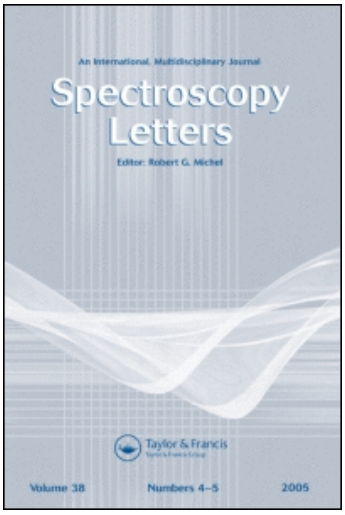

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

The Infrared Spectra of Rhenium Pentamethyl Cyclopentadienyl Complexes: (η^5-C_5Me_5)$Re(CO_3)$ and [(η^5-C_5Me_5)$Re(CO)_3X$] (X=Cl, Br, I)

Guillermo Diaz[a]; A. Hugo Klahn[b]
[a] Facultad de Ciencias, Universidad de Playa Ancha, Valparaiso, Chile [b] Instituto de Quimica, Universidad Catolica de Valparaiso, Valparaiso, Chile

To cite this Article Diaz, Guillermo and Klahn, A. Hugo(1990) 'The Infrared Spectra of Rhenium Pentamethyl Cyclopentadienyl Complexes: (η^5-C_5Me_5)$Re(CO_3)$ and [(η^5-C_5Me_5)$Re(CO)_3X$] (X=Cl, Br, I)', Spectroscopy Letters, 23: 1, 87 — 109
To link to this Article: DOI: 10.1080/00387019008054038
URL: http://dx.doi.org/10.1080/00387019008054038

SPECTROSCOPY LETTERS, 23(1), 87-109 (1990)

THE INFRARED SPECTRA OF RHENIUM PENTAMETHYL CYCLOPENTADIENYL COMPLEXES: $(\eta^5\text{-}C_5Me_5)Re(CO_3)$ AND $[(\eta^5\text{-}C_5Me_5)Re(CO)_3X]^+$ (X = Cl, Br, I)

Keywords: Infrared spectra, Band assignments, Force constants, $(\eta^5\text{-}C_5Me_5)Re(CO)_3$, $[(\eta^5\text{-}C_5Me_5)Re(CO)_3X]^+$

Guillermo Diaz

Universidad de Playa Ancha, Facultad de Ciencias, Casilla 34-V, Valparaiso, Chile

and

A. Hugo Klahn

Instituto de Quimica, Universidad Catolica de Valparaiso Casilla 4059, Valparaiso, Chile

ABSTRACT

The IR spectra of the title compounds are recorded and an assignment of the normal modes in terms of local symmetry is suggested by comparison with those observed in analogous molecules. A set of force constants calculated for simplified models confirms most of the

experimental assignments and reflects the symmetry of the complexes under study. The f_{CO} of the two different CO groups in the cationic complexes indicated that CO groups cis to the halide ligand should be more selective towards nucleophiles.

INTRODUCTION

Most of the vibrational studies in π-olefin metal carbonyl complexes of the type (olefin)$M(CO)_n$, have been done in complexes containing the cyclopentadienyl ligand, Cp = (η^5-C_5H_5). For many years, the vibrational study of $CpMn(CO)_3$ by Hyams, Bailey and Lippincott[1] has been used as reference for interpretation of other related molecules. Pioneering studies have also been performed by Parker et al.[2-4] and Adams et al.[5], who made a critical survey of the IR and Raman spectra of a number of Cp and methylcyclopentadienyl metal carbonyl derivatives. A detailed study of the CO stretching region for these type of compounds has been performed by Butler and Fenster[6] by using ^{13}CO and $C^{18}O$ enriched species. The proposed vibrational assignments were supported by force constant calculations for the energy factored CO stretching blocks of the (FG) matrices.

In cyclopentadienyl rhenium complexes, Lokshin et al.[7] have studied the IR and Raman spectra of $CpRe(CO)_3$ complex. They made an assignment of the normal modes and approximate force constant calculations, considering a pyramidal structure of the type AB_3 for this complex.

More recently, in our laboratory, a vibrational study of the dicarbonyldihalide rhenium complexes containing the pentamethylcyclopentadienyl ligand $Cp^*Re(CO)_2X_2$, (Cp^* = η^5-C_5Me_5, X = Cl, Br and I) was published.[8] We suggested an assignment of the normal modes in terms of the local symmetry. Furthermore, using a modified general valence force field, we performed a normal coordinate analysis, considering simplified models for these complexes. Now, we wish to report a vibrational study of the rhenium cationic complexes $[Cp^*Re(CO)_3X]^+$ (X = Cl, Br and I), with the aim to establish a relationship between the CO force constant and the observed reactivity of these cations towards nucleophiles.[9] We also include in this work a vibrational analysis of the neutral $Cp^*Re(CO)_3$ complex. In addition, we hope to validate the method of local symmetry[10-12] for metal carbonyl complexes, by comparing the number of observed and calculated frequencies.

EXPERIMENTAL

The complexes $Cp^*Re(CO)_3$ and $[Cp^*Re(CO)_3X]^+$ (X = Cl, Br and I), were prepared according to literature procedures[8,13,14] and crystallized from adequate organic solvents. IR spectra were measured using a Perkin-Elmer 599-B instrument in CH_2Cl_2 solution (KBr cells) and in solid state (KBr disc), in the 4000-200 cm^{-1} region. The instrument was calibrated against polystyrene.

RESULTS

a) Vibrational Assignment

The IR spectra of the complexes under study show no serious difference in solid state or in solution. The observed frequencies and the assignments are listed in Table 1.

In Table 2 we have summarized the symmetry of the fragments and the distribution of the corresponding normal modes into irreducible representations of the distinct point groups. Fragments from A) to C) are common for $Cp^*Re(CO)_3$ and $[Cp^*Re(CO)_3X]^+$. The frequencies assignment of these groups has been performed according to those reported in Ref. 8, i.e., bands at ~ 3000 cm^{-1}, ~ 1500 cm^{-1} and ~ 1000 cm^{-1} are ascribed to normal modes of the methyl groups: $\nu(CH)$, $\delta(CH_2)$ and $\rho(CH_3)$, while those at ~ 1400 cm^{-1} and ~ 1100 cm^{-1} are assigned to $\nu(CC)$ and ring breathing vibrations, respectively. Furthermore, the in-plane and out-of-plane bending normal modes: $\delta(CMe)$ and $\gamma(CMe)$, are placed below 400 cm^{-1}. The frequencies due to the ring tilt and Cp^*-Re stretching are customarily found in the 400-300 cm^{-1} region.

For the $Re(CO)_3$ and $Re(CO)_3X$ fragments, the assignment mainly follows that given for $CpRe(CO)_3$[7] and $Cp^*Re(CO)_2X_2$[8], where the CO stretching modes are observed in the 2100-1900 cm^{-1} region, the Re-C stretching vibration between 550-400 cm^{-1}, the Re-CO linear bending modes at ca. 600 cm^{-1} and the C-Re-C and

TABLE 1.

Observed Frequencies (in cm^{-1}) and Assignments for $Cp^*Re(CO)_3$ and $[Cp^*Re(CO)_3X]^+$ (X = Cl, Br, I).

$Cp^*Re(CO)_3$		$[Cp^*Re(CO)_3X]^+$			
	Assignment	Cl	Br	I	Assignment
3000w		3050w	3060w	3060w	
2925mw	ν(CH)E	2995mw	3000mw	3000mw	ν(CH)E
2880w	ν(CH)A_1	2960w	2955w	2960w	ν(CH)A_1
2000s	ν(CO)A_1	2125s	2120s	2100s	ν(CO)A'
		2070s	2060s	2040s	ν(CO)A"
1900s	ν(CO)E	2040sh	2030sh	2020sh	ν(CO)A'(T)
1490mw		1480mw	1495mw	1490mw	
1480mw	$\delta(CH_2)$			1475w	$\delta(CH_2)$
1455mw		1460mw	1450mw	1455mw	
1430mw		1420mw	1420mw	1425mw	
1390ms	ν(CC)E_1'	1385ms	1380ms	1385ms	ν(CC)E_1'
1190w	ν(CMe)	1200vw	1210vw	1210vw	ν(CMe)
1085w	Ring Breathing	1080w	1085w	1090w	Ring Breathing
1040ms	$\rho(CH_3)$	1030ms	1030ms	1035ms	
		1010sh	1015sh	1020sh	$\rho(CH_3)$

(continued)

TABLE 1 (continued)

$Cp^{*}Re(CO)_3$		$[Cp^{*}Re(CO)_3X]^{+}$			
	Assignment	Cl	Br	I	Assignment
620sh		600sh	600sh	600sh	
600s	$\delta(ReCO)A_1,E$	590w	590w	585w	$\delta(ReCO)$
550w		585sh	580sh	580sh	A',A"
		580sh	560sh	570sh	T or cis
520ms		560m	550m	560m	
510sh	$\nu(ReC)A_1,E$	540sh	540sh	545sh	
500sh					
		510m	510m	520m	$\nu(ReC)$
435ms	$\nu(ReC)$?	500sh	505sh	500sh	A',A"
		480m	485m	480m	T or cis
400sh		405mw	405mw	400	
	Ring Tilt	395sh	390sh	390	Ring Tilt
380w		390sh	385sh		
290w	$\nu(Cp^{*}Re)$	340m			$\nu(ReCl)$?
		290w	295w	290w	$\nu(Cp^{*}Re)$
245w	$\delta(CMe)$ or	240w	245w	240w	$\delta(CMe)$ or
215w	$\gamma(CMe)$	210w	210w	215w	$\gamma(CMe)$

T = Carbon trans to halide

TABLE 2

Symmetries of the Normal Modes for the Different Fragments of $Cp^*Re(CO)_3$ and $[Cp^*Re(CO)_3X]^+$.

A) CH_3 vibrations (C_{3v} symmetry)	
ν(CH)	
$\delta(CH_2)$	A_1 (IR/R) + E (IR/R)
$\rho(CH_3)$	
B) Cp^* vibrations (D_{5h} symmetry)	
ν(CMe)[a]	
ν(CC)	
δ(CMe)	A_1' (R) + E_1' (IR) + E_2' (R)
γ(CMe)	
δ(CC)	
γ(CC)	E_2' (R)
C) Cp^*-Re vibrations (C_{5v} symmetry)	
$\nu(Cp^*$ Re)	A_1 (IR/R)
Cp^* tilt	E_1 (IR/R)
Cp^* o.o.p	E_2 (R)
D) Cp^*-$Re(CO)_3$ vibrations (C_{3v} symmetry)	
ν(CO)	
ν(ReC)	A_1 (IR/R) + E (IR/R)
δ(CReC)	

(continued)

TABLE 2 (continued)

δ(ReCO)	A_1 (IR/R) + A_2 (-) + 2 E (IR/R)
δ(Cp*ReCO)	E (IR/R)
E) Cp^{*}-$Re(CO)_3X^{b}$ vibrations (C_s symmetry)	
ν(ReX)	
ν(ReC) T	A' (IR/R)
ν(ReC)	A' (IR/R) + A" (IR/R)
δ(CReX) T	
δ(Cp*ReC) T	A' (IR/R)
δ(Cp*ReX)	
δ(Cp*ReC)	
δ(CReX)	A' (IR/R) + A" (IR/R)
ν(CO) T	A' (IR/R)
ν(CO)	A' (IR/R) + A" (IR/R)
δ(ReCO) T	
δ(ReCO) T $\perp$	A' (IR/R)
δ(ReCO)	
δ(ReCO)$\perp$	A' (IR/R) + A" (IR/R)

[a] Me, Methyl group taken as point mass

[b] Cp* taken as point mass

T Carbon trans respect to X

$\perp$ Perpendicular deformation

Cp^*-Re-C bending vibrations below 200 cm^{-1}. In this region is also expected to find those normal modes involving the halide ligand: ν(ReX), δ(CReX) and $\delta(Cp^*ReX)$, with the only exception of the ReCl stretching vibration, which is currently located at ca. 300 cm^{-1}.

Previously, it has been observed that the CO stretching frequencies of metal carbonyls show a marked dependence on the formal charge of the metal atoms[15-18], and the increase of ca. 100 cm^{-1} per unit positive charge has been explained in terms of changes in the CO bond order. Consequently, we have observed a shift to higher energy in the cationic halide derivatives in comparison to $Cp^*Re(CO)_3$. On the other hand, the two CO stretching vibrations for $Cp^*Re(CO)_3$ are found at lower energy than those reported in Ref. 7 for $CpRe(CO)_3$ (2020-1930 cm^{-1}). The difference can be explained considering the electron donating ability of the methyl substituent in the ring, which should increase the electron density on the metal and further increase the ReCO bond order as compared with unsubstituted complex. This trend has also been observed in the spectra of $(C_6H_6)Cr(CO)_3$ and $(C_6Me_6)Cr(CO)_3$.[19]

For $[Cp^*Re(CO)_3X]^+$ we observe a splitting of the CO band at lower energy, as a consequence of the non-equivalent nature of the CO bonds in this type of complexes. The frequencies recorded in the present work

for the chloride derivative are in good agreement with those reported by King[20] for $[CpRe(CO)_3Cl]^+$ (2110 m, 2040 s and 2020 w cm^{-1}). These frequencies have been assigned to the two A' and one A'' modes considering data reported for related compounds.[21] Accordingly, the highest ν(CO) frequency is assigned to one of the A' modes. The lowest and relatively close ν(CO) are then assigned to the A' and A'' modes. Because force constants of the CO trans to halide ligands are smaller than those of CO groups trans to each other[22-24], we ascribed the band at lowest energy to the A' mode involving the CO group trans to X. This is presumably a result of increased M-C π-bonding in trans position to a poorly π-bonding ligand such as a halide.[25]

On the other hand, also by symmetry reasons, it is expected to find three bands corresponding to the ReCO linear bendings for $Cp^*Re(CO)_3$ (A + 2E), while six bands should be observed for the cationic halide derivatives (4A' + 2A''). These frequencies have been identified in the spectra of the complexes under study, but the symmetry assignment cannot be done without further theoretical analysis.

b) Normal Coordinate Analysis

In order to carry out a normal coordinate treatment on the molecules under study, we have used simplified models to account for most of the uncertain experimental assignments. They have been taken from the $Re(CO)_3$ and

$Re(CO)_3X$ moieties, including the Cp^* ring as a point mass.

The molecular parameters used to build the G matrix[26] have been transferred from those reported for $Cp^*Re(CO)_2X_2$[14], $CpMo(CO)_3Cl$[27] and $(C_6H_6)Cr(CO)_3$.[28] These values have been modified slightly, in order to match the C_3v and C_s point groups adopted for the $Re(CO)_3$ and $Re(CO)_3X$ moieties, respectively. Internal coordinates for these models are shown in Figure 1, while in Table 3 the corresponding symmetry coordinates are listed.

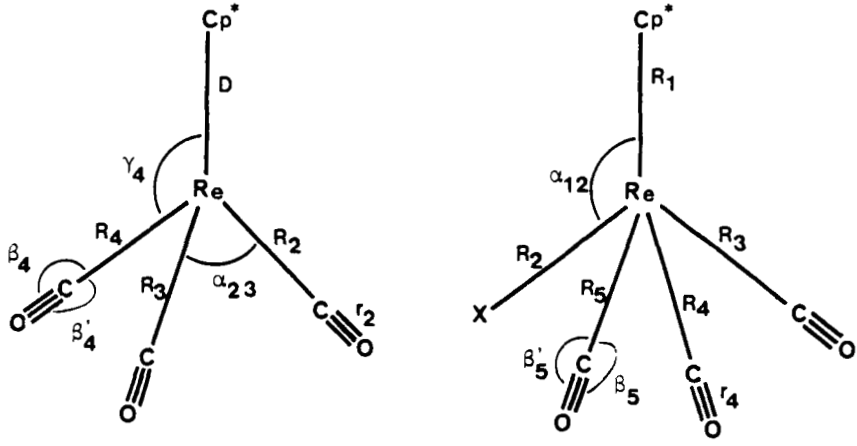

Fig. 1. Simplified Models and internal coordinates for $Cp^*Re(CO)_3$ and $[Cp^*Re(CO)_3X]^+$, where Cp^* has been taken as a point mass.

TABLE 3.

Symmetry Coordinates for the Simplified Models.

a) $Cp^{\bullet}Re(CO)_3$ (C_{3v})

Species:

A_1

$$S_1 = \frac{1}{\sqrt{3}} (r_2 + r_3 + r_4)$$

$$S_2 = D$$

$$S_3 = \frac{\sqrt{R\,r}}{\sqrt{3}} (\beta_2 + \beta_3 + \beta_4)$$

$$S_4 = \frac{1}{\sqrt{3}} (R_2 + R_3 + R_4)$$

$$S_5 = \frac{\sqrt{D\,R}}{\sqrt{6}} (\alpha_{23} + \alpha_{24} + \alpha_{34} - \gamma_2 - \gamma_3 + \gamma_4)$$

A_2

$$S_6 = \frac{\sqrt{R\,r}}{\sqrt{3}} (\beta_2' + \beta_3' + \beta_4')$$

E

$$S_7 = \frac{1}{\sqrt{6}} (2\,r_2 - r_3 - r_4)$$

$$S_8 = \frac{\sqrt{R\,r}}{\sqrt{6}} (2\,\beta_2 - \beta_3 - \beta_4)$$

$$S_9 = \frac{\sqrt{R\,r}}{\sqrt{2}} (\beta_3' - \beta_4)$$

$$S_{10} = \frac{1}{\sqrt{6}} (2\,R_2 - R_3 - R_4)$$

TABLE 3 (continued)

$$S_{11} = \frac{R}{\sqrt{6}} (2\alpha_{34} - \alpha_{23} - \alpha_{24})$$

$$S_{12} = \frac{\sqrt{D\,R}}{\sqrt{6}} (2\gamma_2 - \gamma_3 - \gamma_4)$$

b) $Cp^* ReCO)_3X$ (C_s)

Species:

A'

$$S_1 = R_1$$

$$S_2 = R_2$$

$$S_3 = R_3$$

$$S_4 = \frac{1}{\sqrt{2}} (R_4 + R_5)$$

$$S_5 = \sqrt{R_3R_2}\ \alpha_{23}$$

$$S_6 = \sqrt{R_1R_3}\ \alpha_{13}$$

$$S_7 = \sqrt{R_1R_2}\ \alpha_{12}$$

$$S_8 = \frac{\sqrt{R_1R_5}}{\sqrt{2}} (\alpha_{15} + \alpha_{14})$$

$$S_9 = \frac{\sqrt{R_4R_2}}{\sqrt{2}} (\alpha_{42} + \alpha_{52})$$

(continued)

TABLE 3 (continued)

	$S_{10} = r_3$
	$S_{11} = \frac{1}{\sqrt{2}} (r_4 + r_5)$
	$S_{12} = \sqrt{R_3 r_3}\ \beta_3$
	$S_{13} = \sqrt{R_3 r_3}\ \beta_3'$
	$S_{14} = \frac{\sqrt{R_4 r_4}}{\sqrt{2}} (\beta_4 + \beta_5)$
	$S_{15} = \frac{\sqrt{R_4 r_4}}{\sqrt{2}} (\beta_4' + \beta_5')$
A"	$S_{16} = \frac{1}{\sqrt{2}} (R_4 - R_5)$
	$S_{17} = \frac{\sqrt{R_1 R_5}}{\sqrt{2}} (\alpha_{15} - \alpha_{14})$
	$S_{18} = \frac{\sqrt{R_4 R_2}}{\sqrt{2}} (\alpha_{42} - \alpha_{52})$
	$S_{19} = \frac{1}{\sqrt{2}} (r_4 - r_5)$
	$S_{20} = \frac{\sqrt{R_4 r_4}}{\sqrt{2}} (\beta_4 - \beta_5)$
	$S_{21} = \frac{\sqrt{R_4 r_4}}{\sqrt{2}} (\beta_4' - \beta_5')$

TABLE 4.

Internal Force Constants (mdyn x A^{-1})

$Cp^*Re(CO)_3$	$[Cp^*Re(CO)_3X]^+$
$f_{CO} = 15.1$	$f_{ReX} = 1.65(Cl), 1.55(Br), 1.35(I)$
$f_{CO,CO} = 0.2$	$f_{ReC} = 3.85(T), 3.35(cis)$
$f_{Cp^*Re} = 3.3$	$f_{Cp^*Re} = 3.3$
$f_{ReCO} = 0.455$	$f_{CReX} = 0.21(T), 0.23(cis)$
$f_{ReCO,ReCO} = 0.025$	$f_{Cp^*ReC} = 0.23(T), 0.19(cis)$
$f_{ReC} = 3.6$	$f_{Cp^*ReX} = 0.28$
$f_{CReC} = 0.15$	$f_{Cp^*ReC,Cp^*ReC} = 0.05$
$f_{Cp^*ReC} = 0.12$	$f_{CReX,CReX} = 0.02$
	$f_{CO(T)} = 15.5(Cl), 15.3(Br), 15.2(I)$
	$f_{CO(cis)} = 16.15(Cl), 16.03(Br), 16(I)$
	$f_{CO,CO} = 0.15$
	$f_{ReCO(T)} = 0.45$
	$f_{ReCO(cis)} = 0.41$
	$f_{ReCO,ReCO} = 0.03$

The force constants calculations were not carried out with the intention of determining a reliable force field. The uncertainty in geometrical parameters and, in some cases assignments, does not permit this assumption.

However, it allows us to make an approximation to the extent of coupling between vibrations. It is also useful in finding out the relative order of vibrational modes. In this sense, we have used a modified general valence force field (MGVFF), which emphasizes the diagonal elements of the symmetrized F matrix.

The initial values of the valence force constants have been transferred from those reported for $Cp^*Re(CO)_2X_2$[8], and related molecules.[7,17,29-33] Some of these values have been slightly modified to account for the most certain experimental assignments. The final

TABLE 5.

Calculated Vibrational Frequencies (cm^{-1}) and PED for $Cp^*Re(CO)_3$.

Symmetry	Frequencies	PED
A_1	2010	91% CO
	545	75% ReCO + 23% CReC
	515	91% ReC
	285	95% Cp^*Re
	125	74% CReC + 22% ReCO
E	1985	93% CO
	625	80% ReCO + 16% CReC
	605	90% ReCO ⊥
	505	92% ReC
	110	83% CReC + 14% ReCO
	81	94% Cp^*ReC

TABLE 6.

Calculated Vibrational Frequencies (cm^{-1}) and PED for $[Cp^*Re(CO)_3X]^+$ (X = Cl, Br, I).

Symmetry	Cl	Br	I	PED[a]
A'	2128	2118	2102	95% CO
	2037	2035	2018	97% CO(T)
	605	605	610	96% ReCO(T)
	590	595	595	95% ReCO(T) ⊥
	581	586	585	85% ReCO + 12% Cp^*ReC
	578	581	579	92% ReCO ⊥
	512	513	522	91% ReC(T)
	502	503	498	93% ReC
	282	291	285	80% Cp^*Re + 17% ReX
	325	195	180	73% ReX + 18% Cp^*Re
	109	105	109	55% CReX + 40% Cp^*ReX
	102	85	90	62% Cp^*ReX + 32% CReX(T)
	75	81	76	48% CReX + 45% Cp^*ReX
	60	65	62	58% $Cp^*ReC(T)$ + 30% Cp^*ReX + 12% CReX
	55	48	52	43% Cp^*ReC + 28% Cp^*ReX + 15% CReX(T)
A"	2065	2057	2037	95% CO
	553	557	563	86% ReCO + 15% Cp^*ReC
	546	543	539	90% ReCO ⊥
	475	473	478	95% ReC
	83	92	89	58% CReX + 30% Cp^*ReC
	50	49	52	62% Cp^*ReC + 25% CReX

[a] PED values are very similar for all three halide complexes. Only those calculated for $[Cp^*Re(CO)_3Cl]^+$ are listed.

force constants are given in Table 4. The frequencies calculated from this set are listed in Tables 5 and 6, where the theoretical assignments of the vibrations from the calculated potential energy distribution (PED) are also included.

DISCUSSION

The approximate force fields, essentially confirm the straightforward experimental assignments, with reasonable values of the internal force constants. This fact is a sign that the symmetries adopted for the simplified models are adequate to explain the observed spectra.

In addition, PED allows us to distinguish among the distinct symmetries of some vibrations when there is no experimental evidence available, or when the empirical assignments are controversial. Thus, for $Cp^*Re(CO)_3$ we ascribed the bands observed in the 620-600 cm^{-1} region to the E ReCO bending modes. This result confirms the assignment proposed for $CpMn(CO)_3$ by Parker[4] and Hyams[1] and contrast with the inverse assignment reported by Adams and Squire[5], based on Raman data for the same manganese complex. In this respect, Lokshin et al.[7] claim that this symmetry assignment is difficult because it is not possible to obtain polarization data of the observed bands in the Raman spectra due to their small intensity.

For the $[Cp^*Re(CO)_3X]^+$ complex, our calculations confirm the observed shift of the ReCO frequencies to lower energy in comparison with $Cp^*Re(CO)_3$. This shift has also been observed by Parker[4] in cyclopentadienyl molybdenum complexes. Furthermore, PED shows that the A' ReCO bending modes in trans position are those at higher energy.

With regard to the ReC stretching modes, our results for $Cp^*Re(CO)_3$ allow us to discard the assignment of the band at 435 cm^{-1} to one of these normal modes. The symmetry assignments: 520 (A'), 510 (E) and 500 (E) cm^{-1}, are in agreement with those proposed by Lokshin et al.[7] for $CpRe(CO)_3$. Also, PED for $[Cp^*Re(CO)_3X]^+$ demonstrates that the bands observed in the 510-500 cm^{-1} region belong to the A' species. Furthermore, the band at 510 cm^{-1} can be assigned to the Re-C stretching mode trans to the halide ligand.

The tentative assignment of the Cp^*-Re stretching vibration at ca. 290 cm^{-1}, has also been confirmed. The low value of this frequency in comparison with that reported for $CpRe(CO)_3$[7] can be attributed to the increased mass of the Cp^* ring. As expected, the calculated vibrations, ν(ReX), δ(CReC), $\delta(Cp^*ReC)$, δ(CReX) and $\delta(Cp^*ReX)$, have been found below 200 cm^{-1}, with the only exception of ν(ReCl) which was obtained at 325 cm^{-1}. The latter value would support the assignment of a medium band observed at 340 cm^{-1} to this normal mode. This rather high value, in comparison to that observed for $Re(CO)_5Cl$[17], presumably reflects the increase in oxidation state from Re(I) to Re(III). On the other hand, PED supports indirectly the assignments proposed for ring tilt, δ(CMe) and γ(CMe), since no bands have been calculated at ca. 400 cm^{-1} and in the 260-200 cm^{-1} region.

Finally, the $[Cp^*Re(CO)_3X]^+$ complexes show a decrease of the CO stretching frequencies in going from X = Cl to X =I. These frequencies have been reproduced quite well with our force constants, which are in good agreement with those calculated by King and Houk[24] using the Cotton and Kraihansel method[34], for the tricarbonylhalide complexes $CpMo(CO)_3X$ (X = Cl, Br). Furthermore, our force constants follow the same trend observed in the molybdenum complexes, that is, they decrease slightly in the order Cl > Br > I.

Based on f_{CO} values of the CO groups cis and trans to the halide ligand in these cationic complexes (Table 4) and, considering Angelici's predictions[35], that CO ligands with highest f_{CO} values are more susceptible to react with nucleophiles, it is expected that the more reactive carbonyl groups towards nucleophiles, such as alkoxide ions, are those oriented cis to the halide ligand. However, the isolated products from the reaction of $[Cp^*Re(CO)_3X]^+$ with nucleophiles showed a trans orientation of the remaining CO groups[9]. This result indicates that the cis attack can be viewed as a kinetic product which in turn isomerizes, thermally or photochemically, to the more stable trans isomer.

ACKNOWLEDGMENTS

G. Diaz thanks the Direccion de Investigacion, Universidad de Playa Ancha (Project CNEI 11889), FONDECYT (Grant 0623) and D.T.I. U. de Chile (Project Q

2815-8812). The support of this research by D.G.I., Universidad Catolica de Valparaiso and FONDECYT through operating grants to H.K.O., 125.720/88 and 155/89 respectively, are also appreciated.

REFERENCES

1. I.J. Hyams, R.T. Bailey and E.R. Lippincott, Spectrochim. Acta **1967**; 23A: 273.

2. D.J. Parker and M.H.B. Stiddard, J. Chem. Soc. (A) **1970**; 480.

3. D.J. Parker and M.H.B. Stiddard, J. Chem. Soc. (A) **1970**; 1040.

4. D.J. Parker, J. Chem. Soc. (A) **1970**; 1382.

5. D.M. Adams and A. Squire, J. Organomet. Chem **1973**; 63: 381.

6. I.S. Butler and A.E. Fenster, J. Organomet. Chem **1973**; 51: 307.

7. B.V. Lokshin, Z.S. Klemenkova and Yu.V. Makarov, Spectrochim. Acta **1972**; 28A: 2209.

8. G. Diaz, A.H. Klahn and C. Manzur, Polyhedron **1988**; 7: 2743.

9. A.H. Klahn and C. Manzur, submitted to Polyhedron.

10. F.A. Cotton, A.D. Liehr and G. Wilkinson, J. Inorg. Nucl. Chem. **1955**; 1: 175.

11. H.P. Fritz and J. Manchot, Spectrochim. Acta **1962**; 18: 171.

12. R.T. Bailez and E.R. Lippincott, Spectrochim. Acta **1958**; 10: 307.

13. A.T. Patton, C.E. Strouse, C.B. Knobler and J.A. Gladysz, J. Am. Chem. Soc. **1983**; 105: 5804.

14. F.W.B. Einstein, A.H. Klahn-Oliva, D. Sutton and K.G. Tyers, Organometallics **1986**; 5: 53.

15. E.W. Abel and T.S. Butler, Trans. Faraday Soc. **1967**; 63: 45.

16. E.W. Abel, Quart. Rev. **1963**; 17: 133.

17. R.J.H. Clark and B.C. Crosse, J. Chem. Soc. (A) **1969**; 224.

18. P.D. Harvey, T.S. Butler and D.F.R. Gilson, Inorg. Chem. **1987**; 26: 32.

19. W. Beck, A. Melkinoff and R. Stahl, Chem. Ber. **1966**; 99: 3721.

20. R.B. King, J. Inorg. Nucl. Chem. **1967**; 29: 2119.

21. L.W. Houk and G.R. Dobson, J. Chem. Soc. (A) **1966**; 317.

22. R.F. Fenske and R.L. DeKock, Inorg. Chem. **1970**; 9: 1053.

23. M.B. Hall and R.F. Fenske, Inorg. Chem. **1972**; 11: 1619.

24. R.B. King and L.W. Houk, Can. J. Chem. **1969**; 47: 2959.

25. L.E. Orgel, Inorg. Chem. **1963**; 1: 25.

26. E.B. Wilson Jr., J.C. Decivs and P.C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, **1955**.

27. S. Chaiwasie and R.H. Fenn, Acta Cryst. **1968**; B24: 525.

28. M.F. Bailey and L.F. Dahl, Inorg. Chem. **1965**; 4: 1314.

29. I.J. Hyams, D. Jones and E.R. Lippincott, J. Chem. Soc. (A) **1967**; 1987.

30. V. Devarajan and S.J. Cyvin, Acta Chem. Scand. **1972**; 26: 1.

31. S.J. Cyvin, J. Brunvoll and L. Shafer, J. Chem. Phys. **1971**; 54: 1517.

32. L.H. Jones, R.S. McDowell and M. Goldblatt, Inorg. Chem. **1969**; 8: 2349.

33. K. Kawai and H. Murata, Bull. Chem. Soc. Japan **1960**; 33: 1008.

34. F.A. Cotton and C.S. Kraihanzel, J. Am. Chem. Soc. **1962**; 84: 4432.

35. R.J. Angelici, Acc. Chem. Res. **1972**; 5: 335.

Date Received: 08/28/89
Date Accepted: 10/06/89