of cyclo-octa-1,5-diene- and cyclo-octa-1,3,5-triene-(π-cyclopentadienyl)rhodium(I) in trifluoroacetic acid and by hexafluorophosphoric acid were published.[7] The isomerisations which occur in those systems have led to an extended study of the protonation of these and related complexes and here we report a study of the protonation of cyclo-octa-1,3,5-triene complexes of Co^I, Rh^I, and Ir^I.

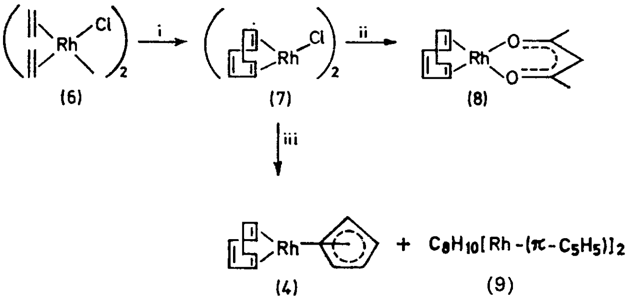
RESULTS

Prior to this investigation the only derivatives of cyclo-octa-1,3,5-triene known were (cyclo-octa-1,3,5-triene)-(π-cyclopentadienyl)cobalt(I) (1) and (bicyclo[4.2.0]octa-2,4-diene)(π-cyclopentadienyl)cobalt(I) (2). Here we describe convenient routes to the rhodium(I) complexes, [(C$_8$H$_{10}$)RhCl]$_2$ (7), (C$_8$H$_{10}$)Rh(acac) (8), and (C$_8$H$_{10}$)Rh(cp) (4) and the iridium(I) complexes [(C$_8$H$_{10}$)IrCl]$_2$ (10) and (C$_8$H$_{10}$)Ir(cp) (5). The routes employed are summarised in Schemes 1 and 2.

Treatment of di-μ-chloro-tetraethylenedirhodium(I) (6),[8] with cyclo-octa-1,3,5-triene in ether yielded the yellow crystalline product di-μ-chloro-bis(cyclo-octa-1,3,5-triene)-dirhodium(I) (7), in excellent yield. The related complexes (cyclo-octa-1,3,5-triene)(acetylacetonato)rhodium(I) (8) and cyclo-octa-1,3,5-triene)(π-cyclopentadienyl)rhodium(I) (4) were prepared from this chloro-bridged dimer by treatment of acetylacetonatothallium and cyclopentadienylthallium respectively. All gave good analytical data and on the basis of ^{1}H n.m.r. data it was established that the triene adopted the 1,2,5,6-π-mode of co-ordination in each case. The iridium complex di-μ-chloro-bis(cyclo-octa-1,3,5-triene)iridium(I) (10) was obtained by direct reaction of the ligand with sodium chloroiridate following the method of Winkhaus and Singer;[9] small yields (5%) of the π-cyclopentadienyl derivative (5) were obtained from (10) by treatment with Tl(cp). Although compound (10) is insufficiently soluble in solvents suitable to permit the measurement of a reliable ^{1}H n.m.r. spectrum, by



SCHEME 1



SCHEME 2 i, C$_8$H$_{10}$; ii, acetylacetonatothallium; iii, cyclopentadienylthallium; iv, C$_8$H$_{10}$, C$_2$H$_5$OH,H$_2$O

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[1] Part XIII, B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J.C.S. Dalton*, 1972, 2084.

[2] J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 1957, 2496, 3413.

[3] W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1963, 2162.

[4] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4821.

[5] M. Cooke, P. T. Draggett, M. Green, B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *Chem. Comm.*, 1971, 621.

[6] B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *J. Chem. Soc.* (*A*), 1971, 422.

[7] J. Evans, B. F. G. Johnson, and J. Lewis, *Chem. Comm.*, 1971, 1252.

[8] R. Cramer, *Inorg. Chem.*, 1962, **1**, 722; *J. Amer. Chem. Soc.*, 1964, **86**, 217.

[9] G. Winkaus and H. Singer, *Chem. Ber.*, 1966, **99**, 3610.

analogy with complex (7) a 1,2,5,6-η-mode of co-ordination may be assumed.

Protonation Studies.—*Cobalt*(I). (Bicyclo[4.2.0]octa-2,4-diene)(π-cyclopentadienyl)cobalt(I) (2) readily dissolves in trifluoroacetic acid to give a stable, red solution; treatment of complex (2) in Et_2O with HPF_6 produces an unstable red-brown salt of formulation $[C_8H_{11}Co(cp)]PF_6$. The ^1H n.m.r. spectrum of this salt in SO_2 is similar to that of (2) in CF_3CO_2H (Table 1) and may be interpreted in terms of the π-octadienyl cation (3). The hexafluorophosphate salt of this cation easily undergoes deprotonation on addition of triethylamine to yield the second isomeric form of (2) *viz.* (cyclo-octa-1,3,5-triene)(π-cyclopentadienyl)cobalt(I) (1). No evidence for the regeneration of (2) from this reaction was obtained. This behaviour is in marked contrast to that shown by the isoelectronic species (bicyclo[4.2.0]octa-2,4-diene)(tricarbonyl)iron(0), (11), which resists protonation under similar conditions. On the other hand proton

TABLE 1

N.m.r. data

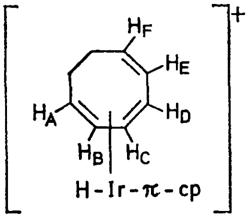
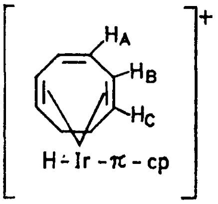
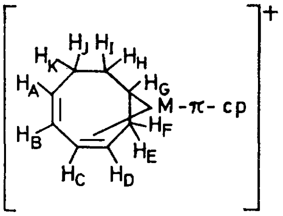
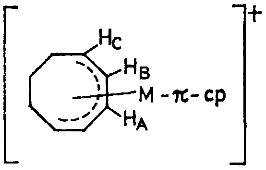
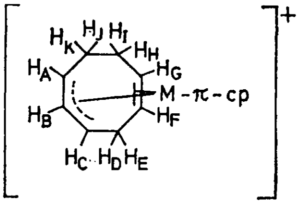
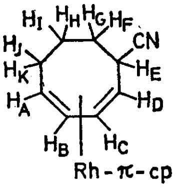
Compound	Proton	Chemical shift (τ)	Multiplicity
 (23) in CD_2Cl_2–CF_3CO_2H	$H_E + H_F$	4·18	d (*J* 6 Hz)
	$H_B + H_C$	4·7	m
	$H_A + H_D$	5·2	m
	methylenes	7·5	m
	cp	4·08	s
	Ir–H	20·8	s
 (22) in CD_2Cl_2–CF_3CO_2H	$2H_A$	3·72	s
	$2(H_B + H_C)$	6·1	m
	methylenes	8·0	m
	cp	4·10	s
	Ir–H	20·0	s
 (16) M = Rh In CF_3CO_2H Deuteriation of H_E	$H_A + H_B$	3·78	m
	H_D	5·35	m
	H_F	6·77	m
	H_E	6·96	dd
	H_C	7·40	m
	H_G	7·50	m
	H_{H-K}	7·9—8·3	m
	cp	4·13	s
(17) M = Ir in CF_3CO_2H Deuteriation of H_E	H_B	3·40	t (*J* 8 Hz)
	H_A	3·85	m
	H_C	4·43	t (*J* 8 Hz)
	H_D	5·1	m
	$H_F + H_G$	7·0	m
	H_E,H_H,H_I,H_J	7·9—8·2	m
	H_K	8·6	m
	cp	4·04	s
 (3) M = Co in CF_3CO_2H	H_A	2·75	m
	$2(H_B + H_C)$	4·84	assym.d.
	methylenes	8·2—8·7	m
	cp	4·44	s
(18) M = Rh in CF_3CO_2H	H_A	2·95	t (*J* 7 Hz)
	$2(H_B + H_C)$	4·6—4·9	m
	methylenes	7·8—8·6	m
	cp	4·16	s

TABLE 1 (*Continued*)

Compound	Proton	Chemical shift (τ)	Multiplicity
(19) M = Ir in CF_3CO_2H	H_A	2·76	t (J 6 Hz)
	$2(H_B + H_C)$	4·6—4·9	m
	methylenes	7·9—8·8	m
	cp	4·12	s
 (14) M = Co in $[^2H_6]$acetone	H_F	3·90	dd
	H_C	4·50	m
	H_G	5·42	t (*J* 8 Hz)
	H_B	6·24	dd
	H_A	6·8	m
	$H_E + H_{I(K)}$	6·8—7·2	m
	$H_H, H_J, H_{K(I)}$	7·8—8·2	m
	H_D	8·8	m
	cp	4·39	s
(20) M = Rh in CF_3CO_2H Deuteriation of H_E	H_F	*	*
	H_C	5·1	m
	H_G	5·4	t (*J* 8 Hz)
	H_B	6·20	dd
	H_A	6·8	m
	$H_E + H_{I(K)}$	6·8—7·2	m
	$H_H, H_J, H_{K(I)}, H_D$	*	*
	cp	4·25	s
(21) M = Ir in CF_3CO_2H Deuteriation of H_E	H_F	*	*
	H_C	5·2	m
	H_G	5·48	t (*J* 7 Hz)
	H_B	6·13	t
	H_A	6·6	m
	H_E	6·8	m
	H_{H-K}, H_D	*	*
	cp	4·20	s
 (24a) In $CDCl_3$	H_C	4·6	m
	H_B	5·10	t (*J* 8 Hz)
	H_D	5·55	t (*J* 8 Hz)
	H_E	5·76	m
	H_A	6·59	tt
	$H_J + H_K$	7·3—7·7	m
	H_{F-I}	7·8—8·5	m
	cp	4·83	s

* Masked by dienyl resonances, or ill defined.

TABLE 2

Kinetic data for reaction (16) ⟶ (18) + (20) at 29·5 °C in CF_3CO_2H

	Loss of (16)	Production of (18)	Production of (20)
$\Delta H^{\ddagger}$	23·7 ± 2 kcal mol^{-1}	22·7 ± 2 kcal mol^{-1}	26·3 ± 1·7 kcal mol^{-1}
$\Delta S^{\ddagger}$	+3·5 ± 6 cal K^{-1} mol^{-1}	−0·5 ± 6 cal K^{-1} mol^{-1}	+7·5 ± 5 cal K^{-1} mol^{-1}
k_H	2·19 ± 0·03 × 10^{-4} s^{-1}	1·64 ± 0·1 × 10^{-4} s^{-1}	0·55 ± 0·05 × 10^{-4} s^{-1}
k_D	1·20 ± 0·02 × 10^{-4} s^{-1}	0·51 ± 0·04 × 10^{-4} s^{-1}	0·71 ± 0·06 × 10^{-4} s^{-1}
k_H/k_{K_D}	1·8 ± 0·1	3·2 ± 0·5	0·8 ± 0·2
(4) In 1 : 1 D$^+$ and H$^+$	1·81 ± 0·04 × 10^{-4} s^{-1}	1·11 ± 0·08 × 10^{-4} s^{-1}	0·70 ± 0·06 × 10^{-4} s^{-1}

addition to (1) to produce the octadienyl ion (3) readily occurs and this behaviour closely parallels that exhibited by the corresponding complex of tricarbonyliron.*

No evidence for the formation of the 1,2,3,5,6-η-cobalt system, which is produced from the reaction of $Ph_3C^+BF_4^-$ with (cyclo-octa-1,5-diene)(π-cyclopentadienyl)cobalt(I) (14),[10] was obtained. The two isomeric forms of the $C_8H_{11}^+$ ligand prepared by the routes outlined above show markedly different chemical behaviour. Thus, whereas the ion (14) easily undergoes nucleophilic addition with for example CN^- to produce the 3-cyano-substituted diene complex, ion (3) is decomposed under the same reaction conditions and the dimer $(C_8H_{11})_2$ is produced. The same sort of behaviour is observed with the (cyclo-octadienyl)(tricarbonyl)iron cation which also reacts with CN^- to produce ultimately $(C_8H_{11})_2$. Reaction of complex (14)

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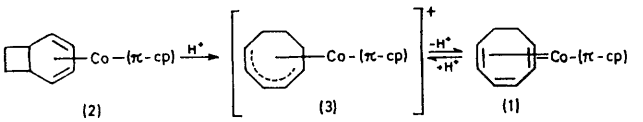
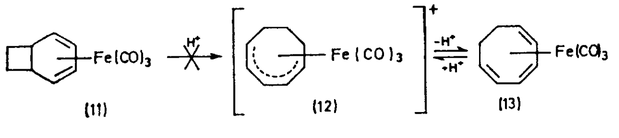
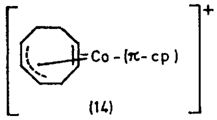
* This difference in behaviour of the two iron complexes (11) and (13) towards protonic acids provides a useful method of separation of the two isomers. Thus addition of HPF_6 to a solution of a mixture of (11) and (13) (always produced under the reaction conditions employed) in ether precipitates the salt (12) but complex (11) remains in solution. Complex (13) may be regenerated by treatment with Et_3N.

[10] J. Lewis and A. W. Parkins, *J. Chem. Soc.* (*A*), 1967, 1150; 1969, 422.

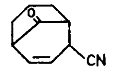
with CN$^-$ follows a different course if carried out in the presence of carbon monoxide. In this case the product is considered to be the transannular ketone (15). Presumably the initial attack by the CN$^-$ occurs such that a







(14)



(15)

σ-π-allyl complex is produced followed by insertion of CO in the metal–carbon bond yielding ultimately the ketone (15).

The 1,2,3,5,6-η-(cyclo-octadienyl)(π-cyclopentadienyl)-cobalt cation does not undergo deprotonation to produce any identifiable species again emphasising the marked dissimilarity in the reactivity of the two isomeric forms of the C_8H_{11} grouping.

Rhodium(I) *and iridium*(I). Of the three rhodium complexes studied only one was successfully protonated. The chloride-bridged dimer, (7), does not dissolve in trifluoroacetic acid, and the acetylacetonate (8), which does dissolve to give initially a red solution, rapidly decomposes. This latter behaviour is similar to that observed when similar β-diketonato-complexes are treated with trityl tetrafluoroborate.[11]

(Cyclo-octa-1,3,5-triene)(π-cyclopentadienyl)rhodium(I), (4), readily forms an air-stable, yellow salt $[C_8H_{11}Rh(\pi\text{-}C_5H_5)]PF_6$ with hexafluorophosphoric acid, and also forms a red solution in trifluoroacetic acid. The n.m.r. spectrum of the CF_3CO_2H solution initially is that of a structure (16), a 1,3,4-η-bonded system. This complex isomerises to a mixture of an octadienyl (18) and an allyl-olefin complex (20) ($t_{\frac{1}{2}}$ *ca.* 45 min at 29·5 °C), in a ratio of 3 : 1. The salt precipitated from ethereal solution at room temperature is approximately of this latter composition. However, when this precipitation is performed at −10 °C, the n.m.r. spectrum of the salt in liquid SO_2 run *ca.* 24 h after preparation is of the composition *ca.* 50% σ–π-olefin, with *ca.* 30% dienyl and *ca.* 20% allyl-olefin metal complex. When the spectrum is recorded of a freshly prepared solution, made up from a 4-day old preparation, then considerable isomerisation had taken place. A similar procedure on a 10-month old sample showed that the solid had now completely isomerised to (18) and (20). Heating a mixture of (18) and (20) in CF_3CO_2H does not alter the proportions of the products, thus indicating that they are not interconvertible. Using [^{2}H]trifluoroacetic acid, the deuterium atom is incorporated into the newly created methylene group, (A), of (16), and appears to be specifically transferred to (B) in (18) and (C) in (20). These two products are, however, now in different ratios, the allyl-olefin-metal complex (20) now predominating. When a freshly prepared [$^2H_1$]trifluoroacetic acid solution is mixed with an equal volume of CF_3CO_2H, the resonance of the added proton rapidly attains half its normal intensity.

The corresponding iridium analogue (5) forms an air-stable, white salt with HPF_6. It also dissolves in trifluoroacetic acid solution, giving a mixture of (17) (80%) and (19) (20%). After eight days in solution only slight change occurs. The salt formed at room temperature also contains (17) and (19), in a ratio of 2 : 1. Heating the trifluoroacetic acid solution at 60 °C for 71 h brings about a similar isomerisation for the rhodium compound. Only *ca.* 4% of (17) is left, and (19) and (21) are in a ratio of *ca.* 3 : 2. In this case dissolution in [$^2H_1$]trifluoroacetic acid yields solely monodeuteriated (17), as in the rhodium complex, and heating this solution to 60 °C for 80 h leads to deuterium transfer to give (19) and (21), in a *ca.* 1 : 1 ratio.

These results demonstrate that the mode of protonation is critical to the nature of the product. Solvent, temperature, and the isotope of hydrogen employed are all important. It also seems that the proton incorporated from the solvent into the σ–π-olefin complex rapidly exchanges with the solvent, and it is this proton which is transferred in the subsequent isomerisations.

The kinetics of this reaction in trifluoroacetic acid were studied by n.m.r. spectroscopy and for both metals the overall reaction was found to be first order with respect to (16) or (17). The rhodium system was studied in greater detail, and it was found that the production of (18) and (20) behaved as parallel first-order reactions. Good linearity for plots of the integrated first-order rate equation was obtained over three half-lives, the standard error being in the order of ±2% for the overall reactions and ±8% for the individual ones. Arrhenius plots of the overall reaction, and the two component ones were determined on rates obtained at 16, 29·5, 39, and 46 °C. Values of $\Delta H^‡$ and $\Delta S^‡$ were calculated at 29·5 °C from the Eyring equation. When the isomerisation was followed in [$^2H_2$]dichloromethane and trifluoroacetic acid (20%) all rates increased to *ca.* 1·6 times the rate in trifluoroacetic acid, and in sulphuric acid (20%) and trifluoroacetic acid, the rates were all between 10 and 20% greater than in the neat acid. In this latter reaction, the solution changed colour to a deep green during the reaction time, but little n.m.r. line broadening was observed. This corresponds with the results of Wilkinson *et al.*[3,4] who found that the cobalt analogue and the cyclo-octatetraene-cobalt and -rhodium complexes were unstable in sulphuric acid.

The overall reaction rate for the iridium system at 60 °C was $1{\cdot}2 \pm 0{\cdot}1 \times 10^{-5}$ s^{-1}, *ca.* 1000 times slower than the rhodium reaction calculated for that temperature. However, the ratio of the two products was approximately equal in both cases.

The parent iridium complex (5) was protonated in [$^2H_2$]dichloromethane solution by trifluoroacetic acid at −80 °C. The n.m.r. from −50 to −10 °C indicated that two metal hydrides were present, one 1,5-bonded (22) and the other 1,3-bonded (23) in ratio of *ca.* 1 : 4. When this solution was heated to 30 °C, it was converted into a mixture of 55% (17) and 45% (19).

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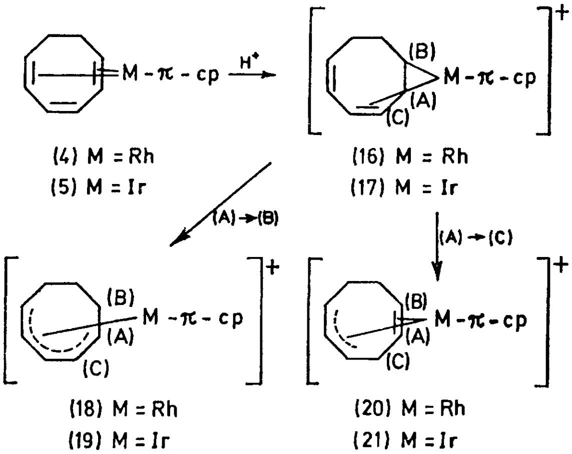
[11] (*a*) M. Green, T. A. Kuc, and S. H. Taylor, *J. Chem. Soc.* (*A*), 1971, 2334; (*b*) B. F. G. Johnson, J. Lewis, and D. A. White, *J. Chem. Soc.* (*A*), 1971, 2699.

Reactions of [$(C_8H_{11})Rh(\pi\text{-}C_5H_5)]PF_6$.—The yellow salt formed by protonation of (4) with HPF_6 deprotonates with triethylamine to reform (4). However, this does not occur in high yield, and it is possible that only the dienyl (18) undergoes the reaction, as in the cobalt system. Cyclo-octa-2,5-dienium(tritylcyclopentadienyl)rhodium hexafluorophosphate does not readily deprotonate, and yields an intractable oil in a manner similar to the allyl-olefin cobalt cation (14).

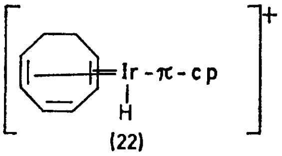


(4) M = Rh
(5) M = Ir

(16) M = Rh
(17) M = Ir

(18) M = Rh
(19) M = Ir

(20) M = Rh
(21) M = Ir



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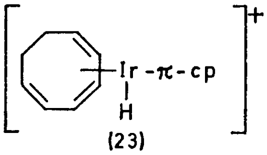

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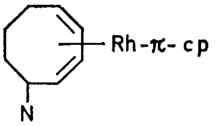
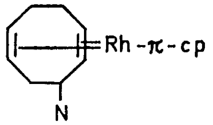
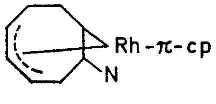


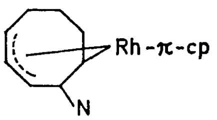
(24) a; N = CN
b; N = H
c; N = OMe



(25) a; N = CN
b; N = H



(26) a; N = CN
b; N = H



(27) a; N = CN
b; N = H

When the mixture of (18) and (20) is treated with sodium cyanide at −10 °C, only one product complex (24) is obtained. However at *ca.* 30 °C two different isomers are also formed, and at *ca.* 22 °C all three are produced. By comparison with the n.m.r. spectrum of 3-cyanocyclo-octa-1,5-diene(cyclopentadienyl)cobalt(I), it appears that one of these additional isomers is (25a). The nature of the second additional isomer has not been determined. It is either complex (26a) or (27a) depending upon the nature of its precursor cation (*i.e.* the allyl-olefin or dienyl salt). On the basis of the yields, (27a) appears the more likely. This would contain the same organic moiety that is suggested in the tricarbonyliron system. Attempts to identify this isomer, using the paramagnetic shift reagent $Eu(dpm)_3$ on the mixture obtained at 30 °C were inconclusive, although shifts were observed.

Similar temperature-dependent behaviour was observed by treating the mixture of salts with sodium borohydride. At room temperature (25b) was obtained together with another isomer. [The n.m.r. spectrum of this contained a resonance at τ 6·85 as well as cp (τ 4·85) and methylene protons], possibly a σ-π-allyl as in cyanide addition. At −10 °C, a complex mixture of products was obtained. Some deprotonation to (4) had occurred (10%), as well as hydride addition to give 25% of (25b), a small amount of the possible σ-π-allyl complex, and the major isomer (24b). [The n.m.r. spectrum of (24b) contained ' inner ' (τ 5·0) and ' outer ' (τ 5·6) diene resonances, as well as the cp (τ 4·87) and methylene signals]. Attempts to synthesise (24b) from cyclo-octa-1,3-diene and di-μ-chloro-tetraethylenedirhodium(I) (1) were unsuccessful. No reaction was observed at room temperature.

Addition of aqueous sodium carbonate to the mixture of salts causes deprotonation to give (4); treatment with sodium methoxide in methanol also gives a large proportion of (4) but some (24c) was detected. The n.m.r. spectrum was similar to that of (24a), although a small amount of another methyl ether isomer was also present.

Other Electrophilic Reactions of $(C_8H_{10})Rh(\pi\text{-}cp)$.—The treatment of (4) with other electrophiles was less fruitful. Under either Friedel–Crafts acetylation or Vilsmeir formylation conditions decomposition of the complex occurred, although *ca.* 1% of cyclo-octa-1,3,5-triene (acetylcyclopentadienyl)rhodium(I) could be detected in the first system, and some of the chloride-bridged dimer (7) in the second. A small amount of cyclo-octa-1,3,5-triene(tritylcyclopentadienyl)rhodium(I) was detected in the reaction of (4) with trityl tetrafluoroborate. An unstable buff-coloured salt was also obtained, its n.m.r. spectrum indicating that trityl addition to the eight-membered ring had occurred.

Attempts to study addition reactions to the uncoordinated olefinic bond were also unsuccessful. Dibromocarbene produced what was probably $Br_2Rh(\pi\text{-}C_5H_5)$,[12] and both peracetic acid and osmium tetroxide caused slow decomposition of the complex.

DISCUSSION

The protonation of (cyclo-octa-1,3,5-triene)(π-cyclopentadienyl)cobalt(I) is different to that of its rhodium(I) and iridium(I) analogues in that only the octadienyl system is produced. It does, however, bear a strong resemblance to the corresponding tricarbonyliron system. The bicyclic system, which is only observed for cobalt(I), shows a completely different chemistry to that of the tricarbonyliron complex in that ring opening occurs to give the octadienyl system.

The evidence obtained for the rhodium(I) and iridium(I) systems suggests that the isomerisations of the $C_8H_{11}^+$ unit, which occur subsequent to the initial protonation step, follow a common path for the two

[12] R. J. Angelici and E. O. Fischer, *J. Amer. Chem. Soc.*, 1963, **85**, 3733.

metals. The protonation of the iridium complex at low temperature indicates that metal hydrides are intermediates and that the triene may, in part, be present co-ordinated in the 1,3-manner. Since the added proton is known to exchange rapidly with the solvent, pre-equilibria probably exist involving the neutral complex, the two bonding isomers of the metal hydrides and the 1,3,4-η complex.

$$e.g.\ \mathrm{H}^+ + (5) \rightleftharpoons (22) \rightleftharpoons (23) \rightleftharpoons (17)$$

The two final, effectively irreversible processes give rise to the two products. There is no direct evidence as to whether the 1,3-bonded hydride exchanges with the solvent, but since cyclo-hexa-1,3-diene(cyclopentadienyl)rhodium(I) [13] protonates to form a metal hydride, which exchanges with the solvent protons, (23) may well behave similarly. It is likely that the dienyl and the allyl-olefin are formed from the metal hydrides too. Hence five possible mechanisms for the isomerisations may be envisaged. (i) Protonation of the neutral diene complexes on the ligand unco-ordinated olefinic bond. (ii) Further protonation of the ligand, giving a dication, followed by the loss of the proton bonded to the metal. (iii) Intramolecular rearrangement so that the dienyl is obtained from the 1,3-hydride and the allyl-olefin comes from the 1,5-hydrido-species. (iv) Intramolecular rearrangement so that the dienyl is obtained from the 1,5-metal hydride and the allyl-olefin from the 1,3-hydrido-species. (v) Intramolecular rearrangement so that both products come from (*a*) 1,3- or (*b*) 1,5-hydrides.

Mechanisms (i) and (ii) are extremes of a mechanism involving bond formation with a proton of the solvent to the ligand and breaking of the metal hydride bond.

The solid-state isomerisation is good evidence for the process being intramolecular at least to a degree. Either there are two reaction paths, a slow intramolecular one and a more rapid one involving solvent protons, or the former solely operates and, not unreasonably, it is much slower in the solid state. The two protons of the newly formed methylene group in the allyl-olefin complex (20) are distinguishable, and one proton is thus seen to be specifically transferred from the σ-π-olefin complex to (20). This suggests that only one mechanism is operating in the reaction. The low values of $\Delta S^\ddagger$ are consistent with an intramolecular mechanism.

The kinetic isotope effects of $k_\mathrm{H}/k_\mathrm{D} = 3{\cdot}2$ for the formation of the dienyl and 0·8 for the production of the allyl-olefin reveal a difference in mechanism between the two parallel reactions. An isotope effect will be due to the combination of two effects: (i) The isotopic substitution of the hydrogen species being transferred. (ii) The change in the solvent medium by isotopic substitution therein.

In aqueous solutions, (ii) is generally believed to be *ca.* 20—30% for reactions not involving small ions. Furthermore for reactions which do not involve ion production or destruction $k_{\mathrm{H_2O}}/k_{\mathrm{D_2O}}$ is assessed as being close to unity.[14] The magnitude of this effect is unknown for trifluoroacetic acid, but probably it will also be small, leaving (i) the dominant effect in determining $k_\mathrm{H}/k_\mathrm{D}$.

The value of 3·2 for dienyl production is sufficiently large to be a primary isotope effect,[14] but too small to permit a linear transition [15] state in which the stretching zero-point energy of a carbon to hydrogen bond is lost. Since the metal hydrides are part of a pre-equilibrium, it appears as though the rate-determining step is during the transfer of the hydrogen from the metal to a carbon atom. So the transition state is either formed by fission of the metal–hydride bond, or its bending to give a metal–hydrogen–carbon transition state in which the bending zero-point energy of the metal hydride bond is lost.

The formation of the allyl-olefin involves a virtual absence of a kinetic isotope effect, suggesting that the breakage of an element–hydrogen(deuterium) bond does not occur in the formation of the transition state. One explanation of this could be that a proton from a methylene group other than that isotopically substituted is transferred. However the n.m.r. spectrum of the monodeuteriated allyl-olefin cannot be rationalised on this basis. So it appears that either bond breaking is indeed relatively unimportant in the rate-determining step or more than one reaction step is required.

The protonation of the closely related cyclohexa-1,3-diene(π-cyclopentadienyl)rhodium(I) [13] has been shown to involve a rapid exchange by transfer of the hydrogen species to the co-ordinated double-bond. Indeed many of the diene protonations in this study involve protonation of a co-ordinated olefinic bond.[7] It is, therefore, not unreasonable to expect that in this case too, transfer is to the co-ordinated olefinic bond. Hence the allyl-olefin must be formed from the 1,3-bonded metal hydride; formation of the dienyl is possible from either. Hence in the alternative mechanisms cited above, either mechanism (iv) or (v*a*) is operating, in which one or both of the products is formed by an intramolecular transfer of the hydrogen from the 1,3-bonded metal hydride to the ligand.

Nucleophilic addition to the mixture of $[(\mathrm{C_8H_{11}})\mathrm{Rh}(\pi\text{-}\mathrm{C_5H_5})]\mathrm{PF_6}$ isomers also appears to be complex. At low temperatures only the dienyl appears to be attacked, at the (terminal) 1-position. But at higher temperatures the allyl-olefin is now attacked at the outer allyl position, and the dienyl also reacts, but the position of attack is now at the 2-position. The relation of these three reactions to each other at a particular temperature is dependent upon the nature of the nucleophile.

Protonation of the octatriene complexes is an unusual reaction. Apart from addition of the trityl cation, no other electrophiles were found to add to, or substitute on, the eight-membered ring. It is interesting that the reactivity of the unco-ordinated double-bond is

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[13] B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J.C.S. Chem. Comm.*, 1972, 235.

[14] 'Isotope Effects in Chemical Reactions,' C. J. Collins and N. S. Bowman, Van Nostrand Reinhold, 1970.

[15] F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265.

less in the rhodium complex than that of the middle olefinic bond of the free ligand. Normally ready reactions of an olefin, *e.g.* epoxidation and *cis*-hydroxylation, are inhibited, and it appears that a slow oxidative decomposition of the complex occurs instead. So it appears that in the complexes studied here, the facility for electrophilic attack observed in the iron(0) system, is lost. These complexes do, however, protonate readily and the metal assists in the interesting ligand isomerisations found.

EXPERIMENTAL

Analyses were performed by the microanalytical department of this laboratory; m.p.s were determined with a Gallenkamp melting point apparatus. I.r. spectra were recorded on a Perkin-Elmer 257 or 457 spectrometer, visible–u.v. spectra using a Unicam SP 800 spectrometer, mass spectra on an A.E.I. MS 12, and ^1H n.m.r. spectra on Perkin-Elmer R12B and Varian Associates HA100 instruments. The kinetic runs were carried out with a HA 100 instrument, employing methanol and ethylene glycol temperature standards. Slopes of the linear first-order and Arrhenius plots were determined by a least-squares fit on a Hewlett-Packard 9100B Calculator using a program of Mr. A. J. P. Domingos. Some of the cyclo-octa-1,3,5-triene used was prepared by Mr. M. H. Mitchell and the $Eu(dpm)_3$ was a gift from Mr. J. K. M. Sanders. All reactions were performed under pure, dry nitrogen, unless stated otherwise.

Preparation of the Diene Complexes.—*Di-μ-chloro-bis-cyclo-octa-*1,3,5-*trienedirhodium*(I) (7). This compound was prepared by standard techniques from di-μ-chloro-tetra-ethylenedirhodium(I) (1) [8] and cyclo-octa-1,3,5-triene,[16] to yield the product as a yellow, crystalline *solid* (91%) [Found: C, 38·8; H, 4·05. $(C_8H_{10}RhCl)_2$ requires C, 39·2; H, 4·1%]: $\nu_{max.}$ (HCB mull) 3030sh, 3025sh, 3010s, 2990s, 2975sh, 2958sh, 2945sh, 2935sh, 2915sh, 2885m, 2845m, and 1635m cm^{-1}; τ ($CDCl_3$) 4·28 (2H, s, unco-ordinated vinyls) 5·85 (4H, m, co-ordinated vinyls), 7·4 (2H, m), and 8·18 (2H, m, ABq + fine coupling-methylenes).

*Acetylacetonatocyclo-octa-*1,3,5-*trienerhodium*(I) (8). Complex (7) (1·0 g) in dichloromethane (15 ml) was shaken with (acac)Ti [17] (1·30 g), with light excluded, for 2 h. The mixture was then filtered, and the solvent was removed from the filtrate. The resulting oil was chromatographed on a silica gel–toluene column (30 × 2 cm); the complex was eluted as a yellow band with toluene–10% methanol. The yellow band yielded a yellow solid which was extracted into dry ether. The ether was removed and the residue was sublimed at 0·2 Torr and 80—100 °C to give the product as a yellow, crystalline *solid* (430 mg), m.p. 134·5—135·5 °C [Found: C, 50·4; H, 5·5%; *M* (mass spec.), 308. $C_{13}H_{17}O_2{}^{103}Rh$ requires C, 50·7; H, 5·5; *M*, 308] $\nu_{max.}$ (Nujol mull) 1620w (C=C) and 1580 and 1520 cm^{-1} (C=O); $\lambda_{max.}$ (n-pentane) 348sh (ε 1600), 301 (5900), 255 (12,100), and 217nm (20,000); τ ($CDCl_3$) 4·18 (2H, s, unco-ordinated vinyls), 4·67 (1H, s, central acac proton), 5·7 (2H, m, co-ordinated vinyls), 5·87 (2H, assym d, co-ordinated vinyls next to free olefinic bond), 7·5 (2H, m, methylenes), 8·07 (6H, s, methyls), and 8·0—8·1 (2H, m, methylenes).

*Cyclo-octa-*1,3,5-*trienecyclopentadienylrhodium*(I) (4). Complex (7) (3·8 g) was shaken in benzene (25 ml) with (cp)Tl [18] (4·0 g), with light excluded, for 4 h. The mixture was filtered and the solvent was removed from filtrate. The resulting solid was dissolved in toluene and chromatographed on a silica gel–toluene column (30 × 2 cm); a yellow band was eluted with toluene which yielded a yellow solid. This sublimed at 60 °C and 0·1 Torr to give the product as a yellow crystalline *solid*, m.p. 98—99 °C (2·93 g, 87%) (Found: C, 57·1; H, 5·45%. $C_{13}H_{15}Rh$ requires C, 56·9; H, 5·45%), mass spec *M*, 274, loosing C_8H_{10} ring in fragments first to give $RhC_5H_5{}^+$; $\nu_{max.}$ (HCB mull) 3100sh, 3090m, 3030sh, 3010sh, 2980s, 2930s, 2920sh, 2880m, 2855sh, 2840m, and 1635m; $\lambda_{max.}$ (n-pentane) 350sh (ε 480), 267sh (3600), 238 (18,000), and 220nm (12,600); τ ($CDCl_3$) 4·42 (2H, s, unco-ordinated vinyls), 4·83 (5H, 5, cp), 5·80 (2H, m, co-ordinated vinyls), 5·94 (2H, assym d, co-ordinated vinyls next to olefin bond), and 7·7—8·0 (4H, m, methylenes).

*Cyclo-octa-*1,3,5-*trienecyclopentadienyliridium*(I) (5). Complex (10) was prepared by the method of Winkaus and Singer [9] from sodium chloroiridate (1120 mg) and cyclo-octa-1,3,5-triene (2 ml). Complex (5) was prepared by the same method as complex (4). Two bands were collected from the chromatography column: (1) a yellow one containing $(C_8H_{12})Ir(\pi\text{-}C_5H_5)$ and a small amount of a yellow complex (*M ca.* 630) and (2) a colourless one. The colourless solid from the second band sublimed at 80 °C and 0·02 Torr as a very pale green crystalline solid (Found: C, 43·2; H, 4·2. $C_{13}H_{15}Ir$ requires C, 42·9; H, 4·15%), Mass spec: 364 ($C_8H_{10}Ir^{193}C_5H_5$) and 362 ($C_8H_{10}Ir^{191}C_5H_5$); C_8H_{10} fragmentation leaves $IrC_5H_5{}^+$; $\nu_{max.}$ (CCl_4 solution) 3100br, w, 3020m, 2980s, 2930m, 2890m, 2850m, and 1630m; $\lambda_{max.}$ (n-pentane) 234sh (ε 5400) and 219nm (12,800); τ ($CDCl_3$) 4·39 (2H, s, unco-ordinated vinyls), 4·80 (5H s, cp), 5·7 (2H, m, co-ordinated vinyls next to methylenes), 6·03 [2H, assym. d, co-ordinated vinyls next to free olefinic band (one side of ABq—other side is further coupled)], and 7·8—8·3 (4H, m, methylenes).

Protonations.—These reactions were performed typically by the action of HPF_6 (*ca.* 0·5 ml) on the neutral complex (200 mg) in dry ether (8 ml). The precipitate which formed was filtered off, washed with dry ether, and dried *in vacuo*; $[(C_8H_{11})Ir(\pi\text{-}C_5H_5)]PF_6$ was recrystallised from dry dichloromethane at −80 °C. The i.r. spectrum of all the salts found (Nujol mull) contained a high ν_{CH} at *ca.* 3030 cm^{-1}, due to the cyclopentadienyl ring, and a broad $PF_6{}^-$ band at 830 cm^{-1}. Although satisfactory analytical data were obtained for $[(C_8H_{11})M(C_5H_5)]$ $[PF_6]$ (M = Rh, Ir) $[(C_8H_{11})\text{-}Co(C_5H_5)]$ $[PF_6]$ was unstable and satisfactory analyses were not obtained.

Neutralisations.—Typical reaction conditions were addition of triethylamine, to excess, to a solution of the salt (250 mg) in acetone (5 ml). The mixture was poured into water (20 ml) and ether (20 ml) and the pH was adjusted with dilute hydrochloric acid (2N) until it was less than 7. The aqueous layer was extracted into ether (3 × 10 ml) and the combined ethereal extract was washed with water (3 × 10 ml), and dried ($MgSO_4$). The solvent was removed and the residue was dissolved in toluene and chromatographed on an alumina '0'–toluene column (13 × 2 cm). The band eluted with toluene yielded the *product*.

Nucleophilic Addition to $[(C_8H_{11})Rh(\pi\text{-}C_5H_5)]PF_6$.—(i) Sodium borohydride reductions were performed in dry

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[16] W. O. Jones, *J. Chem. Soc.*, 1954, 1808.

[17] G. T. Morgan and H. W. Moss, *J. Chem. Soc.*, 1914, 189.

[18] F. A. Cotton and L. T. Reynolds, *J. Amer. Chem. Soc.*, 1958, **80**, 269.

THF, followed by normal extraction and purification procedures as for complex (4), and yielded $(C_8H_{12})Rh(\pi\text{-}C_5H_5)$ [Found: C, 55·85; H, 6·35%; *M* (mass spec.) 276. $C_{13}H_{17}Rh$ requires C, 56·5; H, 6·2%; *M*, 276].

(ii) The salt was added to an aqueous acetone solution of sodium cyanide (four-fold excess) and this was followed by extraction and purification as for (4) except that an alumina column was used; the product was eluted by 10% ether in toluene. The product was obtained as a yellow crystalline *solid* [Found: C, 56·0; H, 5·2; N, 4·5%; *M*, 301. $C_{14}H_{16}NRh$ requires C, 55·8; H, 5·3; N, 4·65%; *M*, 302]; $\nu_{max.}$ (Nujol mull) 2230 cm^{-1} (C≡N).

(iii) Addition of sodium methoxide (four-fold excess) to a suspension of the salt in methanol followed by extraction into ether, sublimation at 60 °C and 0·02 Torr, and crystallisation from pentane at −80 °C gave a mixture of complex (4) and $(C_8H_{11}OCH_3)Rh(\pi\text{-}C_5H_5)$ (Mass spec. *M*, 306).

Other Cyanide Addition Reactions.—(i) $[(C_8H_{11})Co(\pi\text{-}C_5H_5)]\ PF_6$. The allyl-olefin isomer was allowed to react as in the rhodium case above; the product was isolated by extraction into ether, followed by recrystallisation from pentane and ether at −80 °C, similar to the reported preparation.[9] It formed on amber, crystalline solid $(C_8H_{11}CN)Co(\pi\text{-}C_5H_5)$.

Under similar conditions the dienyl isomer yielded a colourless oil (6%). [*M* (mass spec.) 214, corresponding to $C_{16}H_{22}$], $\nu_{max.}$ (CS_2 solution) 1640 cm^{-1} (C=C).

(ii) $[(C_8H_{11})Fe(CO)_3]\ [PF_6]$ (12). The salt (12) (1·51 g) was added to a solution of sodium cyanide (800 mg) in aqueous acetone (20 ml) under CO, and the mixture was stirred for 40 min. The mixture was poured into water (50 ml) and ether (50 ml) and the layers were separated. The aqueous layer was extracted with ether (5 × 20 ml), and the combined ethereal extract was washed with water (4 × 20 ml) and dried ($MgSO_4$) under N_2. The solvent was removed to give a cloudy yellow oil, which was chromatographed on a thick-layer plate with benzene as solvent. Two products were obtained, a fast-moving band yielding a yellow oil, rapidly forming a dark solid, and an oil [*M* (mass spec.) 214, $C_{16}H_{22}$]. A slow-moving band yielded (15) (8%), [*M* (mass spec.) 161], $\nu_{max.}$ (ether solution) 2215 (CN) 1735 (CO) and 1642 (C=C); τ ($CDCl_3$) 3·12 (dd) and 4·09 (t) 2 vinyl H.

Kinetics.—The kinetic runs were performed on 80 mg of (4) dissolved in *ca.* 0·5 ml of trifluoroacetic acid or an equal volume of an alternative solvent. The region from τ 2·5 to 4·3 was scanned and integrated, incorporating $H_A + H_B$ of (16), H_A of (18), and the cyclopentadienyl resonances of (16), (18), and (20).

We wish to thank the S.R.C. for a studentship (to J. E.) and Johnson Matthey and Co. Ltd. for the loan of rhodium and iridium salts.

[2/802 *Received*, 10*th April*, 1972]