The $[M_2(CO)_8]$ Complexes of the Cobalt Group

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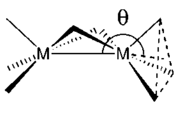
A theoretical study of the carbonyl complexes $[M_2(CO)_8]$ of the group 9 metals (M = Co, Rh, Ir) is presented. Three isomers were found for each metal, with the relative stabilities and energies differing from one metal to another, and two transition states corresponding to their interconversion processes were identified. The minima in the potential energy surface have been fully characterized through a vibrational analysis and the Raman-active metal–metal stretching frequencies, as well as infrared-active carbonyl stretching frequencies. The combination of theoretical, structural, and vibrational data is expected to be useful for the correct characterization of the Rh and Ir complexes for which no experimental structural data have been reported so far.

Introduction

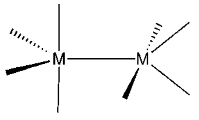
Transition-metal carbonyl complexes constitute a reference set of compounds that have played a crucial role in the development and understanding of modern transition metal chemistry.[1] Dinuclear carbonyls, for instance, are paradigmatic examples used to illustrate the predictive power of the electron counting rules in regard with the existence of metal−metal bonds. Those complexes also constitute the simplest possible realization of a metal cluster and have allowed us to theoretically analyze the effect of the ligands' orientation on metal−metal bonding and their influence in stability.[2,3]

In the particular case of the dicobalt complex $[Co_2(CO)_8]$, a structure with two bridging and six terminal carbonyl groups has been found in the solid state (**1a**).[4,5] The geometry around the metal may be described as square pyramidal with the basal plane comprising two bridging and two terminal carbonyls. With this arrangement, the metal atom obeys the 18-electron rule, completing a pseudo-octahedral coordination sphere with a so-called *bent* metal−metal bond,[5,6] consistent with its diamagnetic behavior.



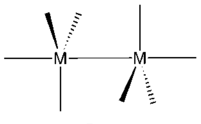
C_{2v}

1a



D_{2d}

1b



D_{3d}

1c

Evidence for the existence of other structures for $[Co_2(CO)_8]$ was early reported by Bor and Noack, based on the study of the carbonyl region of its infrared spectrum, from which they proposed the presence of at least two isomeric forms.[7−9] The first form was associated with the same structure found in the solid state, namely a bridged form with idealized C_{2v} symmetry (**1a**). A second unbridged form with D_{3d} symmetry was proposed, analogous to that found for the isoelectronic $[Fe_2(CO)_8]^{2-}$ anion in the solid state. Later, the existence of a third isomer with eight terminal ligands was detected by infrared spectroscopy.[10−12] Raman spectroscopy also shows the presence of three forms in solution.[13] In summary, it is currently accepted that the vibrational spectra of $[Co_2(CO)_8]$ is consistent with the existence of three isomers: C_{2v} (**1a**), D_{2d} (**1b**), and D_{3d} (**1c**).

No crystal structure has been reported so far for the analogous compounds with other group 9 metals, although some interesting data have been reported in the literature. A bridged form **1a** was proposed for $[Rh_2(CO)_8]$ from its infrared[14−16] and electronic[17] spectra, which are consistent with the existence of two bridging carbonyls. In contrast, no bridging carbonyl groups appear in the infrared spectrum of $[Ir_2(CO)_8]$, for which the unbridged form has been proposed.[18] In both cases, the isomers seem to be unstable toward the formation of tetranuclear species.[19]

Substitution of carbonyls by ER_3 ligands [e.g., PR_3, $P(OR)_3$, or AsR_3] may provide some hints about the structures of the parent compounds. Hence, the $[Co_2(CO)_6(ER_3)_2]$ complexes appear in the D_{3d} structure (**1c**) in the solid state,[20−28] and their conversion in solution into the C_{2v} form has been observed by infrared spectroscopy.[29−31] A similar interconversion has been reported for $[Co_2(CO)_7(ER_3)]$ complexes.[29,32] Rhodium[15,33−35] and iridium[36] complexes of type $[M_2(CO)_{8-n}(ER_3)_n]$ also present an equilibrium between bridged and unbridged forms.

In this paper we present a systematic density functional (DFT) study[37,38] of the $[M_2(CO)_8]$ complexes (M = Co, Rh, or Ir) in an attempt to contribute to a better interpretation of the experimental data available for these complexes. We will focus not only on the calculation of molecular geometries, but also on the relative energies of the three isomers, and on the barriers for their interconversion. We also

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intend to provide some hints for the characterization of the different tautomers from the vibrational spectra, mostly in the carbonyl stretching and metal-metal stretching regions.

Results

Molecular Structure

Density functional calculations were performed on complexes with the formula $[M_2(CO)_8]$ (M = Co, Rh, or Ir), considering in each case the three possible isomers corresponding to idealized symmetries C_{2v}, D_{2d}, and D_{3d} (**1**). The main structural parameters for the optimized structures are presented in Table 1.

Table 1. Calculated structural parameters for the three optimized isomers of $[M_2(CO)_8]$ complexes with M = Co, Rh, and Ir. All distances in Å, angles in degrees, mean experimental values (refs. [4,5]) in parentheses

Isomer	Parameter[a]	Co	Rh	Ir
C_{2v} (**1a**)	$M-M$	2.545 (2.538)	2.830	2.827
	$M-C_{eq}$	1.821 (1.837)	1.985	1.962
	$M-C_{ax}$	1.816 (1.821)	1.997	1.940
	$M-C_{bg}$	1.960 (1.946)	2.106	2.127
	$M-M-C_{eq}$	110.3 (112.7)	112.8	109.9
	$M-M-C_{ax}$	126.5 (123.8)	123.0	126.7
	$C_{eq}-M-C_{ax}$	105.7 (105.0)	105.5	105.8
	$C_{eq}-M-C_{eq}$	93.2 (93.3)	92.7	93.5
	$C_{bg}-M-C_{ax}$	95.5 (95.1)	94.8	94.8
	$C_{bg}-M-C_{bg}$	84.1 (86.0)	82.5	79.2
	$M-C_{bg}-M$	81.0 (81.4)	84.4	83.3
	θ	196.5 (193.1)	192.9	197.6
D_{2d} (**1b**)	$M-M$	2.619	2.882	2.921
	$M-C_{eq}$	1.812	1.973	1.936
	$M-C_{ax}$	1.795	1.941	1.936
	$M-M-C_{eq}$	124.0	120.5	118.1
	$M-M-C_{ax}$	77.1	78.4	79.7
	$C_{eq}-M-C_{ax}$	97.1	95.9	94.8
D_{3d} (**1c**)	$M-M$	2.671	2.851	2.901
	$M-C_{eq}$	1.814	1.975	1.946
	$M-C_{ax}$	1.789	1.934	1.926
	$M-M-C_{eq}$	85.3	85.1	84.8
	$C_{eq}-M-C_{eq}$	119.3	119.3	119.2

[a] Notation: eq = equatorial (D_{2d} and D_{3d}) or basal (C_{2v}); ax = axial (D_{2d} and D_{3d}) or apical (C_{2v}); bg = bridge (C_{2v}).

The optimized geometry of the bridged form of $[Co_2(CO)_8]$ (**1a**) is in good agreement with the experimental data, such as the Co−Co distance (2.545 Å calculated, 2.536 and 2.539 Å experimental) and the pyramidality angle for the apical ligand (100.6° calcd., 100.1° exp.). These data are consistent with a description of the coordination sphere of the metal atom as a square pyramid. The structural parameters calculated here are very similar to those previously reported by Ziegler,[39] only a shorter Co−Co distance was found by us, in better agreement with the experimental value. The orientation of the terminal carbonyl triads (defined by an angle θ of 196.5°, **1a**) is slightly different from the experimental values (193.1±0.5°), but well within the range of experimental values found for the analogous $[Co_2(\mu\text{-}CO)_2(CO)_{6-n}L_n]$ complexes ($188° < \theta < 212°$, Table 2). As predicted for the isoelectronic iron carbonylate,[3] the experimental data for the homoleptic complexes $[Co_2(\mu\text{-}CO)_2(CO)_6]$ and $[Co_2(\mu\text{-}CNR)_2(CNR)_6]$ present a linear correlation between the orientation angle θ and the Co−Co bond length (Figure 1, black circles), corresponding to Equation (1) (regression coefficient $r = 0.958$).

$$Co-Co = 4.187 - 0.00857 \cdot \theta \qquad (1)$$

It thus seems obvious that substitution of the carbonyls by the bulkier isocyanide ligands should favor a larger outward bending of the terminal ligands and shorten the Co−Co distance (which in turn would affect the Co−Co stretching vibration, see below). A similar behavior was found for the isoelectronic mixed ligand complexes $[Co_2(\mu\text{-}CO)_2(CO)_{6-n}L_n]$ (Figure 1, white circles), although some dispersion appears probably due to the bidentate nature of the non-carbonyl ligands. Although the available data is scarcer for Rh and Ir, their complexes follow a similar trend [Figure 1, squares, regression coefficient $r = 0.976$, Equation (2)].

$$M-M = 4.092 - 0.00697 \cdot \theta \qquad (2)$$

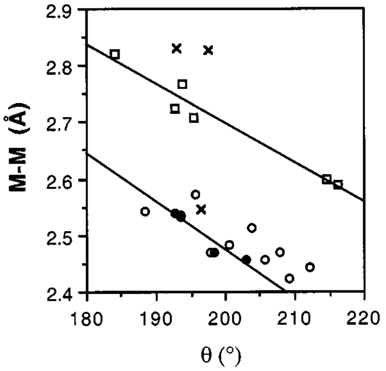


Figure 1. Scatterplot of the experimental values of the orientation angle of the terminal carbonyl groups (θ, see **1**) and the Co−Co distance for the family of $[Co_2(\mu\text{-}CO)_2(CO)_{6-n}L_n]$ complexes; the black circles and the solid line correspond to homoleptic complexes $[Co_2(\mu\text{-}CO)_2(CO)_6]$ and $[Co_2(\mu\text{-}CNR)_2(CNR)_6]$, white circles to the rest of Co complexes in Table 2, squares to Rh and Ir compounds, and crosses to calculated data (Table 1)

Two unbridged forms of symmetries D_{2d} and D_{3d} were also found to be minima in the potential energy surface. The Co−Co bond length in these two isomers is significantly longer than in the bridged one. In the D_{2d} isomer (**1b**), the axial ligands form angles of less than 90° with the equatorial plane, indicating the presence of a weak semibridging interaction (Co···C = 2.83 Å and $Co-Co-C_{ax}$ = 77.1°), similar to that observed in the optimized isoelectronic anion $[Fe_2(CO)_8]^{2-}$ (2.87 Å and 76° for the same parameters),[3] and in $[Mn_2(CO)_8]$ (2.74 Å and 82°).[58]

We have found no D_{2d} structures for carbonyl complexes in the chemical literature, but D_{2d} structures have been proposed for the isoelectronic compounds $[M_2(PF_3)_8]$ (M =

Table 2. Structural data for $[M_2(\mu\text{-}CO)_2L_6]$ complexes of zero-valent metals of the cobalt group with the C_{2v} (**1a**) structure

Compound[a]	M−M [Å]	θ [°]	refcode	ref.
$[Co_2(\mu\text{-}CO)_2(CO)_6]$	2.536	193.6	FOHDEL04	[4,5]
$[Co_2(\mu\text{-}CO)_2(CO)_6]$	2.539	192.6		
$[Co_2(\mu\text{-}CNXyl)_2(CNXyl)_6]$	2.469	198.5	LIDVOJ	[40]
$[Co_2(\mu\text{-}CN\mathit{t}Bu)_2(CN\mathit{t}Bu)_6]$	2.457	203.1	TBICCO10	[41]
$[Co_2(\mu\text{-}CO)_2(CO)_4(\mu\text{-}dppa)]$	2.457	205.6	PPACCP	[42]
$[Co_2(\mu\text{-}CO)_2(CO)_4(\mu\text{-}dmstb)]$	2.471	207.8	PAYKUV	[43]
$[Co_2(\mu\text{-}CO)_2(CO)_4(\mu\text{-}dmars)]$	2.482	200.5	FARSCO10	[44]
$[Co_2(\mu\text{-}CO)_2(CO)_4(dppe)]$	2.541	188.4	BUVSIU	[45]
$[Co_2(\mu\text{-}CO)_2(CO)_4(\mu\text{-}dppbf)]$	2.573	195.8	ROBKIC	[46]
$[Co_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}dppa)_2]$	2.424	209.1	YEZMOF	[47]
$[Co_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}dppm)_2]$	2.443	212.2	HANSUK	[48]
$[Co_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}deppm)]$	2.513	203.7	VAKCEP	[49]
$[Co_2(\mu\text{-}CO)_2(CO)_4(dppp)]$	2.532	193.6	YAWMIS	[50]
$[Co_2(\mu\text{-}CO)_2(CO)_2(dmpv)_2]$	2.471	197.9	YIGXUH	[51]
$[Rh_2(\mu\text{-}CO)_2(CO)_3(PPh_3)_3]$	2.769	193.9	BOPLAT10	[52,53]
$[Rh_2(\mu\text{-}CO)_2(CO)_2(dppp)_2]$	2.709	195.5	CEBBOA	[54]
$[Rh_2(\mu\text{-}CO)_2(CO)_2(dppp)_2]$	2.725	192.7		
$[Rh_2(\mu\text{-}CO)_2(triphos)_2]$	2.822	184.1	FOHMOE	[55]
$[Ir_2(\mu\text{-}CNXyl)_2(CNXyl)_2(\mu\text{-}dmpm)_2$	2.600	214.6	GEFNAG10	[56,57]
$[Ir_2(\mu\text{-}CNXyl\{BH_3\})_2(CNXyl)_2(\mu\text{-}dmpm)_2]$	2.589	216.2	KAXNIG	[57]

[a] Abbreviations: deppm = bis(2-(diethylphosphanyl)ethylphenylphosphanyl)methane; dmars = 1,2-bis(dimethylarsanyl)tetrafluorocyclobutene; dmpv = dimethylphosphanylbenzenevanadium; dmstb = bis(dimethylstibino)methane; dppa = bis(diphenylphosphanyl)amine; dppbf = 4,6-bis(diphenylphosphanyl)dibenzofuran; dppe = 1,2-bis(diphenylphosphanyl)ethane; dppm = bis(diphenylphosphanyl)methane; dppp = 1,3-bis(diphenylphosphanyl)propane; triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane.

Rh, Ir) based on their ^{19}F- and ^{31}P NMR spectra. Also, an approximate Rh−Rh distance of ≈ 2.88 Å has been estimated from X-ray diffraction of a poor crystal,[59] in agreement with the calculated value of 2.882 Å for the corresponding carbonyl complex. In contrast, ^{1}H and ^{31}P NMR spectra of complexes with bulkier ligands, $[M_2\{P(OR)_3\}_8]$ (M = Co, Rh), suggest a D_{3d} symmetry.[60−62]

A third isomer of $[M_2(CO)_8]$ (D_{3d} symmetry, **1c**) with trigonal bipyramidal coordination around the metal atoms was also found to be a minimum in the potential energy surface. Such a structure is found in isoelectronic compounds of the type $[M_2(CO)_6(ER_3)_2]$ (M = Co,[20−28] Rh,[63] and Ir[64]), and the most relevant structural parameters are shown in Table 3. The metal−metal distances in the optimized structures agree well with the experimental data for Co (calcd.: 2.671, exp.: 2.639−2.671 Å) and Rh (calcd.: 2.851, exp.: 2.817−2.827 Å). The equatorial carbonyls are bent towards the second metal atom (i.e., $M{-}M{-}C_{eq}$ angles of less than 90°) for the three metals, and the calculated values are also in good agreement with the experimental ones. The present results for Co agree, within chemical accuracy, with those reported by Ziegler,[39] both in the Co−Co distance (2.634 Å) and the pyramidality angle (85.1°).

Energy Minima and Transition States

The relative energies of the minima and transition states of each metal are presented in Table 4. The three isomers shown in **1** correspond to minima in the potential energy surfaces of the three metals, according to the analysis of calculated vibrational frequencies (see below). As summarized in the introductory section, there is spectroscopic evidence for the coexistence, in solution, of different isomers of the compounds under study, in agreement with the similar energies found in our calculations. However, for such intramolecular reactions to occur thermally, a low activation-

Table 3. Structural data for compounds with the D_{3d} structure and the general formula $[M_2(CO)_6(L)_2]$, where L is a ligand *trans* to the metal−metal bond

Compound	M−M [Å]	$M{-}M{-}C_{eq}$ [°]	refcode	ref.
$[Co_2(CO)_6(AsPh_3)_2]$	2.639	86.2	GOGJAN01	[20,21]
$[Co_2(CO)_6(P\{C_6H_4SO_3\}_3)_2]^{6-}$	2.645	85.8	PIGBUC	[22]
$[Co_2(CO)_6(P\{O\mathit{i}Pr\}_3)_2]$	2.654	86.5	ZENCUQ	[23]
$[Co_2(CO)_6(PPh_2\{C_4F_4AsMe_2\})_2]$	2.663	85.9	ACBPCO	[24]
$[Co_2(CO)_6(PBu_3)_2]$	2.665	87.7	CBUPCO01	[25,26]
$[Co_2(CO)_6(PPh_2\{CH_2COPh\})_2]$	2.666	85.0	WELMOP	[27]
$[Co_2(CO)_6(PMe_3)_2]$	2.671	86.6	DIVZOX	[28]
$[Rh_2(CO)_6(P\mathit{i}Pr_3)_2]$	2.817	83.4	FOFREX	[63]
$[Rh_2(CO)_6(P\{C_5H_9\}_3)_2]$	2.827	84.6	FOFRAT	[63]

Table 4. Calculated energies of the stationary points in the potential energy surfaces of $[M_2(CO)_8]$ (M = Co, Rh, Ir). All data are in kcal·mol^{-1}

Compound	Co	Rh	Ir
Minima			
C_{2v} (**1a**)	1.48	0.00	5.97
D_{2d} (**1b**)	0.00	2.78	0.00
D_{3d} (**1c**)	5.81	8.17	3.53
Transition states			
$C_{2v} \rightleftarrows D_{2d}$ (**2a**)	2.96	4.69	7.91
$D_{2d} \rightleftarrows D_{3d}$ (**2b**)	8.41	10.92	7.43

energy is needed. We have located only two transition states connecting the three minima, indicating two isomerization pathways: **1a** → **1b** and **1b** → **1c** (for schematic energy diagrams see Figure 2). No transition state could be located between C_{2v} and D_{3d} isomers (**1a** → **1c**), indicating that their interconversion must proceed through a D_{2d} intermediate **1b**.

The results of our calculations indicate that the unbridged D_{2d} (**1b**) structure is the most stable one for Co and Ir, but for Rh it is the C_{2v} isomer (**1a**), with **1b** ≈ 2.8 kcal·mol^{-1} above the minimum. Nevertheless, the energy differences between the three isomers are relatively small in most cases, as previously found for the isoelectronic $[Fe_2(CO)_8]^{2-}$ anion.[3] Noack studied the interconversion of bridged to unbridged forms of the cobalt complex in paraffin/alkane solutions between 69 and 295 K,[9] and estimated a reaction enthalpy of about -1.3 ± 0.1 kcal·mol^{-1}, compared with a calculated value of -1.5 kcal·mol^{-1}. The isomerization was monitored through the infrared intensities of the 2044 (or 1857) and 2025 cm^{-1} absorption bands of the bridged and unbridged forms, respectively. A second isomerization ($D_{2d} \rightarrow D_{3d}$) process can be expected according to our results, with a reaction enthalpy of +5.8 kcal·mol^{-1} and low energy barriers (Table 4).

The ligand rearrangement that takes place along the $C_{2v} \rightleftarrows D_{2d}$ path is schematically illustrated in **2a**. Through such a pathway, the bridging and basal CO ligands of the C_{2v} structure (labeled 2, 3, and 4 in **2a**) occupy axial and equatorial positions of the trigonal bipyramid coordination spheres of the D_{2d} isomer. Since the apical ligand (labeled 1 in **2a**) of the C_{2v} isomer also occupies an equatorial position of the D_{2d} trigonal bipyramid, successive rearrangement steps result in exchange of the three types of CO ligands of the C_{2v} structure. Therefore, the $C_{2v} \rightleftarrows D_{2d}$ interconversion is consistent with the observation of a single NMR signal for the carbonyl ligands. This process has a tiny calculated energy barrier of 3.0 kcal·mol^{-1} for $[Co_2(CO)_8]$, lower than the upper limit measured by infrared spectroscopy in hexane matrices at 84 K where interactions with matrix molecules exist ($\Delta G^{\ddagger}$ ≈ 6.4 ± 0.4 kcal·mol^{-1}).[12] The complex $[Co_2(CO)_8]$ has been observed to be fluxional at room temperature, even in the solid state, as seen by the equivalence of all carbonyl ligands in the ^{13}C NMR spectrum.[65] An activation energy for the exchange of bridging and terminal carbonyls has been estimated at 11.7 ± 0.6 kcal·mol^{-1}. The $D_{2d} \rightleftarrows D_{3d}$ conversion (**2b**) for $[Co_2(CO)_8]$ has an energy barrier

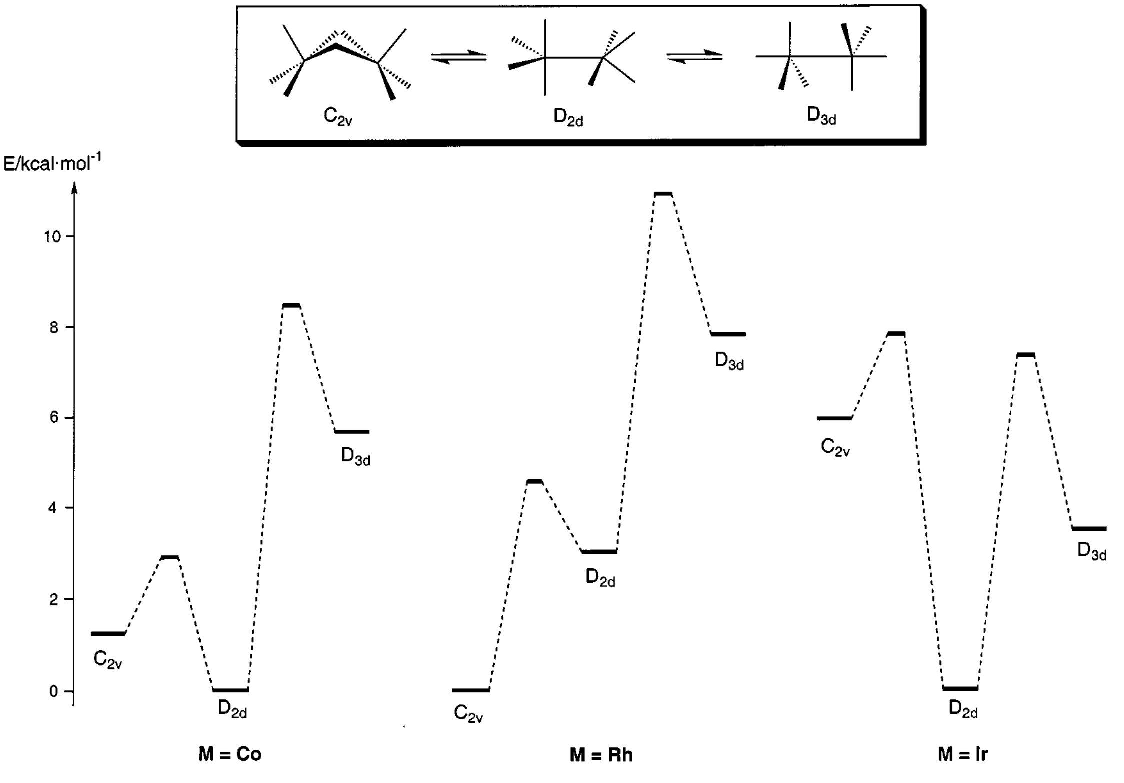
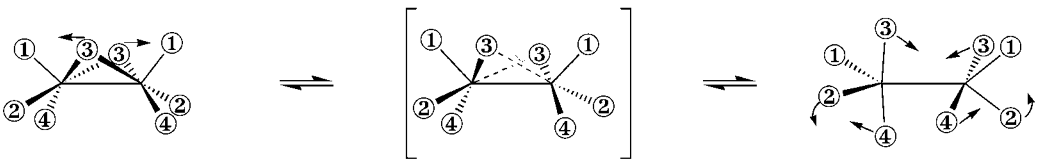
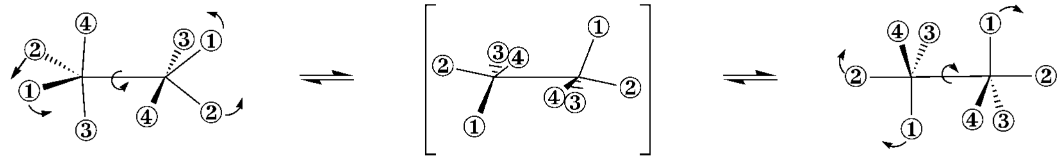


Figure 2. Diagram of the relative energies [in kcal·mol^{-1}] for the differents isomers of the $[M_2(CO)_8]$ complexes (M = Co, Rh, Ir)



2a



2b

of 8.4 kcal·mol^{-1}, and the reverse process has an energy barrier of 2.6 kcal·mol^{-1}. The experimental observation is that this transformation is extremely facile in hexane at 84 K.[12]

For $[Rh_2(CO)_8]$, the most stable structure is that with the bridged C_{2v} symmetry, as previously suggested from infrared and UV/Visible spectroscopic data. In contrast, our calculations for the Ir complex clearly predict the unbridged D_{2d} structure to be the most stable one, in agreement with the absence of absorption bands in the bridging CO region of the infrared spectrum. According to our calculations, the Rh complex presents a low barrier for the $C_{2v} \rightarrow D_{2d}$ transformation (4.7 kcal·mol^{-1}), although this isomerization cannot be experimentally observed due the formation of larger clusters.[15,16,19] The $D_{2d} \rightarrow D_{3d}$ transformation presents a barrier of about 8.1 kcal·mol^{-1}. For the Ir complex, the larger stability of the intermediate D_{2d} structure and the calculated energy barriers of about 7−8 kcal·mol^{-1} allow us to predict that a fluxional process should be observable.

Vibrational Analysis

Metal−Metal Stretching Vibrations

We have studied the vibrational frequencies for the three isomers (**1**): C_{2v}, D_{2d}, and D_{3d}. In all cases they have no imaginary frequencies, and all three structures are minima in the potential energy surface, as found previously in studies on the isoelectronic dianion $[Fe_2(CO)_8]^{2-}$.[3] The calculated metal−metal stretching frequencies of the three isomers are shown in the Table 5. An interesting finding is the existence of a linear correlation between the optimized M−M distance and the corresponding stretching frequency for the three isomers in the case of the Co and Ir complexes [regression coefficients $r = 0.990$ and 0.992, Equation (3) and Equation (4), respectively]. The same trend is found for Rh but the correlation is poorer.

$$\tilde{\nu}_{CoCo} = 1392 - 450 \cdot d_{Co-Co} \tag{3}$$

$$\tilde{\nu}_{Ir-Ir} = 1261 - 389 \cdot d_{Ir-Ir} \tag{4}$$

For $[Co_2(CO)_8]$, the $\tilde{\nu}_{Co-Co}$ band in the solid state[13] appears at 229 cm^{-1}, a value that is consistent with a metal−metal bond supported by two carbonyl bridging ligands,[1] although it appears shifted to 235−239 cm^{-1} in solution. This band can be unequivocally assigned to the C_{2v} isomer, structurally characterized in the solid state, according to our calculated value (221 cm^{-1}), since the corresponding vibration for the two other isomers is expected at significantly lower wavenumbers. Two additional bands appear in solution,[13] at 185 and 158 cm^{-1}. The most intense peak, at 185 cm^{-1}, corresponds to the predominant species in solution, which can be assigned to a D_{2d} structure according to the present computational results (calculated value 179 cm^{-1}) and in excellent agreement with this being the most stable isomer in our calculations. The intensity of the band observed in solution at 158 cm^{-1} increases upon warming[13] and can be assigned to the D_{3d} structure according to the present results (calculated value 162 cm^{-1}). No Raman data have been reported for the analogous Rh and Ir compounds. The calculated frequencies in these cases allow for a clear-cut assignment of the Raman stretching bands that appear at different temperatures to the three isomers: C_{2v}, D_{2d}, and D_{3d} (see Table 5). The successive appearance of the C_{2v}, D_{2d}, and D_{3d} isomers upon warming is consistent with the theoretical finding that the two transition states located allow no direct conversion of the C_{2v} and D_{3d} isomers, but requires going through the D_{2d} intermediate.

Table 5. Theoretical M−M stretching frequencies, ν_{MM} [cm^{-1}] for the three isomers of $[M_2(CO)_8]$, and experimental Raman values for M = Co (refs. [13,66])

Structure	$[Co_2(CO)_8]$ calcd.	$[Co_2(CO)_8]$ exp.	$[Rh_2(CO)_8]$ calcd.	$[Ir_2(CO)_8]$ calcd.
C_{2v}	221	235−239[a] 229−231[b]	183	163
D_{2d}	179	185−186[a]	150	128
D_{3d}	162	157−159[a]	148	131

[a] Solution. − [b] Solid state.

Table 6. Calculated and experimental infrared stretching frequencies in the carbonyl region for $[M_2(CO)_8]$ complexes. Relative intensities given in parenthesis (maximum = 100; for some experimental data: *vs* = very strong; *s* = strong, *m* = medium; *w* = weak; *sh* = shoulder)

C_{2v}	B_2	A_1	B_1	B_2	A_1	B_1	A_1	Notes[a]
Co	1823 (46)	1838 (18)	1993 (0)	2002 (82)	2001 (100)	2022 (100)	2067 (1)	calcd.
	1868 (46)	1878 (18)	2013 (1)	2020 (84)	2021 (100)	2048 (90)	2086 (1)	calcd. (f)
	1857 (42)	1868 (27)	–	2048 (78)	2050 (19)	2076 (100)	2117 (1)	(a)
	1857 (s)	1866 (sh)	–	2042 (vs)	2044 (vs)	2071 (vs)	2112 (w)	(b, c)
	1831 (s)	1844 (s)	–	2025 (s)	2025 (s)	2070 (sh)	2111 (w)	(d)
	1828 (w)	1848 (w)	–	2017 (s)	2031 (s)	2065 (sh)	2107 (m)	(e)
Rh	1816 (51)	1829 (17)	1985 (4)	1991 (86)	1992 (100)	2016 (93)	2051 (3)	calcd.
	1830 (m)	1852 (w)	–	2038 (s)	2043 (s)	2060 (s)	–	(g)
	1845 (s)	1860 (m)	–	–	2061 (s)	2086 (s)	–	(h, i)
Ir	1786 (43)	1800 (23)	1986 (2)	1992 (86)	1997 (100)	2022 (91)	2059 (2)	calcd.
D_{2d}	E	A_1	E	B_2	B_2	A_1		
Co	1957 (21)	1979 (–)	1994 (92)	1971 (3)	2010 (100)	2067 (–)		calcd.
	–	–	2028 (83)[b]	2051 (26)	2073 (59)	–		(a)
	–	–	2023 (vs)	2031 (m)	2069 (vs)	2107		(b, c)
Rh	1953 (10)	1968 (–)	1981 (100)	1976 (18)	1998 (69)	2053 (–)		calcd.
Ir	1958 (0)	1972 (–)	1982 (36)	1982 (100)	2011 (36)	2069 (–)		calcd.
	–	–	2040	2052	2065	–		(g)
D_{3d}	E_g	A_{2u}	E_u	A_{1g}	A_{2u}	A_{1g}		
Co	1962 (–)	1966 (1)	1980 (89)	1998 (–)	2017 (100)	2065 (–)		calcd.
	1992 (–)	1996 (12)	2009 (100)	2016 (–)	2050 (82)	2090 (–)		calcd. (f)
	1999 (24)[b]	2043 (26)	2033 (85)[b]	–	2059 (74)	–		(a)
	1991	–	–	–	2059	–		(b)
Rh	1962 (–)	1959 (5)	1970 (100)	1987 (–)	2024 (79)	2051 (–)		calcd.
Ir	1958 (–)	1963 (12)	1972 (100)	1991 (–)	2035 (67)	2062 (–)		calcd.

[a] (a) Argon matrix at 8 K (solid sample);[12] (b) Hexane solution at 77 K;[12] (c) Paraffin hydrocarbon solvents at variable temperature;[7,8] (d) KBr disk;[67] (e) Spinning-cell FT-Raman (solid state);[66] (f) Calculated with ADF package and BP functional;[58] (g) Co-condensation reaction with CO at 10–15 K (solid sample) for rhodium[16] and iridium;[18] (h) Liquid paraffin-heptane at high pressure of CO (430–490 atm, 243–293 K);[14,15] (i) Adamantane solution at 77 K.[68] – [b] The band appears as a doublet.

Vibrational Spectra in the Carbonyl Region

The second part of our vibrational analysis focused on the carbonyl stretching frequencies (Table 6) since this region of the infrared spectrum is used as a diagnostic tool for carbonyl complexes. The main characteristic of this spectral zone is the number of infrared-active $\tilde{\nu}_{CO}$ modes, although group-theoretical predictions may be not fulfilled because of the existence of allowed bands with low-intensity. The presence of CO bands below 1850 cm^{-1} can be considered as a fingerprint of the presence of bridging carbonyl groups. This feature is clearly present in the calculated spectra for the three metals, as well as in the experimental data of the Co and Rh complexes. In the terminal carbonyl stretching region, two of the three intense bands expected for the C_{2v} isomer are practically coincident and only two peaks should be observed, whereas three bands seem to appear in the D_{2d} form, probably due to intensity stealing between the two B_2 modes. In summary, the three isomers can in principle be identified from the pattern of the CO stretching bands for any of the three metals. These patterns are as follows: (a) the C_{2v} isomer must present two bridging frequencies below 1850 cm^{-1} and three intense bands around 2000–2030 cm^{-1}; (b) the D_{2d} isomer does not present bands below 1900 cm^{-1} but three bands around 2000 cm^{-1} spanning a range of at most 29 cm^{-1}; (c) the D_{3d} isomer does not present bands below 1900 cm^{-1} but has two bands around 2000 cm^{-1}, separated by 37 (for Co) to 63 cm^{-1} (for Ir).

The infrared spectra reported for $[Co_2(CO)_8]$ and $[Rh_2(CO)_8]$ are assigned to the C_{2v} structure, because of the presence of two bridging carbonyl stretching bands between 1820 and 1870 cm^{-1}, together with a set of three strong bands in solid state between 2010 and 2090 cm^{-1}. A similar pattern is found in solution, except that only two terminal carbonyl bands are observed in the case of Rh. The spectra of $[Co_2(CO)_8]$ in an argon matrix at 8 K and in a hexane solution at 77 K, however, are consistent with the pattern expected for the D_{2d} isomer. The spectrum reported in the literature for $[Ir_2(CO)_8]$ can probably be assigned to the D_{2d} isomer, given the absence of bridging carbonyls and the relatively small splitting of the terminal CO bands (25 cm^{-1}, compared to a calculated range of 29 cm^{-1}). With the proposed assignments, deviations of the calculated frequencies relative to the experimental ones of less than 3% result. Interestingly, the isomers that best account for the experimental spectra of the Rh and Ir complexes, and for the Co complex at low temperatures, are those found in our calculations to be the most stable ones.

Conclusions

In the present theoretical work we have analyzed three structures of the dinuclear carbonyl complexes $[M_2(CO)_8]$ (M = Co, Rh, and Ir). The three isomers are stationary points in the corresponding energy surfaces, with the D_{2d} structure being the most stable one for Co and Ir, and C_{2v} the most stable for Rh. However, the other isomers are not very different in energy and are separated by relatively small energy barriers. The calculated structural parameters of the optimized structures are in good agreement with the available experimental data.

Two transition states are found for fluxional process and our calculations show a sequence of transformations $C_{2v} \rightarrow D_{2d} \rightarrow D_{3d}$ without direct pathway connecting the C_{2v} and D_{3d} structures. The conversion between the C_{2v} and D_{2d} isomers has smaller energy barriers for Co and Rh. For the Ir complex, slower processes are to be expected, given the higher calculated energy barriers.

The analysis of the M−M stretching region of the vibrational spectra for the three isomers shows a linear correlation between the M−M wavenumber and the distance for M = Co and Ir. For each of the three metals the M−M stretching of the C_{2v} isomer appears at higher frequencies than the D_{2d} and D_{3d} ones. The calculated peaks show an excellent agreement with the experimental Raman spectrum for Co. In the carbonyl stretching region, two bands are expected at low frequencies for the C_{2v} bridged isomer (1780−1840 cm^{-1}, characteristic of bridging carbonyls), together with three bands between 1995 and 2025 cm^{-1}. For the unbridged D_{2d} and D_{3d} isomers, very similar infrared spectra are expected between 1950 and 2100 cm^{-1}. In all cases, the calculated frequencies differ from the experimental ones by less than 3%.

Experimental Section

Computational Details: Density functional calculations were carried out using the GAUSSIAN94 package.[69] The hybrid B3LYP-DFT method was applied, in which the Becke three parameters exchange functional[70] and the Lee−Yang−Parr correlation functional[71] were used. The double-ζ basis set for the valence and outermost core orbitals combined with pseudo-potentials known as LANL2DZ were used for all the atoms.[72][73] The geometries were fully optimized using gradient techniques. The calculated frequencies shown in this paper are not corrected with any factor to reproduce experimental ones. The zero-point energies of minima and transition states were also calculated, but the relative energies change by less than 10%.

Structural Analysis: Structural data was searched through the Cambridge Structural Database (Version 5.19, February 2000).[74] Our search included compounds with several cores having metal atoms of group 9.

Supporting Information: Tables containing atomic coordinates of structures $[M_2(CO)_8]$ (M = Co, Rh, and Ir) for the three energy minima (**1a**, **1b**, and **1c**) and for the transition states (**2a**, **2b**). This material is available free of charge via the Internet, see also footnote on the first page of this article.

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