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Research Article/ Araştırma Makalesi

A New Method for Analyzing the Force Constants of Tricarbonyl Complexes with C_S Symmetry

Elvan ÜSTÜN[1]*, Cemal KAYA[2]

[1]Department of Chemistry, Ordu University, 52200 Ordu, Turkey
[2]Department of Chemistry, Cumhuriyet University, 58140 Sivas, Turkey

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Abstract

Metal carbonyl complexes that generally used as catalyst in early researches have attracted much attention recently due to their potential pharmaceutical applications as CMIA and CORMs. Metal carbonyls also have used also as bioprobe, protein-labelling agent thanks to unique spectroscopic feature in mid-IR. The position and the number of carbonyl IR bands have affected by chemical environment of carbonyl unit and coordinated ligands. Therefore, the force constants of metal carbonyl complexes could give meaningful qualitative and quantitative information about the electronic influences of the coordinated ligands. Additionally the force constants could be useful criteria when the carbonyl ligands have evaluated in terms of isolobal analogy. In this study, the stretching and the interaction force constants of many metal carbonyl complexes with lots of different seconder ligands have calculated with a new suggested simple method to gain insight into the σ-donor/π-acceptor properties of these coordinated ligands.

***Keywords:** Metal carbonyl complexes; CO-factored force fields, Force constants*

Cs Simetrisindeki Trikarbonil Komplekslerinin Kuvvet Sabitlerinin Yeni Bir Metot ile Analizi

Öz

Erken dönem çalışmalarında genellikle katalizör olarak kullanılan metal karbonil kompleksleri, CMIA ve CORMs olarak potansiyel farmakolojik uygulamalarda kullanıldıkları için son zamanlarda daha fazla dikkat çekmektedirler. Ayrıca metal karboniller, orta-IR bölgesindeki özel spektroskopik özellikleri sayesinde biyoprob ve protein etiketleme ajanı olarak kullanılmaktadır. Karbonil komplekslerinin IR bandlarının sayısı ve yeri, karbonil ve diğer bağlı ligandların oluşturduğu kimyasal çevreden etkilenmektedir. Metal karbonil komplekslerinin kuvvet sabitleri, bağlı ligandların elektronik etkileri konusunda kalitatif ve kantitatif olarak anlamlı bilgiler verebilirler. Bununla birlikte, kuvvet sabitleri, karbonil komplekslerinin izolobal benzerliği ile ilgili kullanışlı bir kriter olarak değerlendirilebilir. Bu çalışmada önerilen yeni ve basit metot ile farklı ikincil ligandlar bulunduran pek çok metal karbonil kompleksinin kuvvet ve etkileşim sabitleri, bu ligandların σ-verici/π-alıcı özellikleri hakkında öngörü oluşturmak için hesaplanmıştır.

***Anahtar Kelimeler:** Metal karbonil kompleksleri; CO-ayrımlı kuvvet alanları, Kuvvet sabitleri*

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* *Corresponding Author/ Sorumlu Yazar: elvanustun@odu.edu.tr*

1. Introduction

Organometallic compounds are known as unstable and toxic and it is true for most of them (Fish & Jaouen 2003). Because of the developments in bioorganometallic chemistry, these complexes are started to use in medicine and called the scientists' attention (Salmain et al. 1999). Metal carbonyl complexes that contain carbon monoxide as ligand are important milestones. Although the applications of these complexes are related to catalyst (Mula et al. 1999), probes in polymerization processes (Morisaki et al. 2004), exploitation of solar energy (Knör & Monkowius 2011), and the pharmaceutical applications as CO-releasing molecules (Motterlini et al. 2002; Üstün et al. 2017; Üstün et al. 2016; Schatzschneider 2014) have accelerated the researches.

Metal carbonyl complexes have unique spectroscopic properties in mid-IR range (Brimm et al. 1954). Metal carbonyls should be sufficiently stable towards hydrolysis, reactive under mild conditions, selective towards particular amino acid side chain and easy to detect quantify once bound of the protein (Gorfti et al. 1996). Thus, characterization of the protein conjugates can be readily performed by IR spectroscopy of the ν(CO) bands of the metal carbonyl moieties. Furthermore, transition metal carbonyl complexes are established as useful bioprobes for studies involving high affinity biological recognition phenomena, such as oestrogen receptor, immunoanalysis and other ligand/protein interactions (Hillard & Jaouen 2011). Additionally, the ^{13}C isotopomers of metal carbonyls are used in labeling of biologically active molecules and clarification of the reaction pathways (Braterman et al. 1964; Bour et al. 2000). Because, the greater mass of ^{13}C (compared with natural ^{12}C) led to lower frequencies of carbonyl stretching bands.

The number and the position of υ(CO) bands depends on the local symmetry and chemical/molecular environment of the metal carbonyl unit and coordinated ligand(s) (Ghaffar et al. 1998). The force constants of carbonyl ligand could be a good quantitative reporter for σ-donor and π-acceptor properties of the coordinated ligands. In recent studies, good correlations between the ^{13}C chemical shift and CO force constants have provided helpful insights into the electronic influences of the ligands. The increasing force constants have thought to be the reason of effective π-back bonding to metal center while the increment of ^{13}C shift is the indication of the π-acidity of the ligands. The interpretations are very meaningful for the ligands that cannot isolated for analyzing σ-donor/ π-acceptor properties (Kendall et al. 2016; Carpenter et al. 2015; Applegate et al. 2016). Furthermore, isolobal analogy between CO and the phosphine, phosphide and arsine type ligands could give valuable qualitative information. Cotton-Kraihanzel force field method has generally used for calculating the force constants of metal carbonyl complexes. However, the method provides relative force constants for similar complexes and generally overestimates the force constants for these type of tricarbonyl complexes (Carpenter et al. 2015). In this study, a new and basic method for solving the force constants in the secular equations of octahedral homoleptic metal carbonyl complexes with many different ligands with C_S symmetry will be suggested. The applicability and the reliability of suggested method will be confirmed by carbonyl IR bands of isotopic enrichment studies.

2. Material and Method

Increasing popularity of the metal carbonyls has made the theoretical studies more common. Nowadays, the structure analysis with quantum mechanics based calculation programs have used commonly; but, CO-factored force fields method (CFFM) had been used since 1980s (Üstün & Kaya 2010). CFFM is an effective and simple method, which can provide useful results.

Group theory predicts that octahedral complexes with C_s symmetry have three bands as $2a' + a''$. All of these bands are IR and Raman active. The secular equations of complexes which obtained by applying CFFM have C-O stretching force constants (k_1 and k_2) and CO-CO interaction constants (k_c, k'_c and k_t) can be seen in Fig 1. Fac-isomer have k_c, k'_c, although mer-isomer have k_c and k_t. It is given only fac-isomer's secular equation in Table 1; because k'_c takes k_t's places in the solution of the secular equations and the solution of k_t is the solution of k'_c, in fact.

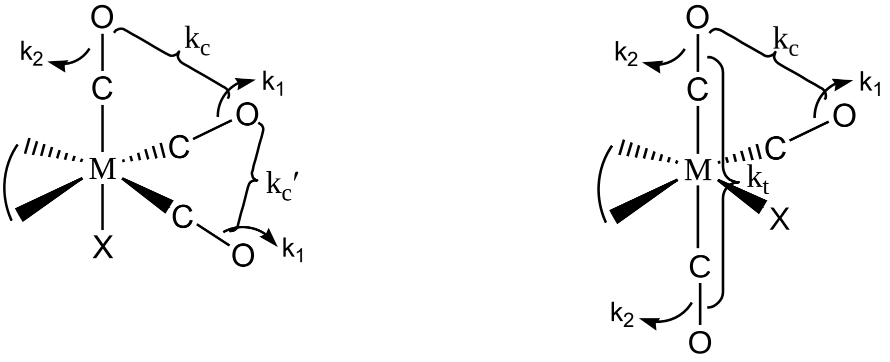

Figure 1. Two different isomers (fac- and mer-) of $M(CO)_3(L\text{-}L)X$ molecules and their force constants

In this study, the approaches which developed for metal carbonyl complexes in type $M(CO)_5$ with D_{3h} symmetry by Kaya et al. (2007) were tried for octahedral tricarbonyl complexes with C_s symmetry.

Table 1. Secular equations of the molecules

Symmetry species	Secular equations[a]
$a'^{(1)}$ $a'^{(2)}$	$\begin{vmatrix} \mu(k_1 + k'_c) - \lambda & \sqrt{2}\mu k_c \\ \sqrt{2}\mu k_c & \mu k_2 - \lambda \end{vmatrix} = 0$
a''	$\lambda = \mu(k_1 - k'_c)$

[a] μ represents the reciprocal or the reduced mass of the CO groups; $\lambda=4\pi^2c^2\nu^2$ where ν is the frequency in cm^{-1}.

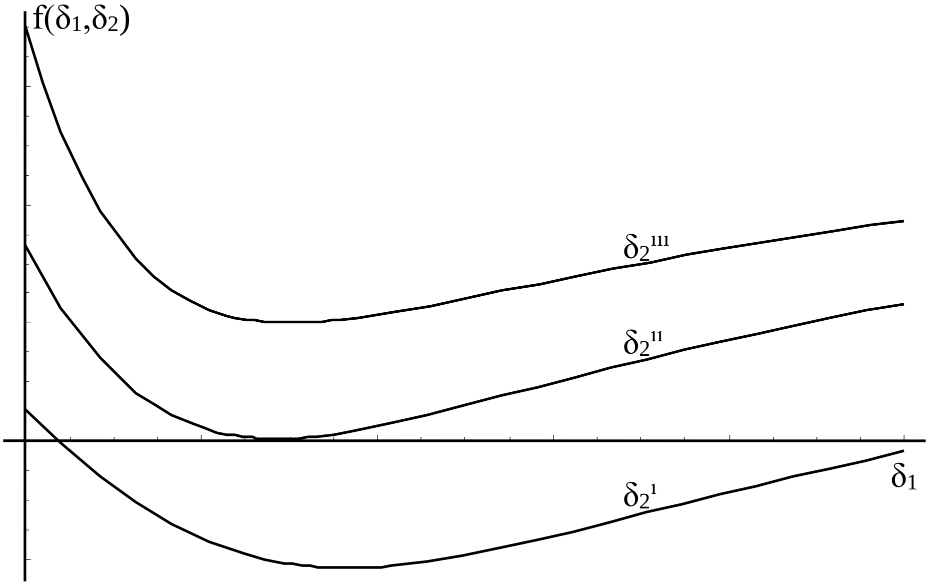

Figure 2. Graph of the function f(δ_1,δ_2) versus different value of δ_2

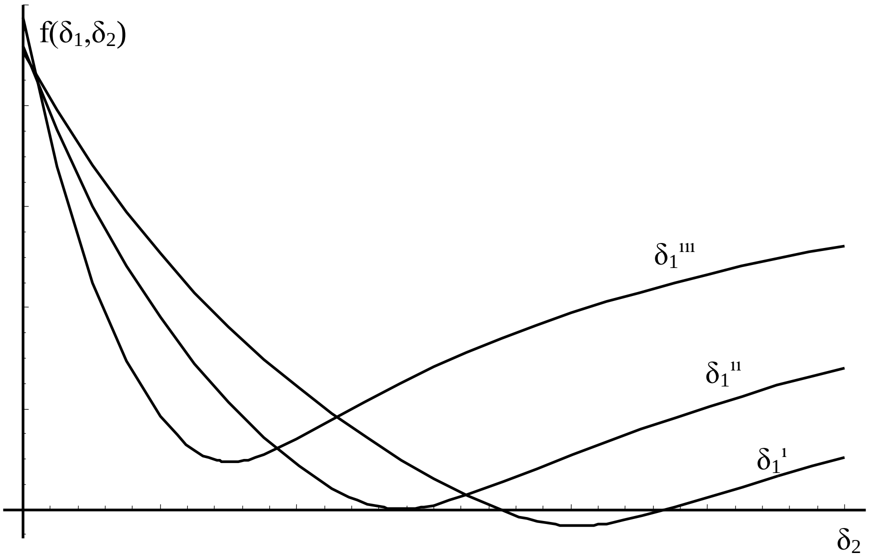

Figure 3. Graph of the function f(δ_1,δ_2) versus different value of δ_1

$$k_1 - k_C^I = \delta_1 k_c \tag{1}$$

$$k_2 = \delta_2 k_c \tag{2}$$

If these approaches have been used in secular equations, the $f(\delta_1,\delta_2)$ function connected with δ_1 , δ_2 and observed frequencies can be gained.

$$f(\delta_1,\delta_2) = \frac{\sqrt{(\delta_1-\delta_2)^2+8}}{\delta_1+\delta_2} - \frac{(\lambda_1-\lambda_2)}{(\lambda_1+\lambda_2)} = 0 \tag{3}$$

If we plot two graph (δ_1 versus δ_2 and δ_2 versus δ_1) for different values of δ , we can see that there are minimums in two graph and can use these minimums for solution (Figure 2 and Figure 3). When we used these minimums, Eq. (4) and (5) are gained for δ_1 and δ_2.

$$\delta_1 = \frac{\sqrt{2}\left[(\lambda_1-\lambda_2)^2+(\lambda_1+\lambda_2)^2\right]}{(\lambda_1-\lambda_2)\sqrt{(\lambda_1+\lambda_2)^2-(\lambda_1-\lambda_2)^2}} \tag{4}$$

$$\delta_2 = \frac{\sqrt{2}\sqrt{(\lambda_1+\lambda_2)^2-(\lambda_1-\lambda_2)^2}}{(\lambda_1-\lambda_2)} \tag{5}$$

It is important that the observed infrared frequencies are only needed for the solution of Eq. (3). If we substitute the Eq. (4) and (5) in secular equations, the equations of force constants were gained. While $\beta = \frac{(\lambda_1-\lambda_2)^2}{(\lambda_1+\lambda_2-2\lambda_3)}$

$$k_1 = \frac{1}{4\mu}(\lambda_1+\lambda_2+2\lambda_3+\beta) \tag{6}$$

$$k_2 = \frac{1}{2\mu}(\lambda_1+\lambda_2-\beta) \tag{7}$$

$$k_C^I = \frac{1}{4\mu}(\lambda_1+\lambda_2-2\lambda_3+\beta) \tag{8}$$

$$k_C = \frac{\sqrt{(\lambda_1-\lambda_2)^2-\beta^2}}{2\sqrt{2}\mu} \tag{9}$$

Secular equations of the molecules can be solved with using of these equations.

3. Result and Discussion

Tricarbonyl complexes with octahedral geometry are more popular than the others recently, especially in theoretical studies, because of the big ligands which are suitable to bind as chelate. For that reason, octahedral metal carbonyls with C_S symmetry have been chosen in this study.

The number of ν(CO) bands depends on the local symmetry of the metal carbonyl unit, whereas their position relies on their chemical and molecular environment. The frequencies of carbonyl complexes can be affected the solvent evenly pH of the solvent. When the molecules are studied in the same chemical condition, IR bands of the molecules are affected only the bonded groups. Bonded group effects can be analyzed C-O stretching force constants and CO-CO interaction constants, quantitatively. The magnitude of stretching force constants show the power of the C-O bond while the magnitude of the interaction constants show the power of the CO-CO interactions. So the differences, which occur due to the ligands expect carbonyl, in a molecule can be interpreted with the force constants of the molecule.

Table 2. Comparison of the frequencies calculated with different methods

Molecules	Method	k_1	k_2	k'_c	k_c
$IrI_2Me(CO)_3$	Lit[a]	18.10	18.40	0.355	0.246
	This study	18.093	18.426	0.346	0.244
$Cr(Ph_3P)(dipy)(CO)_3$	Lit[b]	13.50	14.10	0.47	0.61
	This study	13.510	14.072	0.469	0.625
$Cr(Ph_3P)(phen)(CO)_3$	Lit[b]	13.54	14.14	0.48	0.62
	This study	13.548	14.116	0.480	0.684
$Cr[(EtO)_3P](dipy)(CO)_3$	Lit[b]	13.58	14.19	0.49	0.69
	This study	13.572	14.191	0.492	0.687
$Cr[(EtO)_3P](phen)(CO)_3$	Lit[b]	13.56	14.17	0.49	0.69
	This study	13.558	14.176	0.492	0.687
$Mo[(C_8H_{17})_3P](phen)(CO)_3$	Lit[b]	13.47	14.00	0.53	0.58
	This study	13.474	13.983	0.526	0.588
$Mo(Bu_3P)(phen)(CO)_3$	Lit[b]	13.47	14.01	0.53	0.58
	This study	13.478	13.990	0.531	0.593
$Mo(Ph_3P)(dipy)(CO)_3$	Lit[b]	13.55	14.08	0.53	0.64
	This study	13.555	14.089	0.518	0.626
$Mo(Ph_3P)(phen)(CO)_3$	Lit[b]	13.55	14.08	0.53	0.64
	This study	13.541	14.089	0.528	0.627
$Mo[(PrO)_3P](dipy)(CO)_3$	Lit[b]	13.54	14.21	0.53	0.64
	This study	13.564	14.149	0.529	0.664
$Mo[(PrO)_3P](phen)(CO)_3$	Lit[b]	13.54	14.24	0.54	0.65
	This study	13.576	14.171	0.535	0.676
$Mo[(BuO)_3P](dipy)(CO)_3$	Lit[b]	13.61	14.22	0.52	0.68
	This study	13.608	14.811	0.519	0.679
$Mo[(BuO)_3P](phen)(CO)_3$	Lit[b]	13.61	14.22	0.53	0.69
	This study	13.612	14.218	0.525	0.683
$Mo[(EtO)_3P](phen)(CO)_3$	Lit[b]	13.64	14.25	0.52	0.68
	This study	13.637	14.241	0.520	0.680
$Mo(Ph_3As)(phen)(CO)_3$	Lit[b]	13.51	14.07	0.54	0.59
	This study	13.519	14.042	0.538	0.605
$Mo(Ph_3Sb)(phen)(CO)_3$	Lit[b]	13.51	14.06	0.53	0.53
	This study	13.529	14.005	0.532	0.557
$W(Ph_3P)(dipy)(CO)_3$	Lit[b]	13.44	14.05	0.50	0.60
	This study	13.461	14.009	0.500	0.619
$W[(EtO)_3P](dipy)(CO)_3$	Lit[b]	13.52	14.12	0.50	0.65
	This study	13.503	14.072	0.469	0.632
$W[(EtO)_3P](phen)(CO)_3$	Lit[b]	13.55	14.21	0.50	0.65
	This study	13.569	14.168	0.497	0.669

[a] Ghaffar T, Adams H, Maitlis P M, Sunley G J, Baker M J & Haynes A (1998). Spectroscopic Identification and Reactivity of $[Ir(CO)_3I_2Me]$, A Key Reactive Intermediate in Iridium Catalyzed Methanol Carbonylation. *Chem. Comm.* 1023-1024. [b] Dalton J, Paul I, Smith J G & Stone F G A (1968). Spectroscopic Studies on Organometallic Compounds. Part XVI. Infrared Spectra of Tricarbonylmolybdenum Complexes in The Carbonyl Stretching Region. *J. Chem. Soc.(A)*: 1208-1211.

Solving of the secular equations is essential for analyzing of the force constants of a molecule; but it is often necessary to use some approximations. Now, it is possible that calculate the force constants with only use the observed frequencies by using the method above.

Table 3. Comparison of the calculated and experimental frequencies for $IrI_2Me(CO)_3$

Molecule	Symmetry Type	Exp.	Lit[a]	This study
$M(^{12}CO)_3L$	a′	2156	2156	2156
	a′	2116	2116	2116
	a″	2096	2096	2096
ax-$M(^{13}CO)(^{12}CO)_2L$	a′	2142	2144.2	2143.4
	a′	2081	2079.7	2081.0
	a″	2096	2095.9	2096.0
eq-$M(^{13}CO)(^{12}CO)_2L$	a′		2148.6	2149.1
	a′		2110.7	2110.9
	a″		2060.8	2060.7
eq-eq-$M(^{13}CO)_2(^{12}CO)L$	a′		2141.8	2142.8
	a′		2082.0	2081.5
	a″		2049.2	2049.3
ax-eq-$M(^{13}CO)_2(^{12}CO)L$	a′		2131.7	2131.1
	a′		2082.1	2083.2
	a″		2058.9	2058.9
ax-eq-eq-$M(^{13}CO)_3L$	a′		2107.9	2107.9
	a′		2068.3	2068.8
	a″		2049.2	2049.3

[a] Ghaffar T, Adams H, Maitlis P M, Sunley G J, Baker M J & Haynes A (1998). Spectroscopic Identification and Reactivity of $[Ir(CO)_3I_2Me]$, A Key Reactive Intermediate in Iridium Catalyzed Methanol Carbonylation. *Chem. Comm.* 1023-1024.

In Table 2, the force constants calculated with the method, which recommended above compare with the Cotton-Kraihanzel Force Field (CKFF) Method. There is a good agreement between the Cotton-Kraihanzel Method and the method recommended in this study; in fact, two methods suggest the same results for many of the force constants but the new method explained above can be applied easier than the Cotton-Kraihanzel Method.

Although CKFF method can be used a comparison method, the main valid method that is accepted in literature is ^{13}C isotopomer method. The force constants calculated from the three vibrational frequencies for the unlabeled parent molecule were used to generate the vibrational frequencies for the various isotopically labelled derivatives. However, it is important there is a good agreement between the experimental results and the calculated results. In Table 3, the force constants of $IrI_2Me(CO)_3$ which calculated with the suggested method above have been compared with the experimental results and the calculated results suggested literature; it can be seen there is an excellent agreement. Table 3 show that the suggested method is acceptable for the solution of the secular equations of the octahedral tricarbonyl complexes with Cs symmetry. With this method, the force constants, which have not been calculated before, have been calculated for lots of molecules and shown in Table 4.

Table 4. The IR frequencies and force constants calculated with suggested method of some octahedral metal carbonyl complexes

Molecule	Frequency			Force Constants			
	a'	a'	a''	k_1	k_2	k'_c	k_c
[a]$ReCl(P{\cap}O)(CO)_3$	2039	1938	1935	15.575	15.942	0.450	0.573
[a]$ReBr(P{\cap}O)(CO)_3$	2035	1941	1938	15.591	15.938	0.419	0.533
[a]$ReCl(P{\cap}N)(CO)_3$	2021	1930	1926	15.396	15.740	0.411	0.513
[a]$ReBr(P{\cap}N)(CO)_3$	2024	1925	1921	15.353	15.719	0.446	0.558
[b]$Ru(Me_3Si)(Ph_3P)I(CO)_3$	2088	2022	1999	16.612	17.046	0.469	0.387
[b]$Ru(Me_3Ge)(Ph_3P)I(CO)_3$	2088	2023	2001	16.632	17.055	0.457	0.381
[b]$Ru(Me_3Sn)(Ph_3P)I(CO)_3$	2080	2017	1998	16.549	16.939	0.423	0.368
[b]$Os(Me_3Si)(Ph_3P)Br(CO)_3$	2092	2016	1986	16.502	17.025	0.569	0.445
[b]$Os(Me_3Si)(Ph_3P)I(CO)_3$	2088	2014	1989	16.501	16.976	0.520	0.433
[b]$Os(Me_3Ge)(Ph_3P)Br(CO)_3$	2090	2016	1986	16.493	17.009	0.560	0.434
[b]$Ru(Me_3Si)(Ph_3P)H(CO)_3$	2068	2009	1991	16.408	16.776	0.395	0.343
[b]$Ru(Me_3Sn)(Ph_3P)H(CO)_3$	2061	2009	1989	16.362	16.721	0.381	0.302
[c]$OsH_2Ph_3P(CO)_3$	2079	2027	2018	16.784	16.940	0.186	0.357
[c]$OsH_2Ph_3P(CO)_3$	2079	2024	2061	16.930	17.308	0.381	0.106
[c]$OsH_2Ph_3P(CO)_3$	2075	2029	2005	16.630	17.003	0.390	0.269
[c]$OsD_2Ph_3P(CO)_3$	2076	2004	1989	16.409	16.795	0.428	0.419
[c]$OsD_2Ph_3P(CO)_3$	2073	1999	1983	16.329	16.729	0.444	0.430
[c]$OsD_2Ph_3P(CO)_3$	2070	1994	1978	16.257	16.662	0.452	0.441
[d]fac-$[W(\eta^2\text{-}C_5H_8)_2(CO)_3]$	1973	1887	1863	14.552	15.025	0.532	0.474
[d]mer-$[WH(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_3H_6)]$	2070	2006	1918	15.830	16.766	0.969	0.372
[d]mer-$[WH(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_3H_6)]$	2050	1934	1913	15.440	15.988	0.657	0.659
[d]mer-$[WH(\eta^3\text{-}C_4H_7)(\eta^2C_4H_8)]$	2052	1935	1913	15.453	16.012	0.670	0.665
[e]$W(bpy)(dppm)(CO)_3$	2000	1908	1801	14.284	15.398	1.182	0.513
[e]$W(bpy)(dppf)(CO)_3$	1999	1897	1800	14.235	15.297	1.147	0.567

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4. Conclusion

Metal carbonyl complexes, which is one of the most important complex type of organometallic compounds, have gained increasing attention of scientists due to their potential therapeutic application in human medicine. The most common research area of these complexes are bioprobe improvement, protein labelling and CMIA methods owing to their unique spectroscopic properties in mid-IR region of carbonyl units of these complexes. Both the qualitative and the quantitative method for evaluating the carbonyl bands is calculating the stretching and interaction force constants. In this study, a new method for calculating the force constants of metal carbonyl complexes has suggested and the force constants of many metal carbonyl with lots of different ligands has calculated. These calculations will provide useful insights about the electronic influences of the ligands. In addition, these results could furnish meaningful estimations about the chemical properties of coordinated groups thanks to isolobal analogy theory.

Tricarbonyl complexes with many different ligands with C_S symmetry group were evaluated in this paper and the studies could be extended to different type of metal carbonyl complexes.

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