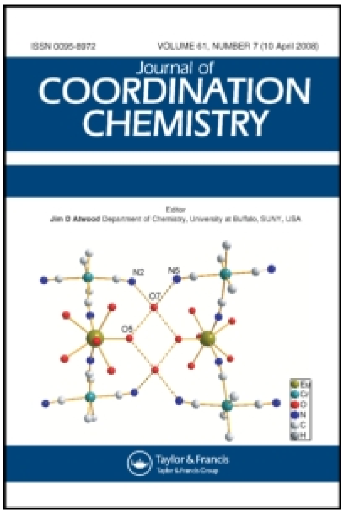


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A NUCLEAR MAGNETIC RESONANCE AND MASS SPECTRAL STUDY OF SOME ALKENE COMPLEXES OF RHODIUM(I) AND IRIDIUM(I): COORDINATED ALKENE ROTATIONAL BARRIERS, APPEARANCE POTENTIALS AND ESTIMATED HEATS OF FORMATION

Michael A. Arthurs[a]; S. Martin Nelson[b]
[a] Department of Chemistry, Dublin Institute of Technology, College of Technology, Kevin Street, Dublin 9, Ireland [b] Department of Chemistry, Queen's University, Belfast, N. Ireland

To cite this Article Arthurs, Michael A. and Nelson, S. Martin(1983) 'A NUCLEAR MAGNETIC RESONANCE AND MASS SPECTRAL STUDY OF SOME ALKENE COMPLEXES OF RHODIUM(I) AND IRIDIUM(I): COORDINATED ALKENE ROTATIONAL BARRIERS, APPEARANCE POTENTIALS AND ESTIMATED HEATS OF FORMATION', Journal of Coordination Chemistry, 13: 1, 29 — 40

To link to this Article: DOI: 10.1080/00958978308079751
URL: http://dx.doi.org/10.1080/00958978308079751

J. Coord. Chem., 1983, Vol. 13, pp. 29–40
0095-8972/83/1301-0029 $18.50/0

A NUCLEAR MAGNETIC RESONANCE AND MASS SPECTRAL STUDY OF SOME ALKENE COMPLEXES OF RHODIUM(I) AND IRIDIUM(I): COORDINATED ALKENE ROTATIONAL BARRIERS, APPEARANCE POTENTIALS AND ESTIMATED HEATS OF FORMATION

MICHAEL A. ARTHURS

Department of Chemistry, Dublin Institute of Technology, College of Technology, Kevin Street, Dublin 9, Ireland

and S. MARTIN NELSON†

Department of Chemistry, Queen's University, Belfast BT9 5AG, N. Ireland.

(Received October 26, 1982; in final form December 20, 1982)

The activation energies ($\Delta G^{\dagger}$) for olefin rotation in ethylene complexes of Rh(I) and Ir(I) have been estimated by signal coalescence from their temperature dependent ^1H nmr spectra in solution. The barriers decrease with increase in the electron accepting nature of the associated ligand (η^5-cyclopentadienyl, pentane-2, 4-dionate, carboxylate and substituted derivatives thereof) in accordance with the expected decrease in the importance of the π-contribution to the metal-olefin bond. Barriers are substantially higher for Ir(I) than for corresponding Rh(I) complexes. The complex temperature dependent spectra of di-μ-chlorotetrakis(4-methylpenta-1, 3-diene dirhodium(I) are interpreted in terms of both intra- and intermolecular processes.

The greater $\Delta G^{\dagger}$ values found for Ir(I) compared to Rh(I) complexes are reflected in the different mass spectral fragmentation patterns for corresponding members of the two series. Appearance potentials and heats of formation are estimated for [cpRh$(C_2H_4)_2$] and [cpRh$(CO)_2$].

INTRODUCTION

Coordinated olefins in complexes of chromium,[1] manganese,[1] iron,[2,3] tungsten,[4] ruthenium,[2] osmium,[5] rhodium[6,7] and platinum[8,9] have been shown to undergo a hindered rotation about the metal-olefin σ-bond axis. The first dynamic nmr study was described by Cramer[10] and subsequently the activation energies, or so-called rotation barriers, of many of these processes have been evaluated using classical kinetic theory.

The measured barrier is considered to comprise contributions from rotation about the metal-olefin π-bond and the metal-olefin σ-bond. The first of these is controlled mainly by steric and electronic factors whereas the second is determined only by steric effects. There have been few systematic studies on the relative importance of the steric and electronic contributions to the overall rotational barrier in different systems. Lewis and co-workers[8] have suggested that the steric contribution is the more important in square planar complexes of Pt(II) whereas in Rh(I) complexes the electronic contribution may be dominant.[6,11]

In this work we have extended the study of η^2-ethylene rotation to a wider range of complexes of Rh(I) and Ir(I) containing substituted η^5-cyclopentadienyl (cp), pentane-2, 4-dionate (pd) and carboxylate groups as counter ligands. To the extent that the metal-

---

† To whom correspondence should be directed.

ethylene bond has an important π-contribution, the introduction of electron withdrawing substituents into the counter ligand would be expected to weaken the metal-olefin π-bond and to lower the rotational barrier. The converse should apply to electron donating substituents.

Variations in metal-alkene π-bonding might be expected to influence the overall stability of the complexes, this, in turn, being reflected in the mass spectra. Apart from the work of King,[12] Kemmitt,[13] and Haegele and co-workers[14] there has been no detailed study of the mass spectra of simple olefin complexes of Rh(I) or Ir(I). The fragmentation patterns for $[\mathrm{cpRh(C_2H_4)_2}]$,[12] $[\mathrm{cpRh(1,5\text{-}C_8H_{12})}]$[12] and $[\mathrm{(1,5\text{-}C_8H_{12})RhX}]_2$,[13] (X = Cl, Br, I) have been reported, and for the halide complexes the first ionisation potentials of the molecular ions have been given. The ionisation process was interpreted as one involving a molecular orbital having little halogen character. Relative ion intensity measurements on $[\mathrm{pdRh(CO)_2}]$ and $[\mathrm{pdRh(C_2H_4)_2}]$ suggest that the former is more stable.[14] In the present study the mass spectra of several ethylene and carbon monoxide complexes of Rh(I) and Ir(I) having η^5-cyclopentadienyl, pentane-2,4-dionate or μ-carboxylate counter ligands are reported. Appearance potentials and approximate heats of formation of $[\mathrm{cpRh(C_2H_4)_2}]$ and $[\mathrm{cpRh(CO)_2}]$ have been estimated.

EXPERIMENTAL

Thallium, sodium and potassium cyclopentadienides were prepared as described previously.[15] The thallium(I) salts of pentane-2, 4-dione and 1,3-diphenyl-propane-1,3-dione were prepared by the method of Taylor and McKillop[16] and those of 1,1,1,5,5,5-hexafluoropentane-2,4-dione and 1,1,1,-trifluoropentane-2,4-dione were prepared by Wojcicki's method.[17] The cyclopentadienyl complexes were prepared by reaction of di-μ-chloro-tetrakis(ethylene)dirhodium(I), or the iridium(I) analogue with a cyclopentadienyl salt as previously described.[15,18]

All but three of the rhodium complexes have been characterised previously.[15,18] Analytical data for the iridium and the new rhodium complexes are given in Table I.

TABLE I
Analytical data for $[(\mathrm{C_2H_4})_2\mathrm{MX}]_n$ complexes where M = Rh and (in parentheses) Ir.

X	Colour	M.p.[a] (θc/°C)	Analyses (%)				M[b]
			Found		Calc.		
			C	H	C	H	
cp[c]	Green	Oil	42.6	3.9	42.8	4.0	224
1,3-diphenylopropane-dionato	Yellow	162	59.9	5.0	59.6	5.0	382
μ-acetato	Red	148 (decomp)	32.2	5.0	33.0	5.0	436
(mcp[d]	Beige	94	35.2	3.8	35.5	4.0	370/372)
(fcp[e]	Beige	94	34.8	3.6	35.1	3.8	340/342)
(pd	Orange	138	31.3	4.5	31.1	4.3	346/348)
(1,1,1,5,5,5F6pd	Red	55	23.6	1.9	23.7	2.0	454/456)

[a] Uncorrected [b] Parent ion in mass spectrum [c] $[(\mathrm{CO})(\mathrm{C_2H_4})\mathrm{Rhcp}]$ complex [d] η^5-methoxycarbonylcp [e] η^5-formylcp.

The pentanedionate complexes were prepared *via* reaction of the appropriate thallium salt, in excess, with $[(C_2H_4)_2RhCl]_2$ or $[(C_2H_4)_2IrCl]_2$ in hexane. Carboxylate complexes were prepared by the method of Haszeldine *et al.*[19] Pentane-2,4-dionatobis(chloroethene)rhodium(I) was synthesised by Cramer's method.[20]

Infrared spectra were measured in the range 4000-250 cm^{-1} (Perkin Elmer 457 grating spectrophotometer) in KBr/CsI discs or as thin films between KBr/CsI plates. ^1H nmr spectra were recorded in deuteriochloroform, perdeuterioacetone or diphenylether using Varian Associates A60D and HA 100 spectrophotometers fitted with variable temperature accessories. The probe temperature was calibrated using methanol below ambient and ethylene glycol above it.[21] Free energies of activation were calculated from the expression (*1*),[6]

$$\Delta G^{\dagger} = -RT_c \ln \frac{\pi \Delta \nu h}{\sqrt{2}kT_c} \qquad (1)$$

where $\Delta\nu$ is the chemical shift of the coalescing resonances in the absence of exchange, T_c is the coalescence temperature, and R, h, and k have their usual thermodynamic significance. ^{13}C nmr spectra were recorded with a Bruker WP-90 instrument with complete proton decoupling.

Mass spectra were obtained with an A.E.I. MS 902 spectrometer with nominal electron energy of 70eV. Appearance potentials were determined using the method of extrapolated voltage difference, first described by Warren[22] and extended by Lappert and co-workers.[23] Ionisation efficiency curves were obtained by reducing the electron voltage in steps from 20eV until no current reading was obtained. Samples were introduced *via* the all-glass heated inlet system of the spectrometer and the argon calibrant *via* the cold inlet. Ionisation efficiency curves were plotted as a function of the current. The value of ΔE obtained by extrapolation to zero current was added algebraically to the ionisation potential of the calibrant gas (15.76 eV). Ionisation potentials were also determined using the 'semi-logarithmic plot' method of Lossing, Tickner and Bryce.[24] The results of six determinations were averaged. The mass spectra and appearance potentials were reproducible to within the quoted error limits for two independent runs comprising six determinations each.

RESULTS AND DISCUSSION

Rotational Barriers for the Ethylene Complexes

^1H and ^{13}C nmr data and derived rotational barriers ($\Delta G^{\dagger}$) for ethylene rotation are given in Table II.

Cyclopentadienyl Complexes

The results show that as the electron withdrawing character of the cyclopentadienyl ring substituent is increased, the rotational barrier ($\Delta G^{\dagger}$) decreases in the order alkyl $\sim$ H $>$ COOR, $\sim$ CN $>$ CHO $>$ $COCO_2R$. These results are consistent with a decrease in the same order of the metal to ethylene π-contribution. They also tend to rule out any significant steric effect (see the cases of *t*-butyl, methyl (2,3), and the three ester substituted rings (6,7,8). The result for the pentamethylcyclopentadienyl complex (1) indicates the moderate effect of alkyl substituents in raising $\Delta G^{\dagger}$. A slightly different substituent order (COOR $\sim$ CHO $>$ CN) has been observed for the electron accepting effect in substituted

TABLE II

$^1H^a$, $^{13}C^a$, and thermodynamic data for $[(C_2H_4)_2MX]_n$ complexes where M = Rh, and (in parentheses) Ir, X = cp, pd or μ-carboxylate.

No	X	^1H $\delta C_2H_4{}^b$ (averaged)	Coalescence Temperature $T_c \pm 2°$	$\Delta G^\dagger$ ± 1.0 kJ mol^{-1}	^{13}C δC_2H_4 ppm	ΔC_2H_4 ppm Coordination shift
1	η^5-Me_5C_5	1.62	$62^{c,d}$	71.5^f	43.90	67.70
2	η^5-C_5H_4iBu	1.85	55	65.7	36.10	85.50
3	η^5-C_5H_4Me	1.85	55	65.7	35.77	85.83
4	η^5-C_5H_5	1.85	55	65.7^f	35.96	85.64
5	$(\eta^5$-$C_5H_5)$	1.23	$100°^d$	>75.0	16.96	104.64)
6	η^5-$C_5H_4CO_2$iPr	2.18	22	58.9		
7	η^5-$C_5H_4CO_2Et$	2.18	22	58.9		
8	η^5-$C_5H_4CO_2Me$	2.18	22	58.9^f	40.64	80.96
9	$(\eta^5$-$C_5H_4CO_2Me$	1.82	119^d	78.8		)
10	$\eta^5C_5H_4CN$	2.29	22	58.9^f	41.62	79.98
11	η^5-C_5H_4CHO	2.32	1	54.5	42.60	79.00
12	$(\eta^5$-C_5H_4CHO	1.91	96^d	74.0	23.26	98.34)
13	η^5-$C_5H_4COCO_2Et$	2.33	− 5	53.3	44.94	76.66
14	$(C_2H_4)(CO)^5C_5H_5$	2.69	0	54.0		
15	pd	2.95	−27	49.8	59.78	61.82
16	(pd	2.67	−18	51.0	40.94	80.66)
17	PhCOCHCOPh	3.00	−31	49.4		
18	F_3-pd	3.00	−35	48.0	60.86	60.74
19	F_6-pd	3.18	-70^e	40.8	63.36	58.24
20	$(F_6$-pd	3.02	-64^e	42.0	44.58	77.02)
21	$(\mu$-$CH_3CO_2)_2$	3.06	-53^e	43.8	60.63	60.97
22	$(\mu$-$C_6H_5CO_2)_2$	3.10	-53^e	43.8		

[a] $CDCl_3$ employed as solvent for all chemical shift measurements (TMS, 40°) [b] $J[^{103}Rh$–$H] = 2.3$Hz (low field) and 1.7 Hz (high field) for all complexes [c] PhOPh [d] o-$C_6H_4Cl_2$ [e] $(CD_3)_2CO$ [f] Previously evaluated, Ref. 6.

ferrocenes.[25] This suggests that the mechanism of transmission of electronic effects in ferrocenes may be rather different.

Figure 1 shows that there is an approximately linear relationship between $\Delta G^\dagger$ and the averaged ^1H and ^{13}C chemical shifts of coordinated ethylene in the Rh(I) complexes. The complex $[cpRh(C_2H_4)(CO)]$ (14) is not included in this plot because the ^1H chemical shift is markedly affected by the anisotropy of the neighbouring CO group. A similar effect was observed for $[cpRh(C_2H_4)(SO_2)]$ for which $\Delta G^\dagger$ has been estimated as 51.2 kJ mol^{-1} and the anisotropic contribution to the coalescence temperature as 10°.[11]

The iridium(I) complex $[cpIr(C_2H_4)_2]$ gave a frozen spectrum for the ethylene protons up to 100° and above this temperature the complex decomposed. This indicates a significantly higher rotational barrier compared to the corresponding rhodium complex. A similar result has been observed for $[(\eta^5$-$C_5Me_5)Ir(C_2H_4)_2]$.[26] However, measurable barriers were obtained for the methoxycarbonyl and formyl derivatives (9, 12). The higher rotational barriers in these iridium(I) systems reinforces the conclusions of Onderdelinden *et al.*,[27] and Jesse *et al.*,[28] on the relative strengths of the rhodium(I)-olefin and iridium(I)-olefin π-interactions.

Pentanedionate and Carboxylate Complexes.

The rotational barriers found for these complexes are appreciably smaller than those

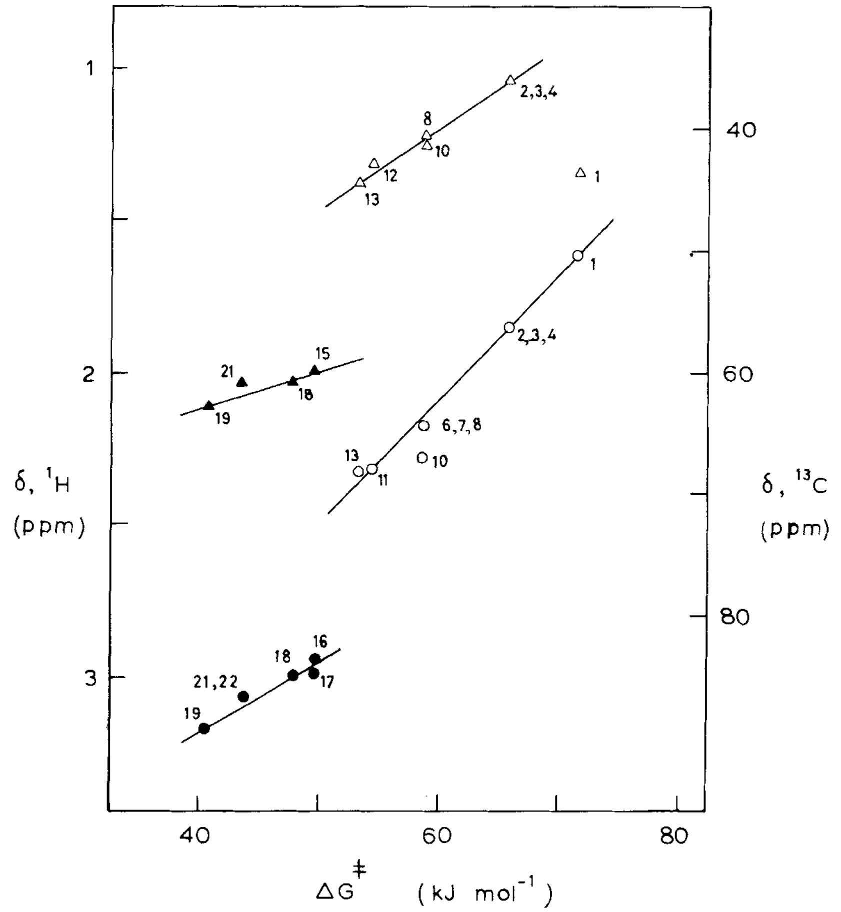


FIGURE 1 Plots of $\Delta G^{\dagger}$ *vs* ^{1}H nmr chemical shift (δ, ^{1}H) and ^{13}C nmr chemical shift (δ, ^{13}C) of coordinated ethylene. Circles refer to (δ, ^{1}H) and triangles to (δ, ^{13}C). Open circles and triangles denote η^5-cyclopentadienyl complexes; filled circles and triangles denote pentane-2, 4-dionate complexes. The numerals refer to the complexes in Table II.

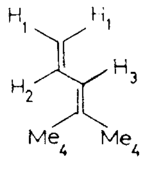
observed for the cyclopentadienyl complexes. Both pentanedionate and carboxylate are expected to cause a substantial reduction in electron density at the metal through the electron withdrawing effect of the oxygen atoms. This in turn is manifested as a decrease in the importance of the π-component in the metal-olefin bond. In view of the substantial weakening of this π-component it is not surprising that the effect is attenuated. The overall spread in $\Delta G^{\dagger}$ values is only 9 kJ mol^{-1} compared to 26 kJ mol^{-1} for the cp complexes. The levelling effect on $\Delta G^{\dagger}$ of replacing cp by pd is particularly evident in a comparison of the data for $[(C_2H_4)_2Rhpd]$ with $[(C_2H_4)_2Irpd]$ (15, 16) and of $[(C_2H_4)_2Rh(F_6\text{-}pd)]$ with $[(C_2H_4)_2Ir(F_6\text{-}pd)]$ (19,20). On the other hand the greater ^{13}C coordination shift (*ca* 19 ppm) observed for ethylene in the Ir(I)-cp complexes is maintained in the pd complexes. It has been estimated that the overall bond energy difference for the metal-olefin bond in $[pdRh(C_2H_4)_2]$ and $[pdIr(C_2H_4)_2]$ is approximately 25 kJ mol^{-1}.[27] Thus, if $\Delta G^{\dagger}$ is considered to be a measure of the metal-olefin π-bond energy the implication of the present results is that the metal-olefin σ-bond is stronger in all the Ir(I) complexes.

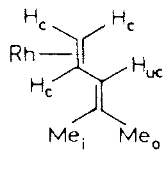
Pentane-2-4-dionatobis(vinylchloride)rhodium(I).

The ^{1}H nmr spectrum of [$(C_2H_3Cl)_2$Rhpd] in $CDCl_3$ at −60° showed four groups of resonances: a sharp singlet at δ 5.33 due to the pd proton, two sets of complex multiplets centred at δ 4.02 and δ 2.99 arising from the vinyl chloride protons, and a doublet at δ 2.13 due to the methyl groups of the chelating pd ligand. Increase in temperature caused the fine structure of the olefin multiplets to disappear and the signals to coalesce. The methyl group doublet also began to coalesce. These observations indicate interconversion of the stereoisomers present. Ten such isomers have been described for [$(C_2H_3OCH_3)_2$Rhpd].[29] If the reasonable assumption is made that at the temperature of the experiment isomer interconversion can only occur by rotation an attempt may be made to estimate an average rotational barrier. However, the presence of unequal isomer concentrations and the multiplicity of resonances made an accurate determination of the coalescence temperature difficult. Despite these difficulties an approximate value of 57 ± 3 kJ mol^{-1} was obtained. The increase in the rotational barrier compared to the parent (unsubstituted) ethylene complex is expected to have both electronic and steric contributions. Both are expected to act in the same sense but the total barrier will not necessarily be the sum of the steric and electronic effects and it is not possible to analyse these separately at present.[31] A detailed study of [cpRh$(C_2H_3F)_2$] by Cramer indicated a free energy difference between the six stereoisomers of 0.4 kJ and a rotational barrier of 67 kJ mol^{-1}.[30]

Di-μ-chlorotetrakis(4-methylpenta-1,3-diene)dirhodium(I).

This complex is unusual in that the diene is monodentate *via* the less substituted double bond; the crystal and molecular structure has been described.[32] The ^{1}H nmr spectrum of the free diene in $CDCl_3$ at 37° consists of four sets of resonances, *viz* δ 6.5 (multiplet, H_2), δ 5.85 (broad multiplet, H_3), δ 5.05 (broad triplet H1, H_1') and δ 1.79 (singlet, Me_4, Me_4'). In the complex at the same temperature the spectrum consists of resonances at δ 5.35 (multiplet H_{uc}), δ 3.70 (multiplet, H_c), and δ 1.70 (doublet Me_o, Me_i).





The doublet for the methyl group is considered to arise from the protons of the 'inside' methyl groups (Me_i) resonating at slightly higher field than those of the 'outside' group (Me_o) due to long-range shielding by the adjacent olefin. The spectrum of the complex is temperature dependent. The H_c multiplet broadens as the temperature is raised from −40°. Simultaneously the components of the methyl group doublet begin to move together. The effects are fully reversible up to 35° and are first-order with respect to the concentration of the complex. Both effects are indicative of diene rotation about the metal-olefin bond axis. However, it was not possible to measure the rotational barrier because of irreversible spectral changes which set in above *ca* 45°. These involved a shift of both H_c and H_{uc} resonances to lower field (δ 4.14 and δ 5.70, respectively) together with the appearance of a singlet at δ 1.80 for the methyl groups.

It was suspected that these changes might be due to chelation of the diene with accompanying liberation of free diene. Addition of free diene to a $CDCl_3$ solution of the complex at −30° gave rise to a spectrum which was a simple combination of the individual constituents. On warming the solution to 40° the resulting spectrum comprised a singlet at δ 1.77 for the methyl groups, and merged resonances at δ 5.67 and δ 4.48 for the olefin protons. This indicates slow intermolecular exchange at –30° and rapid exchange at 40°. Thus, the increased exchange rate upon addition of free diene suggests a bimolecular (associative) mechanism, as indeed is to be expected for such '16-electron' complexes. The non-reversible changes in the ^{1}H nmr spectrum of this complex in the absence of added diene, being quantitatively similar to those observed in its presence, may result from chelation of the 4-methyl-penta-1,3-diene ligand with accompanying release of one or more free diene molecules (see Scheme). Two types of product are possible, the di-μ-chlorocomplexes (2) or (3), and the mononuclear halogen bridge-cleaved species (4) or (5). The non-reversibility of the exchange process may then stem from the partial decomposition of any of these chelated diene complexes. Considerable intramolecular steric interaction is to be expected for complexes containing this diene coordinated as a bidentate because of the presence of the *anti*-methyl group. Although a stable complex of this type containing the η^5-cyclopentadienyl group as counter ligand has been prepared,[32] di-μ-chloro complexes of Rh(I) generally have lower thermal stability.

An alternative explanation of the non-reversible changes in the spectra in terms of diene isomerisation to *trans*-2-methylpenta-1,3-diene, observed previously[33] in various inert solvents at temperatures above *ca* 70°, is rejected because of the lack of agreement of the observed spectra with that expected for this reaction.

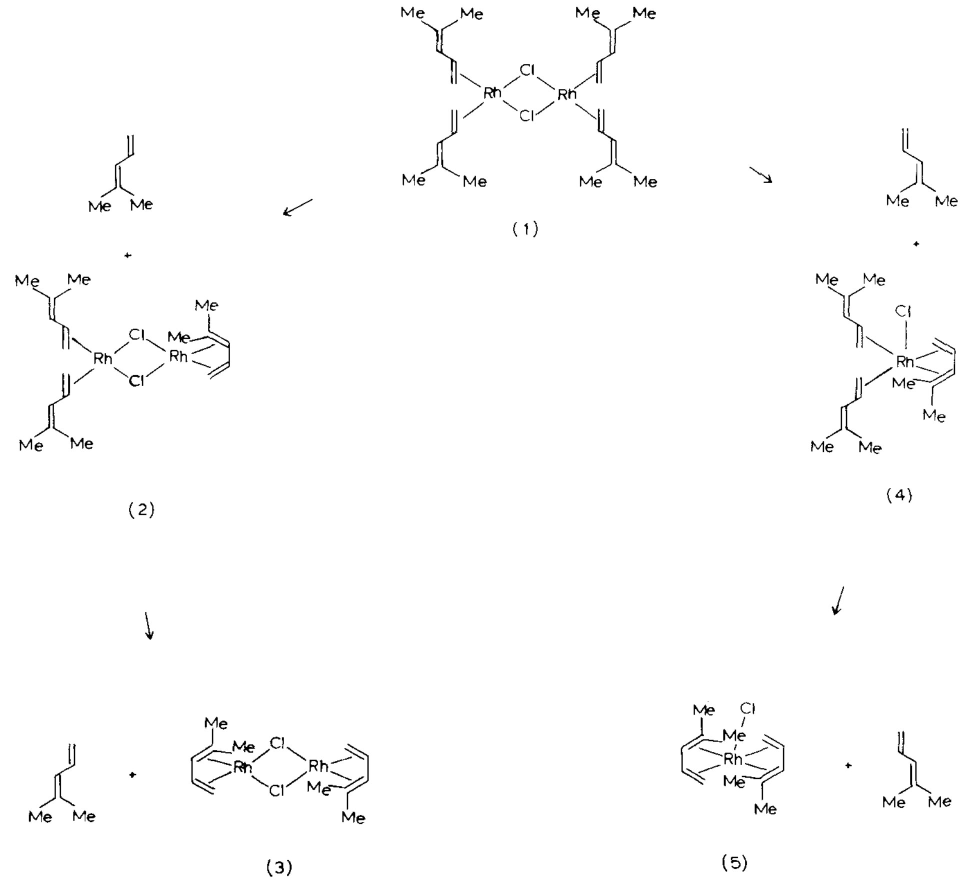


TABLE III

Relative abundances, principal positive ions and metastable transitions (m*) in $[L_2M(\eta^5\text{-}C_5H_5)]$ complexes.

$L = C_2H_4$, Relative Abundances			L = CO, Relative Abundances		
Ion	M = Rh	M = Ir	Ion	M = Rh	M = Ir
$[(C_2H_4)_2M\,cp]^+$	19.0	42.0	$[(CO)_2Mcp]^+$	30.3	58.0
$[(C_2H_4)Mcp]^+$	39.6	37.6	$[(CO)Mcp]^+$	39.0	31.0
$[(C_2H_2)Mcp]^+$	a	100.0	$[Mcp]^+$	100.0	100.0
$[Mcp]^+$	100.0	34.3	$[MC_3H_3]^+$	30.0	21.0
$[MC_3H_3]^+$	17.4	11.0	$[M(CO)]^+$	3.3	a
$[MC_2H_2]^+$	a	2.6	$[MC]^+$	12.0	a
$[MC]^+$	3.5	1.4	$[M]^+$	18.0	a

Metastable Transitions			Neutral fragment lost	m* Rh	m* Ir[b]
$[L_2Mcp]^+$	→	$[LMcp]^+ + L$	C_2H_4 or CO	171.5	260.5
$[LMcp]^+$	→	$[Mcp]^+ + L$	C_2H_4 or CO	144.0	232.7
$[(C_2H_2)Mcp]^+$	→	$[Mcp] + C_2H_2$	C_2H_2		234.4
$[Mcp]^+$	→	$[MC_3H_3] + C_2H_2$	C_2H_2	120.0	208.6
$[Mcp]^+$	→	$[M^+] + C_5H_5$	C_5H_5	63.1	

[a] Ions having less than 1% abundance are not recorded, sample heater temperature, 60–80°; ionization chamber temperature 90–110°. [b] Refers to ^{193}Ir isotope.

Mass Spectra

Table III lists the relative abundances and main processes involved in the fragmentation of the $[(C_2H_4)_2Mcp]$ and $[(CO)_2Mcp]$ complexes (M = Rh or Ir). The m/e values quoted in the Tables and in the text for ions containing iridium refer to ^{193}Ir. All relative abundances refer to an arbitrary value 100 chosen for the base peak in each spectrum. Experimental conditions were made as near identical as possible for the four compounds and the results show that the Ir(I) complexes are more stable than their Rh(I) analogues. This is the expected result for the ethylene complexes on the basis of the findings of Brown and Fitzpatrick.[34]

In addition to the simple stepwise loss of olefin, as found for $[(C_2H_4)_2Rhcp]$, the corresponding Ir(I) complex also shows competitive olefin dehydrogenation under the same conditions. The base peak is $[(C_2H_2)Ircp]^+$ and the same type of behaviour is fond for the pentanedionate complex $[(C_2H_4)_2Irpd]$. Thus, loss of one olefin molecule gives $[(C_2H_4)Irpd]^+$ which then fragments by two competing processes. The major process involves loss of H_2 to give $[(C_2H_2)Irpd]^+$. This is followed by further competing processes, CO loss from the β-diketonate group being preferred to C_2H_2 loss.

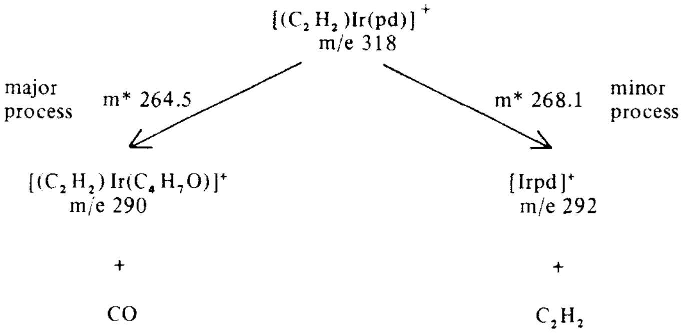


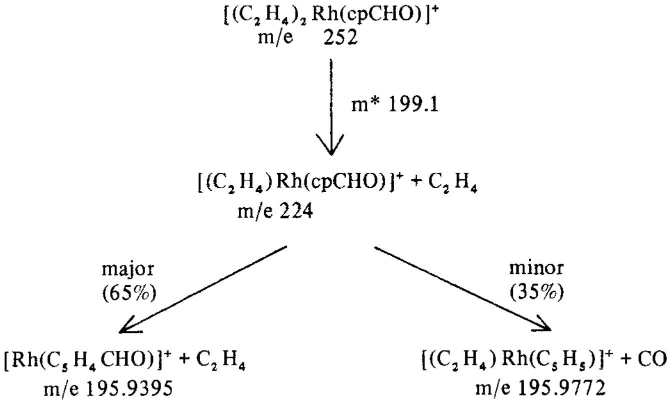
TABLE IV

Relative Abundancees (70eV), principal positive ions and metastable transitions (m*) in $[L_2Rh\,\eta^6C_5H_4CO_2CH_3]$ compounds.

Ion	Relative Abundances $L = C_2H_4$	$L = CO$	Metastable Transitions m* $L = C_2H_4$	$L = CO$	Process	Natural Fragment Lost
$[L_2RhcpCO_2Me]^+$	30.0	58.0				
$[LRhcpCO_2Me]^+$	62.0	88.0	228.8	228.7	$[L_2RhcpCO_2Me]^+ \rightarrow [LRhcpCO_2Me]^+$	L
$[L_2RhcpCHO]^+$	a	5.0				
$[RhcpCO_2Me]^+$	100.0	86.0	201.0	201.1	$[LRhcpCO_2Me]^+ \rightarrow [RhcpCO_2Me]^+$	L
$[LRhcpCHO]^+$	a	4.0				
$[RhcpCHO]^+$	34.0	58.0	169.9	169.9	$[RhcpCO_2Me]^+ \rightarrow [RhcpCHO]^+$	CH_2O
$[Rhcp]^+$	86.0	100.0	144.0	144.0	$[RhcpCHO]^+ \rightarrow [Rhcp]^+$	CO
$[RhC_3H_3]^+$	26.5	30.5	120.0	120.0	$[Rhcp]^+ \rightarrow [RhC_3H_3]^+$	C_2H_2
$[RhCO]^+$	a	5.0				
$[RhC]^+$	12.5	18.0				
$[Rh]^+$	18.7	16.0				

[a]Ions having less than 4% relative abundance are not recorded, sample heater temperature 60–80°, ionization chamber temperature 90–110°.

In contrast, the fragmentation of the corresponding Rh(I) complex involves sequential loss of the olefin ligands followed by CO loss from the pd chelate ring. This difference between the two metals is also seen in the fragmentation of the $[(C_2H_4)_2M(cpCHO)]$ complexes. For M = Rh, loss of one ethylene is followed by competition between loss of the second ethylene and CO loss from the counter ligand.



For $[(C_2H_4)_2Ir(cpCHO)]$ on the other hand, the most important fragmentation processes are, first, loss of a single ethylene followed by loss of H_2, and finally loss of CO to give $[(C_2H_2)Ir(C_5H_5)]^+$. These observations by high resolution and metastable peak analysis imply that the metal-olefin bonds are stronger in the iridium complexes, as concluded also from the results of the nmr study described above.

The relative abundances and fragmentation patterns for $[L_2Rh(\eta^5\text{-}C_5H_4COOCH_3)]$ ($L = C_2H_4$ or CO) are given in Table IV. The different fragmentation found for the *bis-*

carbonyl derivative suggests that it is the more stable. Some fragmentation of the cyclopentadienyl ring side chain competes with CO loss in $[(CO)_2Rh(cpCO_2Me)]$ whereas no significant fragmentation of the side chain occurs in the ethylene complex until after both olefin ligands are lost.

Appearance Potentials

The proposed processes and derived heats of formation for the principal ions formed in the fragmentation of $[(C_2H_4)_2Rhcp]$ and $[(CO)_2Rhcp]$ are given in Table V. Heats of formation used in these calculations are $[Rh]^+$, 1285[35]; C_2H_4, 51.9[36]; CO, −110.4[36]; C_2H_2, 226.8[36]; C_3H_3, 351.5[37]; and C_5H_5, 209.2[38] kJ mol^{-1}. On the assumption that no excess energy is involved in the fragmentation to the metal ion and that the resulting neutral fragments are formed in their ground states, the heats of formation (ΔH_f) of $[(C_2H_4)_2Rhcp]$ and $[(CO)_2Rhcp]$ are calculated to be −91 and −319 kJ mol^{-1}, respectively. These values may be compared with those obtained by Winters and Kiser[39] for $[(CO)_2Cocp]$ ($\Delta H_f = -62.8$ kJ mol^{-1}) and $[(CO)_3Mncp]$ ($\Delta H_f = -280.3$ kJ mol^{-1}). It is noteworthy however, that a more recent calorimetric study of $[(CO)_2Cocp]$ and $[(CO)_3Mncp]$ gave values for the standard heats of formation (ΔH_f°) of −169 and −478 kJ mol^{-1} respectively.[40]

From the data in Table V the heat of reaction for the reaction (*2*)

$$[Rhcp]^+_{(g)} = [Rh]^+_{(g)} + cp_{(g)} \qquad (2)$$

may be evaluated to give the bond strength $D_{(Rh-cp)^+}$. Values of 492 and 453 kJ mol^{-1} are obtained from the data pertaining to $[(C_2H_4)_2Rhcp]$ and $[(CO)_2Rhcp]$, respectively. The discrepancy presumably reflects uncertainty inherent in the method. Values obtained for the dissociation energies in metallocenes $D_{(M-cp)}$ range from 301.2 kJ mol^{-1} in $[Mncp_2]$ to 470 kJ mol^{-1} in $[Rucp_2]$.[41]

Data for the dissociation (*3*),

$$[L_2Rhcp]^+_{(g)} = [LRhcp]^+_{(g)} + L_{(g)} \qquad (3)$$

for which ΔH_{react} represents the bond strength D_{Rh-L}, give values of 132 kJ mol^{-1} for $[(C_2H_4)_2Rhcp]$ and 145 kJ mol^{-1} for $[(CO)_2Rhcp$. Cramer[42] has estimated a maximum value of 130 kJ mol^{-1} for $D_{[Rh-(C_2H_4)]}$ in $[(C_2H_4)_2Rhcp]$ from gas phase pyrolysis studies, while Brown, Connor and Skinner[43] have given an average value of 163 kJ mol^{-1} for $D_{[Rh-CO]}$ from studies of the thermal decompositions of $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}$. Vrieze and co-workers found a corresponding difference of 32 kJ mol^{-1}

TABLE V

Appearance potentials of the principal positive ions formed from $[L_2Rhcp]$ complexes.

m/e	Appearance potential ± 0.2 eV		Proposed Process	ΔH_f(ion) kJ mol^{-1}	
	L = C_2H_4	L = CO		L = C_2H_4	L = CO
224	7.9	8.6	$[L_2Rhcp] \rightarrow [L_2Rhcp]^+$	671	510
196	9.3	10.1	$\rightarrow [LRhcp]^+ + L$	754	765
168	12.4	11.8	$\rightarrow [Rhcp]^+ + 2L$	1001	1040
142	16.4	15.6	$\rightarrow [RhC_3H_3]^+ + C_2H_2 + 2L$	1160	1180
103	17.5	16.5	$\rightarrow [Rh]^+ + C_5H_5 + 2L$	−91[e]	−319[a]

[a] heat of formation of $[L_2Rhcp]$ ± 20 kJ mol^{-1}.

from a calorimetric study of $[(C_2H_4)_2Rhpd]$ and $[(CO)_2Rhpd]$.[28] However, dissociation enthalpies are not expected to remain unchanged on alteration of the counter ligand.

The alternative process, (*4*),

$$[L_2Rhcp]^+_{(g)} \rightarrow [Rh]^+_{(g)} + C_3H_{3(g)} + C_2H_{2(g)} + 2L_{(g)} \qquad (4)$$

for the formation of $[M]^+$ has been considered. This leads to values of $D_{(Rh-cp)}$ of 84 and 123 kJ mol^{-1} for $[(CO)_2Rhcp]$ and $[(C_2H_4)_2Rhcp]$, respectively, and $D_{(Rh-L)}$ of 135 and 145 kJ mol^{-1} for $[(C_2H_4)_2Rhcp]$ and $[(CO)_2Rhcp]$, respectively. This fragmentation process is rejected on the grounds that large positive values for the heats of formation of both compounds result, a fact at variance with their known stability. Moreover, this analysis requires that the Rh-(C_2H_4) and Rh-(CO) bonds are stronger than the Rh-cp bond which cannot be true.

ACKNOWLEDGEMENTS

We thank Dr. T.R. Spalding of University College, Cork, for helpful comment, and Dr. A. Wade and Mr. G. Jordan for experimental assistance.

REFERENCES

1. H. Alt, M. Herberhold, C.G. Kreiter and H. Strack, *J. Organometallic Chem.*, **77**, 353 (1974).
2. J.W. Faller and B.V. Johnson, *J. Organometallic Chem.*, **98**, 101 (1975).
3. D.L. Reger and C.J. Coleman, *Inorg. Chem.*, **18**, 3270 (1979).
4. H. Alt, J.A. Schwarzle and C.G. Kreiter, *J. Organometallic Chem.*, **153**, C7 (1978).
5. B.F.G. Johnson and J.A. Segal, *Chem. Comm.*, 1312 (1972).
6. R. Cramer and J.J. Mrowca, *Inorg. Chim. Acta*, **5**, 528 (1971).
7. J. Kriz and K. Bouchal, *J. Organometallic Chem.*, **64**, 255 (1974).
8. J. Ashley-Smith, Z. Douek, B.F.G. Johnson and J. Lewis, *J.C.S. Dalton*, 128 (1974).
9. K.S. Wheelock, J.H. Nelson, L.C. Cusachs and H.B. Jonassen, *J. Amer. Chem. Soc.*, **92**, 5110 (1970).
10. R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964).
11. R. Cramer, J.B. Kline and J.D. Roberts, *J. Amer. Chem. Soc.*, **91**, 2519 (1969).
12. R.B. King, *J. Organometallic Chem.*, **14**, 19 (1968).
13. I.M.T. Davidson, M. Jones and R.D. Kemmitt, *J. Organometallic Chem.*, **17**, 169 (1969).
14. D. Haegele, V. Schurig and D.M. Desiderio, *Inorg. Chem.*, **13**, 1960 (1974).
15. M. Arthurs, S.M. Nelson and M.G.B. Drew, *J.C.S. Dalton*, 779 (1977).
16. E.C. Taylor, G.W. Lacy and A. McKillop, *J. Amer. Chem. Soc.*, **90**, 2421 (1968).
17. F. Hartman, P.L. Jacoby and A. Wojcicki, *Inorg. Synth.*, **12**, 82 (1970).
18. M. Arthurs, M. Sloan, M.G.B. Drew and S.M. Nelson, *J.C.S. Dalton*, 1794 (1975).
19. R.N. Hazeldine, R.J. Lunt and R.V. Parish, *J. Chem. Soc. (A)*, 3696 (1971).
20. R. Cramer, *J. Amer. Chem. Soc.*, **89**, 4621 (1967).
21. A.L. Van Geet, *Anal. Chem.*, **42**, 679 (1970).
22. J.W. Warren, *Nature*, **165**, 811 (1950).
23. M.F. Lappert, M.R. Litzow, J.P. Pedley, P.N.K. Riley and A. Tweedale, *J. Chem. Soc. (A)*, 3105 (1968).
24. F.P. Lossing, A.W. Tickner and A.W. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).
25. G.G. Dvoryantseva, S.L. Portnova, K.I. Grandberg, S.P. Gubin and Y.N. Sheinker, *Doklady Akad. Nauk. S.S.S.R.*, **160**, 1075 (1965).
26. K. Moseley, J.W. Kang and P.M. Maitlis, *J. Chem. Soc. (A)*, 2875 (1970).
27. A.L. Onderdelinden and A. van der Ent, *Inorg. Chim. Acta*, **6**, 420 (1972).
28. A.C. Jesse, A. Baks, J. Stufkens and K. Vrieze, *Inorg. Chim. Acta*, **29**, 177 (1978).
29. M. Herberhold, C.G. Kreiter and G.O. Wiedersatz, *J. Organometallic Chem.*, **120**, 103 (1976).
30. R. Cramer and G.S. Reddy, *Inorg. Chem.*, **12**, 346 (1973).
31. C.E. Holloway, G. Hulley, B.F.G. Johnson and J. Lewis, *J. Chem. Soc. (A)*, 1653 (1970).

32. M.G.B. Drew, S.M. Nelson and M. Sloan, *J.C.S. Dalton*, 1484 (1973).
33. M. Arthurs, C.M. Regan and S.M. Nelson, *J.C.S. Dalton*, 2053 (1980).
34. D.A. Brown and N. Fitzpatrick, *J. Chem. Soc. (A)*, 315 (1967).
35. W.H. Evans et al, *"Selected Values of Chemical Thermodynamic Properties"*, Natl. Bur. Std., *Washington D.C.*, 1969.
36. F.D. Rossini *et al.*, *"Selected Values of Chemical Thermodynamic Properties"*, *ibid*, 1952.
37. J.B. Farmer and F.P. Lossing, *Canad. J. Chem.*, **33**, 861 (1955).
38. F.A. Cotton and G. Wilkinson, *J. Amer. Chem. Soc.*, **74**, 5764 (1952).
39. R.E. Winters and R. Kiser, *J. Organometallic Chem.*, **4**, 19 (1965).
40. J.R. Chipperfield, J.C.R. Sneyd and D.E. Webster, *J. Organometallic Chem.*, **178**, 177 (1979).
41. T.R. Spalding, *"Spectroscopic Methods in Organometallic Chemistry"*, (W.O. George, Ed.), *London*, Butterworths, p. 129, 1970.
42. R. Cramer, *J. Amer. Chem. Soc.*, **94**, 5681 (1972).
43. D.L.S. Brown, J.A. Connor and H.A. Skinner, *J.C.S. Faraday Trans.*, **71**, 699 (1975).