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Vibrational spectroscopic and force field studies of (η^5-Cp)ML_3-type complexes (M = Mn, Re; L = CO, O)

É. Bencze [a,b], J. Mink [a,c,*], C. Németh [a], W.A. Herrmann [b], B.V. Lokshin [d], F.E. Kühn [b,*]

[a] *Institute of Isotope and Surface Chemistry, Chemical Research Center of the Hungarian Academy of Sciences, PO Box 77, H-1525 Budapest, Hungary*
[b] *Anorganisch-chemisches Institut, Technischen Universität München, Lichtenbergstrasse 4, D-85748 Garching, Germany*
[c] *Analytical Chemistry Department, Veszprém University, PO Box 158, H-8201 Veszprém, Hungary*
[d] *A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova Str. 28, 117813 Moscow, Russia*

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Abstract

High- and low-oxidation state $CpML_3$-type (M = Mn, Re; L = O, CO) cyclopentadienyl complexes have been investigated by vibrational spectroscopy (FTIR, FT-FIR, FT-Raman) and normal coordinate calculations. The vibrational spectra of $CpMn(CO)_3$, $CpRe(CO)_3$ complexes were revised and reinterpreted. For the oxo-complexes and Cp*-carbonyl compounds, $Cp^*Mn(CO)_3$ and $Cp^*Re(CO)_3$, a complete spectral assignment is proposed. The results of the normal coordinate analysis are in good agreement with the spectral evidence. The vibrational spectroscopic findings help to explain earlier observations, e.g. the significantly lower stability of $CpReO_3$ in comparison to Cp^*ReO_3. Characteristic force constants have been determined for Cp and Cp* ligands. A method is described for estimating an approximate force constant for the metal cyclopentadienyl (Cp) ligand bond stretch in half sandwich type of complexes, based on the use of an effective 'spectroscopic' mass of the Cp-ligand.

Keywords: Cyclopentadienyl; Manganese; Oxo complexes; Rhenium; Vibrational spectroscopy

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1. Introduction

High-oxidation state organometallic oxides [1] have been studied intensively, especially since the organorhenium(VII) basic complexes CH_3ReO_3 [1–4] and (η^5-C_5Me_5)ReO_3 (Me = CH_3) [1,5] were first reported. Today, a wide variety of these complexes exist [1,6–8]. In addition to the knowledge on the preparation of these compounds, their structure and chemical behavior, and specific catalytic properties, there is considerable interest in further studying the vibrational spectroscopic and bonding properties of these and similar compounds.

Considerable research has been focused on the vibrational properties of cyclopentadienyl (Cp) complexes of low-oxidation state metals [9]. In recent years, density functional theory (DFT) calculations were proven to give reliable vibrational IR frequencies and intensities. Our recent DFT calculations and experimental (IR, Raman) re-investigations of Cp^-, Cp^{*-} (Cp* = pentamethylcyclopentadienyl) and the CpM and Cp*M (M = Li, Na, K) systems [10] led to considerable modification of the generally accepted assignment of Cp^- ring vibrations [11]. Thus, based on these results and the recent results of DFT calculations on Cp^-, CpLi and Cp_2Fe species [12], we concluded that vibrational re-investigation of some well-known molecules, like $C_5H_5Mn(CO)_3$, $C_5D_5Mn(CO)_3$ [13], $CpRe(CO)_3$ [14] is necessary. To our knowledge, no detailed vibrational data, no Raman polarization measurements have been reported of high-oxidation state organometallic oxides, such as $CpReO_3$ and Cp^*ReO_3. Moreover, there are

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* Corresponding authors. Tel.: +49-89-289-13080; fax: +49-89-289-13473 (F.E.K.). Tel.: +36-1-329-2551; fax: +36-1-392-2551 (J.M.).

E-mail addresses: fritz.kuehn@ch.tum.de (F.E. Kühn), mink@iserv.iki.kfk.hu (J. Mink).

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very few or no vibrational experimental reports on Cp* complexes, such as Cp*Re$(CO)_3$ [15] and Cp*Mn$(CO)_3$.

We have re-recorded the spectra of some complexes and report new vibrational data of others not previously studied. This report is an attempt to rationalize the different assignments of the Cp ring vibrations and establish a reliable assignment of the Cp* ring vibrations. We have compared the spectra of Cp complexes with those of Cp* derivatives and analyzed the spectral differences between these two types of compounds.

Normal coordinate analysis (NCA) and force constant calculation of organometallic compounds is not trivial. It is extremely difficult in the case of $CpML_3$-type molecules, where two molecular moieties are connected with different local symmetry. If one considers the real symmetry of the whole $CpML_3$-type compound, definition of some internal coordinates (e.g. the metal-ring symmetric and asymmetric ('tilt') stretching or the deformations of the ML_3 fragment) becomes complicated. There are two different approaches to the inclusion of the complete ring–ligand coordinate into the force field. One is to introduce five metal–carbon stretching coordinates, whereas the other is based on introduction of a 'dummy' atom in the middle of the Cp-ring for modeling the metal–ligand stretching coordinate. In the second case, the Cp 'tilt' motions can be expressed on the basis of the moments of inertia of the Cp ring by introducing a special internal coordinate. For sandwich-type Cp_2M [16,17] and half sandwich-type CpM [10] complexes, the first method has been used. Our experience in force constant calculations of $CpML_n$-type complexes has found that the second method is preferable. This allows the easy introduction of deformational internal coordinates for the ML_n moiety. Evaluating the applicability of the 'dummy' atom model is also examined in this present paper. Relatively few approximate force field calculations have been reported in the literature, e.g. energy factored CO stretching force constants were obtained for CpMn$(CO)_3$ [18] and CpRe$(CO)_3$ [19], and a simplified calculation has been performed for $CpReO_3$ and Cp^*ReO_3 [20] species. However, 'extensive' force constant calculations for these systems are not available.

Herein, we report the 'complete' force constant calculations and vibrational analysis of the molecules CpMn$(CO)_3$ and its deuterated derivative, Cp*Mn$(CO)_3$, CpRe$(CO)_3$, Cp*Re$(CO)_3$, $CpReO_3$, and Cp^*ReO_3 with a view to understanding their structural and bonding properties.

Table 1
Experimental and calculated (NCA) normal vibrations (cm^{-1}) of CpMn$(CO)_3$ and $C_5D_5Mn(CO)_3$ complexes

Point group				$C_5H_5Mn(CO)_3$		$C_5D_5Mn(CO)_3$		Assignment	PED (%)[b]
C_s	C_{5v}	C_{3v}	Number	Experimental[a]	Calculated	Experimental[a]	Calculated		
A′	a_1		**1**	3125	3123.2	2349	2351.1	ν(CH)	$98r+2R$
A′	a_1		**2**	1117	1117.1	1051	1049.7	ν(CC)	$97R+3r$
A′	a_1		**3**	837	836	613	614.0	γ(CH)	100ρ
A″	a_2		**4**	1267	1261.4	980	991.6	β(CH)	100β
A′	e_1		**5a**	3109	3113.7	2340	2336.1	ν(CH)	$98r+1\alpha+1R$
A′	e_1		**6a**	1425	1430.5	1260	1260.0	ν(CC)	$70R+27\beta+3r$
A′	e_1		**7a**	1010	1014.1	775	776.0	β(CH)	$74\beta+18R+7\alpha+1r$
A′	e_1		**8a**	842	846.1	685	680.5	γ(CH)	$94\rho+6\tau$
A′	e_2		**9a**	3120	3118.8	2340	2340.5	ν(CH)	$98r+2R$
A′	e_2		**10a**	1364	1366.7	1311	1312.2	ν(CC)	$80R+14\alpha+3\beta+3r$
A′	e_2		**11a**	1065	1068.1	832	820.4	β(CH)	$55\beta+44R+1r$
A′	e_2		**12a**	930	928.1	853	851.7	α(CCC)	$80\alpha+14R+6\beta$
A′	e_2		**13a**	922	920.7	720	722.4	γ(CH)	$91\rho+9\chi$
A′	e_2		**14a**	616	621.9	560	550.6	δ(CCC)	$79\chi+21\rho$
A′		a_1	**15**	2027	2025.0	2023	2025.0	ν_s(CO)	$94D+6d$
A′		e	**20a**	1944	1942.1	1940	1942.1	ν_{as}(CO)	$94D+6d$
A′		a_1	**16**	667	666.8	663	666.2	δ(MnCO)	$69\varepsilon+13\omega+12\rho+6d$
A″		a_2	**19**	410	400.8	400	400.2	δ(MnCO)	$100\varepsilon'$
A′		e	**21a**	635	632.2	629	632.0	δ(MnCO)	$50\varepsilon'+36d+12\gamma+2\omega$
A′		e	**22a**	542	541.1	540	541.1	δ(MnCO)	$91\varepsilon+5\omega+3d+1\gamma$
A′		a_1	**17**	493	495.7	494	493.2	ν_s(MnC)	$41d+35\rho+23\varepsilon+1D$
A′		e	**23a**	491	486.3	488	486.3	ν_{as}(MnC)	$55d+41\varepsilon'+3\gamma$
A′		e	**24a**	111	112.9	111	112.3	δ(CMnC)	$44\gamma+39\omega+7d+6\varepsilon+5\varepsilon'$
A′		a_1	**18**	104	106.1	104	105.4	δ(CMnC)	$84\omega\gamma+13\varepsilon+2\rho+1\mathrm{d}$
A′		e	**25a**	104	95.1	104	94.4	δ(CMnC)	$47\omega+41\gamma+6d+6\varepsilon'$
A′	a_1		**26**	347	345.8	337	341.6	ν_s(MnCp)	$51S+48d+1D$
A′	e_1		**27a**	372	380.9	362	356.4	ν_{as}(MnCp)	$98\tau+2\rho$

[a] Experimental frequencies from Ref. [13].

[b] For internal coordinates notation see Fig. 1.

Table 2
Experimental IR and Raman frequencies (cm^{-1}) of $Cp^*Mn(CO)_3$

IR		Raman		Assignment	
Solid	Solution (CH_2Cl_2)	Solid	Solution (CH_2Cl_2)		
2982 m	2982 w	2986 m		e_1	ν_{as} (CH_3)
2963 m	2963 w	2965 ms	2966 w, dp		
2922 b,s	2917 b,wm	2925 vs	2921 m, p	a_1	ν_s (CH_3)
2863 wm	2963 w,sh				
2047 ms	2046 w,m				
2004 vvs	2003 vvs	1994 s	2001 vs, p	a_1	ν_s (CO)
		1930 vvs			
1910 vvs	1914 vvs	1907 vvs	1917 vs, dp	e	ν_{as} (CO)
1485 wm	1484 w	1484 sh		e	$\delta_{as}(CH_3)$
1469 sh		1470 wm			
1451 wm	1454 w	1449 m	1454 m, dp		
1427 wm	1428 w	1428 m	1428 s, p	a_1	$\nu(CC)+\nu(C\text{-}CH_3)$
1409 sh		1416 vw		e_1	$\nu(CC)+\nu(C\text{-}CH_3)$
1382 s	1386 m	1384 w	1385 wm, p	a_1	$\delta_s(CH_3)$
		1369 w	1373 sh, dp	e_2	$\nu(CC)+\nu(C\text{-}CH_3)$
			1336 w, p		
1262 m	1265 m				
1214 vw					
1163 vvw					
1098 wm					
1073 wm	1073 w		1071 vw, dp	e_2	$\nu(CC)+\nu(C\text{-}CH_3)$,
				e	$\rho_r(CH_3)$
1030 sm	1033 wm	1030 w	1035 w, p	e	$\rho_r(CH_3)$
914 vvw	895 vw				
876 vw					
803 b.m				e_1	$\nu(CC)+\nu(C\text{-}CH_3)$
674 s	676 s			a_1	δ(Mn-CO)
639 vs	640 vs		643 wm	e_2	δ(CCC),
				e	δ(Mn-CO)
590 sh		594 m	593 s, p	a_1	$\nu(CC)+\nu(C\text{-}CH_3)$
			590 sh, dp		
547 sh	545 sh	550 wm	549 m, dp	a_2	β($C\text{-}CH_3$)
538 sm	539 sm	545 sh		e	δ(Mn-CO),
503 m	508 wm	505 s	501 vs, p	a_1	ν_s(Mn-CO)
498 m				e	ν_{as}(Mn-CO)
469 w					
438 w,m		441 w	445 w, dp	e_2	α(CCC)
	389 vs	392 vvs, p		a_1	ν_s(Mn-Cp*)
386 w				a_2	δ(Mn-CO)
		300 w			
292 m		286 w		e_1	ν_{as}(Mn-Cp*)
201 s,b		210 s	210 s, dp	e_1	β($C\text{-}CH_3$)
			205 s, p	a_1	$\gamma(C\text{-}CH_3)$,
				e_2	β($C\text{-}CH_3$)
		145 w		e_1	$\gamma(C\text{-}CH_3)$
		124 s	133 m, dp	a_1	δ(CMnC)
109 w				e_2	$\gamma(C\text{-}CH_3)$
				e	δ(CMnC)
83 vw				Lattice modes	
62 vw					

b, broad; s, strong; w, weak; m, medium; vs, very strong; vw, very weak; vvw, very-very weak; wm, weak-medium; ms, medium-strong; sh, shoulder; p, polarized; dp, depolarized.

2. Experimental

Complexes $CpMn(CO)_3$, $CpRe(CO)_3$, $Cp^*Re(CO)_3$ are commercially available from Strem. $Cp^*Mn(CO)_3$ [21], $CpReO_3$ [22,23a] and Cp^*ReO_3 [24] were synthesized using established literature procedures.

The $CpReO_3$ complex is sensitive to light and elevated temperatures [23b]. All manipulations were performed using Schlenk procedures or using glove box techniques (purged with dry N_2).

Mid-IR spectra of the complexes were recorded with a BIO-RAD FTS-60A spectrometer, both in solid (KBr pellets) and solution (CH_2Cl_2) phase. Far-IR measurements were performed on a BIO-RAD FTS-40 or FTS-175 systems as Nujol mulls or polyethylene pellets, using a 6-μm Mylar beamsplitter. Raman spectra were measured with a BIO-RAD Digilab dedicated FT-Raman spectrometer using the near infrared 1064 nm excitation from a Nd:YAG laser. Raman polarization measurements of solutions (CH_2Cl_2) were also carried out.

3. Results and discussion

3.1. Vibrational spectra

FTIR and FT-Raman spectra of $CpMn(CO)_3$ and its deuterated derivative have been measured and tentatively assigned by Parker [13]. The local symmetry approach i.e., C_{5v} point group for CpM moiety is a reasonable approximation [13]. From the 14 fundamental modes of the Cp ring, 12 frequencies are in agreement with our assignments. In the e_2 species for the ν_{11} vibration, we suggest 1065 cm^{-1} as C–H in-plane-deformation instead of the 1215 cm^{-1} band. For the ν_{13} C–H out-of-plane deformation vibration, the 922 cm^{-1} band shows better agreement with the calculated frequency [10] than Parker's assignment (1065 cm^{-1}) [13].

We have obtained more discrepancies in $C_5D_5Mn(CO)_3$ vibrations. The medium Raman band at 1311 cm^{-1} was assigned to the ν_{10} (e_2) vibration, instead of the band at 1260 cm^{-1} [13]. Frequencies for the e_2 species, 1311, 832, 853, and 720 cm^{-1} were assigned to ν_{10}, ν_{11}, ν_{12}, and ν_{13} vibrations, respectively. The tentative assignments suggested by Parker were 1260, 1094, 720, and 850 cm^{-1} for the same series of the fundamental vibrations [13]. Further confirmation of our assignments was obtained from the Teller–Raleigh product rule. The theoretical product ratio of 0.403 is in satisfactory agreement with the observed 0.446. The previous assignments [13] give a product ratio of 0.340 more different from the theoretical value. Vibrations due to the $-Mn(CO)_3$ moiety can be unambiguously assigned. These show no sensitivity to deuterium substitution of the Cp-ring. The experimental and calculated fundamental frequencies, their assignments and potential energy distribution are presented in Table 1.

Table 2 reports the experimental fundamental frequencies of Cp*Mn$(CO)_3$ and the tentative assignment proposed on the basis of our previous work [10]. The complex was measured both in solid and solution (CH_2Cl_2) phases, including Raman polarization measurements, too. Comparing the –Mn$(CO)_3$ group frequencies in CpMn$(CO)_3$ and Cp*Mn$(CO)_3$ compounds, it can be observed that these frequencies are not showing considerable sensitivity to the ligand exchange.

Our assignment of the CpRe$(CO)_3$ complex is in good agreement with the previous work of Lokshin et al. [14] (see Table 3). However, based on our earlier results [10], we suggest some modifications of the ring vibrations. We assigned the in-plane C–H deformations at 1006 cm^{-1} (e_1) and 1061 cm^{-1} (e_2), respectively, instead of 1198 and 1006 cm^{-1}. We have also re-assigned the C–H out-of-plane vibration (e_2) to 912 instead of 1061 cm^{-1}. The Raman spectra highlighted a weak band at 598 cm^{-1}, which we interpreted as being the ring out-of-plane torsional mode contrary to Lokshin's assignment of 380 cm^{-1}, which we believe to be too low for this vibration [10].

Only the FTIR spectrum (4000–200 cm^{-1}) is available for the Cp*Re$(CO)_3$ [15]. The assignment of the vibrations is not complete and in some cases the vibrations are interpreted wrongly, e.g. the ring breathing at 1085 cm^{-1} and the asymmetric Re–Cp* stretching at 380 cm^{-1} which appears as polarized band in our Raman measurements. Table 4 presents the vibrational spectra and our tentative assignment for the Cp*Re$(CO)_3$ molecule.

IR measurements of CpReO$_3$ [22] and Cp*ReO$_3$ [20], both in solid and solution (CH_2Cl_2) phase, allowed the identification of the Re=O vibrations only. The CpReO$_3$ complex is a poor Raman scatterer and the fluorescence complicates analysis of the spectra. Also, it is insoluble in most common spectroscopic solvents (CCl_4, CS_2, CH_2Cl_2, acetonitrile, benzene). Accordingly, our assignment (Table 5) is based on IR and Raman measurements of the compound in its solid state. The Cp*ReO$_3$ spectra were recorded both in solid and solution (CH_2Cl_2) phase and the assignment is presented in Table 4, together with the tricarbonyl analogue molecule, Cp*Re$(CO)_3$.

Considering the IR and Raman band intensities, the activity of the vibrations, the Raman polarization measurements, and the previous work on similar complexes

Table 3
Experimental and calculated (NCA) fundamental frequencies (cm^{-1}) of CpRe$(CO)_3$ complex

Point group				CpRe$(CO)_3$		Assignment	PED (%) [a]
C_s	C_{5v}	C_{3v}	Number	Experimental	Calculated		
A′	a_1		**1**	3125	3123.9	ν(CH)	$98r+2R$
A′	a_1		**2**	1106	1102.6	ν(CC)	$93R+7r$
A′	a_1		**3**	826	826.1	γ(CH)	100ρ
A″	a_2		**4**	1225	1231.4	β(CH)	100β
A′	e_1		**5a**	3066	3068.2	ν(CH)	$98\mathrm{r}+1\alpha+1R$
A′	e_1		**6a**	1421	1420.9	ν(CC)	$68R+27\beta+5r$
A′	e_1		**7a**	1006	1007.1	β(CH)	$81\beta+14R+5\alpha$
A′	e_1		**8a**	839	838.0	γ(CH)	$95\rho+5\tau$
A′	e_2		**9a**	3105	3104.5	ν(CH)	$98r+2R$
A′	e_2		**10a**	1354	1353.6	ν(CC)	$84R+12\alpha+1\beta+1r$
A′	e_2		**11a**	1061	1065.4	β(CH)	$54\beta+45R+1r$
A′	e_2		**12a**	932	930.3	α(CCC)	$88\alpha+8R+3\beta$
A′	e_2		**13a**	912	913.0	γ(CH)	$92\rho+8\chi$
A′	e_2		**14a**	598	597.4	δ(CCC)	$76\chi+24\rho$
A′		a_1	**15**	2025	2025.1	ν_s(CO)	$93D+7d$
A′		e	**20a**	1926	1926.1	ν_{as}(CO)	$93D+7d$
A′		a_1	**16**	610	610.3	δ(ReCO)	$78\varepsilon+18\omega+2\rho+1d$
A″		a_2	**19**	378	380.1	δ(ReCO)	$100\varepsilon'$
A′		e	**21a**	600	601.0	δ(ReCO)	$75\varepsilon'+15d+7\gamma+3\omega$
A′		e	**22a**	513	513.2	δ(ReCO)	$72\varepsilon+9\omega+4d+1\gamma$
A′		a_1	**17**	503	501.8	ν_s(ReC)	$81d+10\rho+5\varepsilon+4D$
A′		e	**23a**	509	507.7	ν_{as}(ReC)	$67d+18\varepsilon'+14\gamma$
A′		e	**24a**	120	120.1	δ(CReC)	$82\gamma+12\varepsilon'+3\varepsilon+2d$
A′		a_1	**18**	110	112.3	δ(CReC)	$78\omega\gamma+21\varepsilon+1\rho$
A′		e	**25a**	76	83.1	δ(CReC)	$96\omega+4\varepsilon$
A′	a_1		**26**	328	327.3	ν_s(ReCp)	$77S+22d+1\varepsilon$
A′	e_1		**27a**	352	352.0	ν_{as}(ReCp)	100τ

[a] For internal coordinates notation, see Fig. 1.

[10,13,14], our assignments seem to be justified. Two strongly polarized bands are observed in the Cp* derivatives' Raman spectra analogous to those of the alkali metal Cp* complexes [10]. These bands are due to the strong coupling of the two symmetric skeletal modes of the Cp ring and ring-methyl symmetric stretches and they are split strongly with a separation of ca. 800 cm^{-1} (ca. 1430 and 590 cm^{-1}). It is noteworthy that the Cp complexes exhibit the M–Cp symmetric stretchings at lower wavenumbers than the asymmetric ones in contrast with the Cp* complexes. Also, the M–Cp* symmetric stretchings occur at higher frequencies than the M–Cp ones, suggesting that the M–Cp* bonds are stronger than M–Cp.

The ML$_3$ substituents do not show a profound influence on the intra-ring vibrational frequencies. Thus, these frequencies are transferable for different complexes.

Table 4
Experimental frequencies (cm^{-1}) of Cp*Re(CO)$_3$ and Cp*ReO$_3$

Cp*Re(CO)$_3$				Cp*ReO$_3$					
IR		Raman		IR		Raman		Assignment	
Solid	Solution (CH$_2$Cl$_2$)	Solid	Solution (CH$_2$Cl$_2$)	Solid	Solution (CH$_2$Cl$_2$)	Solid	Solution (CH$_2$Cl$_2$)		
				2999 vw	2996 w	2998 m			
2985 w	2984 w	2986 wm	2986 wm, dp	2980 vw	2985 w	2980 sh		e	$\nu_{as}(CH_3)$
2966 w	2965 vw	2967 m	2967 m, dp	2961 w	2963 vw	2962 m			
2926 w	2918 w	2925 s	2922 vs, p	2923 wm	2924 m	2925 s	2926 vs, p	a_1	$\nu_s(CH_3)$
		2874 sh	2876 w, dp	2866 vw	2867 vw	2869 wm			
2861 vw	2861 vvw			2855 vw		2852 wm			
		2804 vw	2806 vw						
		2753 vw	2759 w, p					a_1	2 × 1388
		2727 vw	2732 w, p					a_1	2 × 1370
1999 vvs	2007 vvs	1995 s	2007 s, p					a_1	$\nu_s(CO)$
1989 sh		1987 sh							
		1921 vvs							
1905 vvs	1909 vvs		1909 s, dp					e	$\nu_{as}(CO)$
1897 vvs		1897 vvs							
1866 m		1866 w							
				1503 m	1492 w	1501 wm		e	$\delta_{as}(CH_3)$
1483 wm	1482 w	1485 sh	1487 w	1483 sh		1481 sh			
1472 w	1468 sh	1466 wm	1466 w, dp	1473 w		1470 sh		e	$\delta_{as}(CH_3)$
1453 wm	1454 wm	1449 m	1450 w, dp		1450 w	1457 wm		e_1	$\nu(CC)+\nu(C\text{-}CH_3)$
1425 w	1426 m	1419 m	1421 m, p	1439 s	1431 vw	1430 m	1429 s, p	a_1	$\nu(CC)+\nu(C\text{-}CH_3)$
1405 w		1406 w	1408 sh		1415 vvw	1407 vw		e_2	$\nu(CC)+\nu(C\text{-}CH_3)$
1384 m	1387 s	1383 w	1388 w, dp	1380 m	1380 ms		1385 w, p	a_1	$\delta_s(CH_3)$
		1367 w	1370 w, dp	1372 s		1371 m			
				1361 s	1366 sh	1360 w	1366 w, dp	e_1	$\nu(CC)+\nu(C\text{-}CH_3)$
1160 vw		1158 vw	1159 vvw	1167 vvw		1166 vw			
1108 w		1086 vw		1105 vvw		1099 vvw			
1072 w	1073 w	1065 vw		1073 w	1073 vw	1073 w	1073 vw, dp	e_1	$\nu(CC)+\nu(C\text{-}CH_3)$, $\rho_r(CH_3)$
1033 wm	1035 wm	1031 w	1035 w, p	1024 m	1027 w	1021 m	1027 m, p	a_1, e	$\rho_r(CH_3)$
952 vvw		951 vw		962 vvw	955 vw	961 vvw			
				910 vs	919 vs	905 vvs	918 vvs, p	a_1	$\nu_s(ReO_3)$
				886 vvs	886 vvs	887 vs	886 s, dp	e	$\nu_{as}(ReO_3)$
						873 vs			
		878 vvw	879 vw						
				845 vvw	833 vw		845 vvw		
798 vvw		796 vvw	795 vvw	803 m	802 m	801 w	804 w, dp	e_1	$\nu(CC)+\nu(C\text{-}CH_3)$
630 sh		632 w	634 vw, dp	612 w		610 w		e_2	$\delta(CCC)$

Table 4 (*Continued*)

611 m	615 s	608 sh	615 wm					a_1	δ(ReCO)
594 m	595 s	589 m	587 s, p	594 vw	590 vvw	594 s	591 vs, p	a_1, e	ν(CC)+ν(C-CH$_3$), δ(ReCO)
545 w		543 wm	544 wm, dp	547 w	544 vvw	544 m	545 m, dp	a_2	β(C-CH$_3$)
513 s	515 vs		515 sh, p					e	δ(ReCO)
508 sh	507 sh	501 vs	507 vs, p					a_1	ν(ReCO)
			495 sh, dp	491 vw				e	δ(ReCO)
430 m	433 m	435 w	439 w, dp					e_2	α(CCC)
						429 sh			
				420 m	418 vw	420 w	422 w, dp	e_2	α(CCC)
				396 s	400 s	395 vs	400 vs, p	a_1	$δ_s$(ReO$_3$)
378 wm	380 w	377 wm	381 wm, p					a_1, a_2	$ν_s$(ReCp*), δ(ReCO)
						353 s	355 m, p	a_1	$ν_s$(ReCp*)
				337 m	340 m	337 s	340 m, dp	e	$ν_{as}$(ReCp*)
		293 w		297 vvw		296 vw		e	$ρ_r$(ReO$_3$)
		281 w	280 w					e	$ν_{as}$(ReCp*)
				205 m	201 w	205 w	204 w	e, e_1	$δ_{as}$(ReO$_3$), β(C-CH$_3$)
192 w	190 w							e_1	β(C-CH$_3$)
		185 s	182 m, dp					e_2	β(C-CH$_3$)
				182 m		183 w		a_1, e_2	γ(C-CH$_3$), β(C-CH$_3$)
172 wm	171 w	175 sh	173 s, p					a_1, e_1	γ(C-CH$_3$)
				161 wm	166 vw	164 vs	160 w	e	γ(C-CH$_3$)
	144 w	144 w						e	δ(CReC)
	115 w								δ(CReC)
			104 s, dp					a_1, e	δ(CReC)
			76 vw, dp					Lattice mode	

s, strong; w, weak; m, medium; vs, very strong; vw, very weak; vvw, very-very weak; wm, weak-medium; ms, medium-strong; p, polarized; dp, depolarized.

3.2. Normal coordinate analysis (NCA)

NCA of the title complexes is not trivial and, therefore, is not carried out routinely. In CpML$_3$ type complexes, two molecular fragments are connected with different local symmetries. The –CpM moiety shows C_{5v} symmetry, while the –ML$_3$ (L = O, CO) is of C_{3v} symmetry. In order to carry out a 'complete' normal coordinate analysis, we have introduced a 'dummy' atom in the geometrical center of the Cp ring (see also Section 1). This makes it possible to describe in a simpler mode the Cp–M–L$_3$ skeletal deformations. However, it should be emphasized that this is not suitable for defining the ring 'tilt'. We have already mentioned that for this type of internal coordinate system, the ring 'tilt' can be expressed as the inverse of the moments of inertia of the Cp ligand. The internal coordinates are presented in Fig. 1. The 'tilt' is noted as a librational mode, τ. For the carbonyl complexes, in addition to those coordinates which can be seen in Fig. 1, we have introduced three more stretchings (denoted D for C≡O), and six deformation coordinates for Re–C–O groups, namely three linear bendings (ε) and three more linear bendings (ε'), perpendicular to the ε coordinates. In the case of Cp* molecules, the methyl groups were considered to be point masses.

Thirty-five normal vibrations were calculated for the trioxo complexes, whereas 44 were calculated for the tricarbonyl complexes. In all cases, the ring torsion

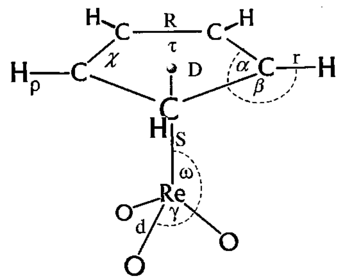

Fig. 1. Internal coordinate notation for Cp(Cp*)ML$_3$-type derivatives. Notation: R, CC stretching; r, CH stretching; S, ReD stretching; D, ReL stretching; α, CCC bending; β, CCH bending; ω, LReD bending; γ, LReL bending; χ, out-of-plane ring torsion; ρ, out-of-plane bending; τ, tilt.

Table 5
Experimental (IR, Raman) frequencies of $CpReO_3$ (cm^{-1})

$CpReO_3$			
IR	Raman	Assignment	
3100 vs	3103 s	a_1	$\nu(CH)$
	3092 w	e_2	$\nu(CH)$
3075 sh			
3025 vvw		e_1	$\nu(CH)$
3015 vvw			
2964 w			
2924 w			
2850 vw			
2775 w			
1429 vs	1419 m	e_1	$\nu(CC)$
1400 sh	1392 wm		
	1329 vvw	e_2	$\nu(CC)$
1261 m		a_2	$\beta(CH)$
	1243 vvw		
	1230 w		
1180 wm	1182 vw		
1158 vw	1132 vvw		
1094 m			
1080 m	1075 m	a_1	$\nu(CC)$
	1049 w	e_2	$\gamma(CH)$
1017 vs	1018 vw	e_1	$\beta(CH)$
958 vw	957 vvw		
	938 w	e_2	$\alpha(CCC)$
926 vs	914 vvs	a_1	$\nu_s(ReO_3)$
	897 m	e_2	$\gamma(CH)$
886 vvs	885 m	e_2	$\nu_{as}(ReO_3)$
871 sh	875 m		
855 vs	856 vw	e_1	$\gamma(CH)$
835 sh	835 w	a_1	$\gamma(CH)$
801 w	793 vvw		
668 w			
589 m		e_2	$\delta(CCC)$
470 w			
419 vvw			
384 w	386 w	a_1	$\delta_s(ReO_3)$
	375 m	e_1	$\nu_{as}(ReCp)$
351 m			
345 m	343 s		
	318 vs	a_1	$\nu_s(ReCp)$
276 w	277 sh	e	$\rho_r(ReO_3)$
	270 m		
	237 vvw		
	218 w		
193 m		e	$\delta_{as}(ReO_3)$
	185 m		

s, strong; w, weak; m, medium; vs, very strong; vw, very weak; vvw, very-very weak; wm, weak-medium; ms, medium-strong; sh, shoulder.

coordinate was neglected, assuming free rotation of the ring. The molecules belong to the C_s point group, but vibrational assignments were made considering their local symmetries, C_{5v} and C_{3v}.

The irreducible representation is $20A' + 15A''$ for Cp(Cp*)ReO_3, and $25A' + 19A''$ for the Cp(Cp*)-$M(CO)_3$ (M = Mn, Re) complexes. If we consider the molecules as having planar symmetry (C_s), then 20 or 25 polarized bands should appear in the Raman spectra for oxo- or the tricarbonyl complexes. In reality, only eight polarized bands appear in the spectra of tricarbonyl complexes. This is in good agreement with that expected on applying the local symmetry concept of C_{5v} and C_{3v} point groups. This experimental evidence justifies the introduction of special symmetry coordinates. It is also necessary to introduce special coordinates for the doubly degenerate ring 'tilt' in addition to implementing the local symmetries. These symmetry coordinates are presented in Table 6.

Geometrical parameters were taken from the literature. $CpMn(CO)_3$ [25], $CpRe(CO)_3$ [26], $CpReO_3$ [23], Cp*$Mn(CO)_3$ [27], Cp*$Re(CO)_3$ [28], Cp*ReO_3 [20]. The starting force fields were also adopted from the literature: Ref. [10] for the Cp, Cp* rings, Refs. [14–20] from approximate calculations for the $-ML_3$ moiety. These results were refined to the experimental frequencies of the $CpMn(CO)_3$ complex, for which frequencies for the deuterated derivative are also available. Thus, a reliable force field for $CpMn(CO)_3$ compound was calculated. The force constants reported for the $CpMn(CO)_3$ molecule were considered as initial force fields for the other derivatives and were refined for the corresponding experimental frequencies. Tables 1, 3, 7–9 outline the results (calculated fundamental frequencies) obtained for complexes $CpMn(CO)_3$, $CpRe(CO)_3$, Cp*$Mn(CO)_3$, $CpReO_3$ and Cp*ReO_3, respectively.

It was found that none of the vibrations, which belong to degenerate symmetry species (e, e_1, e_2) show any splitting either in calculations or in experimental observations. Therefore, frequencies of vibrations belonging to A″ species (**5b**–**27b**) are practically identical to those of **5a**–**27a**, with the same potential energy distributions (PED). Hence, these vibrations are omitted from the tables. Accordingly, in Tables 1, 3, 7–9 only the A′ components of the degenerate vibrations are presented together with those of the asymmetric unpaired vibrations (e.g. ν_4 (β(CH)) and ν_{19} (δ(MCO)) in the case of tricarbonyl complexes, and ν_4 (β(CH)) for trioxo derivatives) which appear only in symmetry block A″.

The frequencies calculated are found to be in very good agreement with the experimental observations (Table 10). The PED values indicate that the in-plane vibrations of the Cp ring are coupled strongly in both Cp and Cp* rings. In the latter case, the degree of coupling is considerably higher. Furthermore, in Cp* molecules, considerable interaction can be observed between the M–Cp* symmetric stretching and the symmetric out-of-plane C–CH_3 deformation, the so called 'umbrella' mode (Table 11).

Table 6
Symmetry coordinates of CpM and $M(CO)_3$ moieties

Point group			Symmetry coordinate	Point group			Symmetry coordinate
C_s	C_{5v}	Number		C_s	C_{5v}	Number	
CpM moiety							
A′	a_1	**1**	$5^{-1/2}(r_1+r_2+r_3+r_4+r_5)$				
	a_1	**2**	$5^{-1/2}(R_1+R_2+R_3+R_4+R_5)$				
	a_1	**3**	$5^{-1/2}(\rho_1+\rho_2+\rho_3+\rho_4+\rho_5)$				
				A″	a_2	**4**	$10^{-1/2}(\beta_1-\beta_2+\beta_3-\beta_4+\beta_5-\beta_6+\beta_7-\beta_8+\beta_9-\beta_{10})$
	e_1	**5a**	$Ar_1+Br_2-Cr_3-Cr_4+Br_5$		e_1	**5b**	$Er_2+Dr_3-Dr_4-Er_5$
	e_1	**6a**	$CR_1-BR_2-AR_3-BR_4+CR_5$		e_1	**6b**	$DR_1+ER_2-ER_4-DR_5$
	e_1	**7a**	$2^{-1/2}(E\beta_3-E\beta_4+D\beta_5-D\beta_6-D\beta_7+D\beta_8-E\beta_9+E\beta_{10})$		e_1	**7b**	$2^{-1/2}(A\beta_1-A\beta_2+B\beta_3-B\beta_4-C\beta_5+C\beta_6-C\beta_7+C\beta_8+B\beta_9-B\beta_{10})$
	e_1	**8a**	$A\rho_1+B\rho_2-C\rho_3-C\rho_4+C\rho_5$		e_1	**8b**	$E\rho_2+D\rho_3-D\rho_4-E\rho_5$
	e_2	**9a**	$Ar_1-Cr_2+Br_3+Br_4-Cr_5$		e_2	**9b**	$Dr_2-Er_3+Er_4-\mathrm{D}r_5$
	e_2	**10a**	$BR_1-CR_2+AR_3-CR_4+BR_5$		e_2	**10b**	$\mathrm{E}R_1-DR_2+DR_4-ER_5$
	e_2	**11a**	$2^{-1/2}(D\beta_3-D\beta_4-E\beta_5+E\beta_6+E\beta_7-E\beta_8-D\beta_9+D\beta_{10})$		e_2	**11b**	$2^{-1/2}(A\beta_1-A\beta_2-C\beta_3+C\beta_4+B\beta_5-B\beta_6+B\beta_7-B\beta_8-C\beta_9+C\beta_{10})$
	e_2	**12a**	$A\alpha_1-C\alpha_2+B\alpha_3+B\alpha_4-C\alpha_5$		e_2	**12b**	$D\alpha_2-E\alpha_3+E\alpha_4-D\alpha_5$
	e_2	**13a**	$A\rho_1-C\rho_2+B\rho_3+B\rho_4-C\rho_5$		e_2	**13b**	$D\rho_2-E\rho_3+E\rho_4-D\rho_5$
	e_2	**14a**	$E\chi_1-D\chi_2+D\chi_4-E\chi_5$		e_2	**14b**	$\mathrm{B}\chi_1-C\chi_2+A\chi_3-C\chi_4+B\chi_5$
	a_1	**26**	S				
	e_1	**27a**	$E\tau_2+D\tau_3-D\tau_4-E\tau_5$		e_1	**27b**	$A\tau_1+B\tau_2-C\tau_3-C\tau_4+B\tau_5$
C_s	C_{3v}	Number		C_s	C_{3v}	Number	
$M(CO)_3$ moiety							
A′	a_1	**15**	$3^{-1/2}(d_1+d_2+d_3)$				
	a_1	**16**	$3^{-1/2}(\varepsilon_1+\varepsilon_2+\varepsilon_3)$				
	a_1	**17**	$3^{-1/2}(D_1+D_2+D_3)$				
	a_1	**18**	$6^{-1/2}(\omega_1+\omega_2+\omega_3-\gamma_1-\gamma_2-\gamma_3)$				
				A″	a_2	**19**	$3^{-1/2}(\varepsilon'_1+\varepsilon'_2+\varepsilon'_3)$
	e	**20a**	$6^{-1/2}(2d_1-d_2-d_3)$		e	**20b**	$2^{-1/2}(d_2-\mathrm{d}_3)$
	e	**21a**	$2^{-1/2}(\varepsilon'_2-\varepsilon'_3)$		e	**21b**	$6^{-1/2}(2\varepsilon'_1-\varepsilon'_2-\varepsilon'_3)$
	e	**22a**	$6^{-1/2}(2\varepsilon_1-\varepsilon_2-\varepsilon_3)$		e	**22b**	$2^{-1/2}(\varepsilon_2-\varepsilon_3)$
	e	**23a**	$6^{-1/2}(2D_1-D_2-D_3)$		e	**23b**	$2^{-1/2}(D_2-D_3)$
	e	**24a**	$6^{-1/2}(2\gamma_1-\gamma_2-\gamma_3)$		e	**24b**	$2^{-1/2}(\gamma_2-\gamma_3)$
	e	**25a**	$6^{-1/2}(2\omega_1-\omega_2-\omega_3)$		e	**25b**	$2^{-1/2}(\omega_2-\omega_3)$

$A=0.632456$; $B=0.195440$; $C=0.511667$; $D=0.371748$; $E=0.601501$. The above list involves symmetry coordinates for $–ReO_3$ moiety as well, namely 17, 18, 23, 24 and 25 type of linear combinations.

Table 7
Experimental and calculated (NCA) fundamental frequencies (cm^{-1}) of $Cp^*Mn(CO)_3$ complex

Point group				$Cp^*Mn(CO)_3$		Assignment	PED (%) [a]
C_s	C_{5v}	C_{3v}	Number	Experimental	Calculated		
A′	a_1		**1**	1428	1427.9	$\nu(CC^*)$ [b] $+\nu(CC)$	$53R+47r$
A′	a_1		**2**	593	584.6	$\nu(CC^*)+\nu(CC)$	$54r+46R$
A′	a_1		**3**	205	200.9	$\gamma(CC^*)$	100ρ
A″	a_2		**4**	549	547.3	$\beta(CC^*)$	100β
A′	e_1		**5a**	1416	1421.8	$\nu(CC^*)+\nu(CC)$	$38r+33r+26\alpha+3\beta$
A′	e_1		**6a**	803	803.8	$\nu(CC^*)+\nu(CC)$	$51R+47r+2\beta$
A′	e_1		**7a**	210	213.6	$\beta(CC^*)$	$55\beta+29R+16r$
A′	e_1		**8a**	145	153.2	$\gamma(CC^*)$	$98\rho+2\tau$
A′	e_2		**9a**	1373	1372.0	$\nu(CC^*)+\nu(CC)$	$76r+19R+3\alpha+2\beta$
A′	e_2		**10a**	1071	1070.3	$\nu(CC^*)+\nu(CC)$	$85R+11\beta+4r$
A′	e_2		**11a**	205	211.6	$\beta(CC^*)$	$97\beta+3R$
A′	e_2		**12a**	445	454.6	$\alpha(CCC)$	$50\alpha+45r+5R$
A′	e_2		**13a**	109	112.8	$\gamma(CC^*)$	$85\rho+15\chi$
A′	e_2		**14a**	643	643.3	$\delta(CCC)$	$61\chi+39\rho$
A′		a_1	**15**	2001	2004.1	$\nu_s(CO)$	$92D+8d$
A′		e	**20a**	1917	1917.5	$\nu_{as}(CO)$	$93D+7d$
A′		a_1	**16**	676	675.1	$\delta(MnCO)$	$88\varepsilon+11\omega\gamma+1d$
A″		a_2	**19**	392	390.1	$\delta(MnCO)$	$100\varepsilon'$
A′		e	**21a**	643	645.2	$\delta(MnCO)$	$80\varepsilon'+16\gamma+4d$
A′		e	**22a**	545	552.1	$\delta(MnCO)$	$79\varepsilon+11d+8\omega+2\gamma$
A′		a_1	**17**	501	500.3	$\nu_s(MnC)$	$92d+5S+3D$
A′		e	**23a**	498	495.2	$\nu_{as}(MnC)$	$79d+15\varepsilon+6\varepsilon'$
A′		e	**24a**	133	126.1	$\delta(CMnC)$	$81\gamma+15\varepsilon'+2\varepsilon+2d$
A′		a_1	**18**	109	112.3	$\delta(CMnC)$	$91\omega\gamma+7\varepsilon+2d$
A′		e	**25a**	109	98.4	$\delta(CMnC)$	$83\omega+9d+6\varepsilon+2\gamma$
A′	a_1		**26**	392	387.3	$\nu_s(MnCp^*)$	$94S+4d+2\varepsilon$
A′	e_1		**27a**	286	285.8	$\nu_{as}(MnCp^*)$	$62\tau+38\rho$

[a] For internal coordinates notation see Fig. 1.

[b] C*, C-atom of the CH_3-groups.

3.3. Force field of cyclopentadienyl ligands

It is always important to produce so called transferable force constants, which can be adopted to similar molecules or molecular fragments. Table 12 contains seven diagonal and four off-diagonal force constants of averaged values obtained for three Cp and three Cp* complexes. We believe that these sets of internal valence force constants can be used as starting force field for other 'half-sandwich' Cp or Cp* complexes.

3.4. Method of 'spectroscopic' masses of Cp and Cp* ligands

It has clearly been demonstrated that to perform a rigorous and complete force field calculation of Cp and Cp* complexes is not an easy problem. Therefore, we have made an attempt to calculate metal–ring stretching force constants based on a simple diatomic-approximation. If one uses molecular weights of Cp and Cp* and atomic weights of the metals, the approximate calculation gives force constants 2.11, 2.76 and 3.05 N cm^{-1}, whereas the rigorous calculation give 3.39, 3.66 and 4.03 N cm^{-1} for CpMn(CO)$_3$, CpReO$_3$, and CpRe(CO)$_3$, respectively. Generally, the above diatomic approximation underestimates strongly the metal–Cp stretching force constants. We have made an attempt to improve the accuracy of the approximate calculations by using so called 'spectroscopic' masses of Cp ligands, instead of their molecular weight. It has turned out that the spectroscopic mass of Cp ligand is higher than its molecular weight and slightly increases from the first (72.8), second (77.1) and third (83.2) rows of transition metals (Table 13) in the periodic table. The effective G-matrix element has been calculated as a sum of the inverse masses of Cp ligand and the –M(CO)$_3$ or –ReO$_3$ moieties of the complex.

Based on those estimated spectroscopic masses of Cp ligands we calculated metal–ligand force constants for CpNiNO [29] and CpV(CO)$_4$ [30] complexes. The other five Cp derivatives in Table 13 have been used as reference molecules to obtain 'spectroscopic' masses of Cp ligand.

We believe that force constants obtained by using 'spectroscopic' masses come close to the results of rigorous solutions. The method can be used as a fast and simple way to judge the approximate metal–Cp bond strength and the force constant can be used as a

Table 8
Experimental and calculated (NCA) fundamental frequencies (cm^{-1}) of Cp*Re(CO)$_3$ complex

Point group				Cp*Re(CO)$_3$		Assignment	PED (%) [a]
C_s	C_{5v}	C_{3v}	Number	Experimental	Calculated		
A′	a$_1$		**1**	1421	1419.8	ν(CC*) [b] + ν(CC)	$51R+50r$
A′	a$_1$		**2**	587	588.2	ν(CC*) + ν(CC)	$51r+50R$
A′	a$_1$		**3**	173	173.1	γ(CC*)	100ρ
A″	a$_2$		**4**	544	546.3	β(CC*)	100β
A′	e$_1$		**5a**	1408	1412.8	ν(CC*) + ν(CC)	$59r+40\alpha+1r$
A′	e$_1$		**6a**	795	796.3	ν(CC*) + ν(CC)	$50R+43r+7\beta$
A′	e$_1$		**7a**	190	187.7	β(CC*)	$78\beta+21R+1r$
A′	e$_1$		**8a**	173	171.7	γ(CC*)	$83\rho+17\tau$
A′	e$_2$		**9a**	1388	1382.2	ν(CC*) + ν(CC)	$55r+25\alpha+18R+2\beta$
A′	e$_2$		**10a**	1073	1078.8	ν(CC*) + ν(CC)	$85R+13\beta+2r$
A′	e$_2$		**11a**	185	186.8	β(CC*)	$81\beta+19R$
A′	e$_2$		**12a**	439	439.4	α(CCC)	$73\alpha+23r+3R+1\beta$
A′	e$_2$		**13a**	104	108.1	γ(CC*)	$67\rho+25\chi$
A′	e$_2$		**14a**	634	634.0	δ(CCC)	$64\chi+36\rho$
A′		a$_1$	**15**	2007	2007.1	ν_s(CO)	$92D+8d$
A′		e	**20a**	1909	1909.0	ν_{as}(CO)	$93D+7d$
A′		a$_1$	**16**	615	616.9	δ(ReCO)	$77\varepsilon+18\omega\gamma+2d+2S$
A″		a$_2$	**19**	381	380.1	δ(ReCO)	$100\varepsilon'$
A′		e	**21a**	595	595.0	δ(ReCO)	$74\varepsilon'+21\gamma+5\varepsilon$
A′		e	**22a**	495	494.4	δ(ReCO)	$71\varepsilon+13d+8\varepsilon'+7\omega$
A′		a$_1$	**17**	507	513.9	ν_s(ReC)	$91d+4\varepsilon+3D+2S$
A′		e	**23a**	515	518.2	ν_{as}(ReC)	$85d+12\varepsilon+2\omega+1\varepsilon'$
A′		e	**24a**	144	136.2	δ(CreC)	$77\gamma+17\varepsilon'+4\varepsilon+1\omega$
A′		a$_1$	**18**	104	124.3	δ(CreC)	$79\omega\gamma+13\varepsilon+7S$
A′		e	**25a**	104	103.5	δ(CreC)	$90\omega+10\varepsilon$
A′	a$_1$		**26**	381	374.3	ν_s(ReCp*)	$97S+2\varepsilon$
A′	e$_1$		**27a**	280	279.6	ν_{as}(ReCp*)	$54\tau+47\rho$

[a] For internal coordinates notation see Fig. 1.

[b] C*, C-atom of the CH$_3$-groups.

Table 9
Experimental and calculated (NCA) fundamental frequencies for $\mathrm{CpReO_3}$ ($\mathrm{cm^{-1}}$)

Point group				$\mathrm{CpReO_3}$		Assignment	PED (%) [a]
C_s	C_{5v}	C_{3v}	Number	Experimental	Calculated		
A′	a_1		**1**	3103	3098.6	$\nu(\mathrm{CH})$	$98r+2R$
A′	a_1		**2**	1075	1076.6	$\nu(\mathrm{CC})$	$91R+9r$
A′	a_1		**3**	835	835.0	$\gamma(\mathrm{CH})$	100ρ
A″	a_2		**4**	1230	1229.9	$\beta(\mathrm{CH})$	100β
A′	e_1		**5a**	3015	3018.4	$\nu(\mathrm{CH})$	$99r+1\alpha$
A′	e_1		**6a**	1429	1431.5	$\nu(\mathrm{CC})$	$78R+21\beta+1r$
A′	e_1		**7a**	1182	1182.6	$\beta(\mathrm{CH})$	$62\beta+24R+15\alpha$
A′	e_1		**8a**	855	855.0	$\gamma(\mathrm{CH})$	$95\rho+5\tau$
A′	e_2		**9a**	3075	3074.4	$\nu(\mathrm{CH})$	$97r+2R+1\beta$
A′	e_2		**10a**	1329	1330.7	$\nu(\mathrm{CC})$	$74\mathrm{R}+17\alpha+9\beta$
A′	e_2		**11a**	1018	1015.4	$\beta(\mathrm{CH})$	$52\beta+46R+2r$
A′	e_2		**12a**	958	949.9	$\alpha(\mathrm{CCC})$	$57\alpha+27R+16\beta+2r$
A′	e_2		**13a**	1049	1047.8	$\gamma(\mathrm{CH})$	$93\rho+7\chi$
A′	e_2		**14a**	589	589.0	$\delta(\mathrm{CCC})$	$74\chi+26\rho$
A′		a_1	**15**	926	928.3	$\nu_s(\mathrm{ReO_3})$	$100d$
A′		a_1	**16**	384	388.3	$\delta_s(\mathrm{ReO_3})$	$71\omega\gamma+29\rho$
A′		e	**17a**	886	886.0	$\nu_{as}(\mathrm{ReO_3})$	$100d$
A′		e	**18a**	276	276.7	$\rho_r(\mathrm{ReO_3})$	$92\gamma+8\omega$
A′		e	**19a**	193	202.3	$\delta_{as}(\mathrm{ReO_3})$	$92\omega+8\gamma$
A′	a_1		**20**	318	319.4	$\nu_s(\mathrm{ReCp})$	$59S+41\omega\gamma$
A′	e_1		**21a**	375	374.9	$\nu_{as}(\mathrm{ReCp})$	100τ

[a] For internal coordinates notation see Fig. 1.

Table 10
Experimental and calculated (NCA) fundamental frequencies for $\mathrm{Cp^*ReO_3}$ ($\mathrm{cm^{-1}}$)

Point group				$\mathrm{Cp^*ReO_3}$		Assignment	PED (%)[a]
C_s	C_{5v}	C_{3v}	Number	Experimental	Calculated		
A′	a_1		**1**	1427	1426.9	$\nu(\mathrm{CC})$ [b] $+\nu(\mathrm{CC^*})$	$53R+47r$
A′	a_1		**2**	591	585.8	$\nu(\mathrm{CC^*})+\nu(\mathrm{CC})$	$53r+47R$
A′	a_1		**3**	183	179.0	$\gamma(\mathrm{CC^*})$	100ρ
A″	a_2		**4**	545	545.0	$\beta(\mathrm{CC^*})$	100β
A′	e_1		**5a**	1407	1406.9	$\nu(\mathrm{CC})+\nu(\mathrm{CC^*})$	$64R+33r+3\beta$
A′	e_1		**6a**	804	803.9	$\nu(\mathrm{CC})+\nu(\mathrm{CC^*})$	$48R+44r+8\beta$
A′	e_1		**7a**	205	205.2	$\beta(\mathrm{CC^*})$	$82\beta+17R+1r$
A′	e_1		**8a**	122	121.7	$\gamma(\mathrm{CC^*})$	$92\rho+8\chi$
A′	e_2		**9a**	1366	1363.3	$\nu(\mathrm{CC^*})+\alpha(\mathrm{CCC})$	$57r+24\alpha+17R+2\beta$
A′	e_2		**10a**	1073	1069.5	$\nu(\mathrm{CC})$	$89R+8r+3\beta$
A′	e_2		**11a**	183	193.3	$\beta(\mathrm{CC^*})+\nu(\mathrm{CC})$	$82\beta+17R+1\alpha$
A′	e_2		**12a**	422	424.7	$\alpha(\mathrm{CCC})$	$74\alpha+21r+4R+1\beta$
A′	e_2		**13a**	109	108.8	$\gamma(\mathrm{CC^*})$	$99\rho+1\chi$
A′	e_2		**14a**	610	610.0	$\delta(\mathrm{CCC})$	$70\chi+30\rho$
A′		a_1	**15**	918	917.9	$\nu_s(\mathrm{ReO_3})$	$100d$
A′		a_1	**16**	400	392.5	$\delta_s(\mathrm{ReO_3})$	$79\omega\gamma+21S$
A′		e	**17a**	886	886.0	$\nu_{as}(\mathrm{ReO_3})$	$100d$
A′		e	**18a**	296	296.8	$\rho_r(\mathrm{ReO_3})$	$95\gamma+5\omega$
A′		e	**19a**	205	204.8	$\delta_{as}(\mathrm{ReO_3})$	$95\omega+5\gamma$
A′	a_1		**20**	355	352.5	$\nu_s(\mathrm{ReCp^*})$	$67\mathrm{S}+33\omega\gamma$
A′	e_1		**21a**	340	340.0	$\nu_{as}(\mathrm{ReCp^*})$	$83\tau+17\rho$

[a] For internal coordinates notation see Fig. 1.

[b] C*, C-atom of the $\mathrm{CH_3}$-groups.

starting value for the refinement procedure of a full solution.

4. Conclusions

Some important calculated force constants are presented in Table 10. From these data the following conclusions can be drawn. (a) The higher energy d orbitals of the heavier Re atom, which has a bigger atomic radius and is richer in electrons, allows a bigger overlap with the Cp ring orbitals than the Mn atom. This is reflected by the larger Re–Cp(Cp*) force constants compared with the Mn–Cp(Cp*) force constants. In $CpM(CO)_3$ complexes, the M–C force constants (both M–Cp and M–CO) are always larger in the case of Re than Mn-complexes. (b) Increasing the Re oxidation number in the trioxo complexes (Re(VII)) results in the concomitant weakening of the σ-coordination. Since the ReO_3 moiety is strongly electron-withdrawing, the metal–ring bond is weakened in comparison to the carbonyl complexes. This is evidenced by the larger K(MCp) force constants for the $CpRe(CO)_3$ complex relative to $CpReO_3$. In the case of the Cp* complexes, this weakening effect is more significant. (c) CH_3 groups increase the electron-density of the Cp ring, which has a direct consequence of increasing the charge on the metal. Therefore, the metal–ligand interaction becomes stronger, which is indicated by the larger force constants for Cp* complexes relative to Cp ones. Additionally the Re(Mn)–CO bond order increases, and the $C{\equiv}O$ bond order decreases, which is in accordance with the larger K(Re(Mn)–CO) and smaller K($C{\equiv}O$) force constants for Cp* complexes. (d) The larger force con-

Table 11
Some characteristic force constants of Cp(Cp*)ML_3 complexes

Force constant	Internal coordinate	$CpMn(CO)_3$	$Cp^*Mn(CO)_3$	$CpRe(CO)_3$	$Cp^*Re(CO)_3$	$CpReO_3$	Cp^*ReO_3
Stretching [a]							
K(CC)	R	7.52	7.74	7.43	6.67	7.25	6.67
K(CH(C*)) [b]	r	5.20	5.25	5.13	5.34	4.95	5.34
K(CD) [c]	S	3.39	6.85	4.03	6.91	3.66	3.81
K(MC*) [d]	d	2.80	3.63	3.62	3.86	–	–
K(ReO)	d'					6.99	6.99
K(CO)	D	15.97	15.85	15.89	15.69	–	–
Stretching–stretching [a]							
F(CC,CC)	R_1R_2 [e]	0.66	0.78	0.74	0.84	0.59	0.84
F(CC,C′C′)	R_1R_3 [f]	−0.85	−0.68	−0.32	−0.73	−0.75	−0.73
F(MC*, MC*)	dd	0.02	0.03	0.09	0.18		
F(ReO,ReO)	$d'd'$					0.36	0.36
F(CO,CO)	DD	0.17	0.18	0.23	0.24		
F(CC,CH(C*))	Rr	−0.28	−0.24	−0.26	−0.25	−0.42	−0.43
Bending [g]							
H(CCC)	α	1.62	1.32	1.42	0.91	1.88	0.86
H(CCH(C*))	β	0.39	0.46	0.33	0.43	0.51	0.45
H(DMC*)	ω	0.34	0.62	0.62	0.70		
H(DReO)	ω'					1.11	1.20
H(C*MC*)	γ	0.49	0.76	0.76	0.88		
H(OReO)	γ'					1.09	1.14
$H(MCO)_{ip}$ [g]	ε	0.79	0.70	0.81	0.71	–	–
$H(MCO)_{op}$ [h]	ε'	0.53	0.60	0.47	0.54	–	–
H(CCCH(C*))	ρ	0.36	0.39	0.27	0.33	0.54	0.20
H(CCCC)	χ	0.63	0.38	0.66	0.49	0.62	0.50
Cp tilt	τ	0.31	0.41	0.27	0.41	0.27	0.37
Bending–bending [i]							
h(DReO,DReO)	$\omega'\omega'$					0.25	0.34
h(OReO,OReO)	$\gamma'\gamma'$					0.33	0.26

[a] 10^2 N m^{-1}.
[b] C*, C-atom of the CH_3-groups.
[c] D, 'dummy' atom in the geometric center of C_5-ring.
[d] C*, C-atom which belongs to CO-groups.
[e] R_1R_2, adjacent C–C bonds.
[f] R_1R_3, opposite C–C bonds.
[g] ip, M–C–O in–plane linear deformation.
[h] op, M–C–O linear deformation, perpendicular to the plane.
[i] 10^{-18} N m rad^{-2}.

Table 12
Averaged internal valence force constants for Cp and Cp* ligands

Force constant	Internal coordinate	$C_5H_5^-$	$C_5(CH_3)_5^-$
Stretching [a]			
K(CC)	*R*	7.52	7.03
K(CH(C*)) [b]	*r*	5.10	5.31
Stretching–stretching [a]			
F(CC,CC)	R_1R_2 [b]	0.66	0.82
F(CC,C′C′)	R_1R_3 [c]	−0.64	−0.71
F(CC,CH(C*))	Rr	−0.32	−0.30
Bending [d]			
H(CCC)	α	1.64	1.03
H(CCH(C*))	β	0.41	0.45
Out of plane, torsional			
H(CCCH(C*))	ρ	0.39	0.31
H(CCCC)	χ	0.64	0.46
Cp tilt	τ	0.28	0.40
Stretching–bending [e]			
h(CC, CCC) [f]	$R\alpha$	0.80	0.92

[a] 10^2 N m^{-1}.
[b] R_1R_2, adjacent C–C bonds.
[c] R_1R_3, opposite C–C bonds.
[d] 10^{-18} N m rad^{-2}.
[e] 10^{-8} N m rad^{-1}.
[f] $R_1\alpha_5$, interaction of α_i with R_j having common bonds.

stants for the Cp* complexes relative to Cp ones can be interpreted as a measure of the molecules' stability. As in the case of oxo derivatives, the smaller force constant obtained for $CpReO_3$ (3.66×10^2 N m^{-1}) can be a good explanation of its lower stability in comparison to Cp^*ReO_3 (3.81×10^2 N m^{-1}). (e) Generally, it can be concluded, that due to the metal–ligand bond strengthening, the ring force constants become smaller (both for the in-plane and out-of-plane coordinates). Averaged 11 characteristic force constants have been selected for Cp and Cp* ligands, which can be transferred to other-complexes. By introducing effective 'spectroscopic' masses for Cp ligand, metal–Cp stretching force constants can be estimated by a very simple ('diatomic') calculation.

Table 13
Calculated metal–ligand stretching force constants using 'spectroscopic' masses of Cp ligands

Molecule	'Spectroscopic' mass of Cp	Effective G matrix elements	Symmetric Cp–M stretching (cm^{-1})	Calculated Cp–M force constants (N cm^{-1})	
				Approximate	Full solution
CpNiNO	72.8	0.024972	322 [a]	2.45	–
$CpV(CO)_4$	72.8	0.019871	329 [b]	3.21	–
$CpMo(CO)_2NO$	77.1	0.018465	324 [c]	3.35	3.36
$CpMn(CO)_3$	72.8	0.020931	347	3.38	3.39
$C_5D_5Mn(CO)_3$	79.8	0.019726	337	3.39	3.39
$CpReO_3$	83.2	0.016293	318	3.65	3.66
$CpRe(CO)_3$	83.2	0.015723	328	4.03	4.03

[a] Frequency taken from Ref. [29].
[b] Ref. [30].
[c] Ref. [31].

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