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Carbon Dioxide Coordination Chemistry. 1.[1] Vibrational Study of *trans*-$Mo(CO_2)_2(PMe_3)_4$ and $Fe(CO_2)(PMe_3)_4$

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This paper describes the spectroscopic characterization of carbon dioxide complexes and discusses the role of isotopic labeling for this purpose. In part 1, complete assignments of FTIR and Raman spectra are proposed for *trans*-$Mo(CO_2)_2(PMe_3)_4$ and $Fe(CO_2)(PMe_3)_4$. Frequency shifts observed by means of isotopic enrichments with ^{13}C and/or ^{18}O are related to the coordination mode of the CO_2 moiety. It appears that two vibrational modes are highly sensitive to the CO_2 geometry in the complex: the symmetrical stretching mode $\nu(CO)$, at about 1150 cm^{-1}, and the out-of-the-plane bending mode $\gamma(C{=}O)$, located around 550 cm^{-1}. Normal coordinate analysis allows us to conclude that the CO_2 moiety is bonded in a side-on manner in *trans*-$Mo(CO_2)_2(PMe_3)_4$, whereas the bonding is intermediate between an η^1-C and a side-on arrangement in $Fe(CO_2)(PMe_3)_4$.

Introduction

Activation of CO_2, which is potentially the most abundant source of C_1 compounds, may be reasonably expected to be brought about by transition-metal catalysis. So, there has been intense interest in the coordination of carbon dioxide by transition-metal complexes with respect to incorporation in reduction processes.[2,3] Carbon dioxide complexes are therefore recognized as important intermediates in a large number of reactions.[4,5] These are of importance in homogeneous catalysis and because of their structures, which, when available, provide information on the nature of metal–ligand bonds. Despite considerable research, however, formation of fairly stable CO_2 complexes is quite rare and only a small number of them have been characterized by diffraction methods.[6–12]

The main models for the different possible bonding modes can be summarized as follows: (a) η^1 attachment occurs through the carbon atom (C coordination),[9,11,12] from Hoffmann and colleagues,[13] when "the metal is electronically saturated by its coligands and the fragment has a free coordination site". (b) η^1 attachment occurs through the oxygen atom (end-on coordination). No structural evidence for end-on conformation has ever been observed. It is strongly dependent on interactions of electrostatic origin[13] and has been spectroscopically characterized for $CuCO_2$ in matrix.[14] (c) η^2 attachment occurs through one C=O bond (side-on coordination), which is the most encountered coordination mode until now.[6–8,10] It can be described by the Chatt–Dewar–Duncanson model, with bonding resulting from both CO_2 to metal charge transfer and electron back-bonding from the metal to antibonding orbitals of CO_2.

In all cases, the coordinated CO_2 molecule is bent (all measured values of the OCO angle being around 130–140°), with a lengthening of the CO bonds corresponding to lower bond orders.

The nature of the bond between CO_2 and transition metal is of fundamental importance to organometallic chemistry. The availability of FTIR spectroscopy now makes it essential to employ ^{13}C and ^{18}O isotopic enrichment for unequivocal spectroscopic identification of coordinated CO_2, for confirmation of its source, and for probing the bonding in CO_2–transition-metal complexes. So, an FTIR matrix isolation study[14] has been previously performed by us in order to spectroscopically characterize the three coordination modes of CO_2 on different transition metals. All of them were observed, and attempts have been made, by means of normal coordinate analysis, to correlate structure with spectroscopic properties, especially with isotopic frequency shifts observed on the ν_1 and ν_3 modes (respectively symmetric and asymmetric CO stretching modes) in ^{13}C- and ^{18}O-labeled compounds.

This led to the following relationships: (a) The C-coordination mode is characterized by small splittings of the ν_1 and ν_3 modes (namely $\bar{\nu}_3 - \bar{\nu}_1 \le 400$ cm^{-1}). If $\sum\Delta\bar{\nu}$ represents the sum of the frequency shifts observed in the ν_1 and ν_3 modes in labeled complexes, we have $\sum\Delta\bar{\nu}(^{13}C) \ge \sum\Delta\bar{\nu}(^{18}O)$ with $60 < \sum\Delta\bar{\nu}(^{18}O) < 70$ cm^{-1}. (b) The end-on coordination mode presents large $\nu_3 - \nu_1$ splittings and very large isotopic shifts by ^{18}O labeling as $\sum\Delta\bar{\nu}(^{13}C) < \sum\Delta\bar{\nu}(^{18}O)$ with $\sum\Delta\bar{\nu}(^{18}O) \ge 70$ cm^{-1}. (c) Finally, the side-on coordination mode can be distinguished from the end-on one only by considering isotopic frequency shifts, as $\nu_3 - \nu_1$ is of the same order of magnitude but $\sum\Delta\bar{\nu}(^{13}C) \ge \sum\Delta\bar{\nu}(^{18}O)$ with $\sum\Delta\bar{\nu}(^{18}O) \le 60$ cm^{-1}.

An extension of these relations to organometallic compounds would be of great interest to better understand mechanisms in CO_2 reactions, especially to characterize authentic CO_2 complexes in catalytic cycles, usually modeled by using fairly stable complexes. The availability of these compounds led to the current investigation of their vibrational spectra and a simplified normal coordinate analysis to probe the nature of the bonding that exists in these CO_2–transition-metal complexes. To investigate the nature of the chemical bonding, a series of compounds is more informative than an isolated case and three such studies are reported here. Part 1 will be devoted to vibrational study of $Mo(CO_2)_2(PMe_3)_4$[15] and $Fe(CO_2)(PMe_3)_4$,[16] whereas $Cp_2Ti(CO_2)(PMe_3)$[17] will be studied in part 2. The study of $Ni(CO_2)(PCy_3)_2$[6] is still in progress in our laboratory.

The spectroscopic characterization of these complexes is described to provide the first basis for spectroscopic investigations of metal–CO_2 bonding in organometallic compounds.

Experimental Section

trans-$Mo(CO_2)_2(PMe_3)_4$ was prepared according to the method published by Carmona and colleagues.[15] $Fe(CO_2)(PMe_3)_4$ was obtained by

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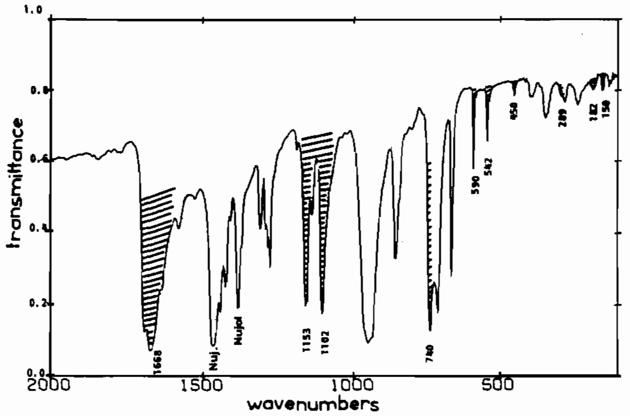

Figure 1. FTIR spectrum (100–2000 cm^{-1}) of *trans*-$Mo(CO_2)_2(PMe_3)_4$ (Nujol mull). (The hatching represents CO_2 absorptions.)

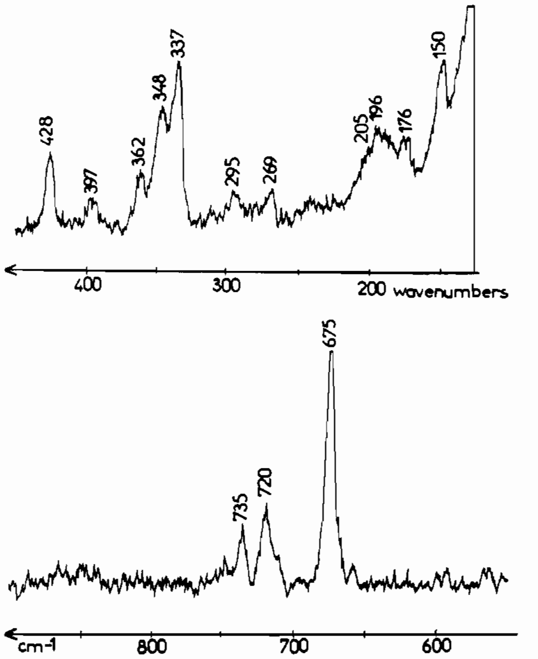

Figure 2. Raman spectrum (150–850 cm^{-1}) of *trans*-$Mo(CO_2)_2(PMe_3)_4$ at 77 K (λ_{exc} = 568.2 nm, 30 mW, resolution 4 cm^{-1}).

the procedure described by Karsch and Aresta.[18] PMe_3 was obtained from Strem Chemicals and used without further purification. CO_2 (99.995%) was supplied by L'Air-Liquide and used without further purification. Isotopically substituted carbon dioxide $^{13}CO_2$ (enriched up to 99.5%) and $C^{18}O_2$ (enriched up to 97.7%), provided by CEA-ORIS, were used to identify CO_2 vibrational modes and to measure frequency shifts. Solvents were purchased from commercial sources, distilled, and bubbled with argon before use. Air-sensitive compounds and solutions were handled under argon with the use of Schlenk equipment in conjunction with a vacuum-inert-gas manifold and glovebox. FTIR spectra were recorded by using a Bruker 113 V Fourier transform interferometer. Frequencies are accurate to ±1 cm^{-1}. Solid samples were studied as Nujol (previously dried on sodium wire and bubbled with argon) mulls. Solutions were handled by means of an home-built variable temperature and path length liquid cell described elsewhere.[19]

Raman spectra were recorded on a Coderg T800 spectrometer; exciting lines were provided by a Spectra-Physics krypton ion laser. Solid samples were studied as microcrystalline powders in sealled capillary tubes at 77 K by means of a liquid-nitrogen cryostat to avoid thermal decomposition by laser exposure.

Results

***trans*-$Mo(CO_2)_2(PMe_3)_4$.** The FTIR and Raman spectra of solid *trans*-$Mo(CO_2)_2(PMe_3)_4$ are presented on Figures 1 and 2, respectively. As the vibrational spectrum of coordinated PMe_3 is quite similar to that of the free molecule,[20] it is easily recognizable in the spectra and will be described separately, only in the region of interest, below 2000 cm^{-1}. The symmetric deformations $\delta_s(CH_3)$ are observed at 1305, 1288, 1280, and 1275 cm^{-1} as medium-intensity bands, whereas asymmetric bending modes $\delta_a(CH_3)$ are obscured by Nujol absorptions around 1430 cm^{-1}. At 950 cm^{-1} is located a very strong band, which is assigned to the rocking motions (A_1, E) of the methyl groups $r(CH_3)$. The A_2 mode, which is inactive in free PMe_3 (C_{3v} group), appears at 855 cm^{-1} in the coordinated molecules, when the symmetry is lowered.[21,22] The strongest band in the Raman spectrum at 675 cm^{-1} is assigned to in-phase symmetric stretching $\nu_s(PC_3)$, while the infrared out-of-phase $\nu_s(CH_3)$ is observed at 665 cm^{-1}, with medium intensity. The asymmetric stretchings of PC bonds ν'_s- and $\nu_a(PC_3)$ are located in the congested region around 720 cm^{-1} and are observed at 735 and 720 cm^{-1} as weak bands in the Raman spectrum. The deformations $\delta(PC_3)$ are expected in the 200–300-cm^{-1} region, with the symmetric components located at higher wavenumbers than the asymmetric ones.[23,24] Assignments will be discussed further. Apart from PMe_3 absorptions, we can see bands that are shifted by isotopic labeling experiments. The very strong absorption at 1668 cm^{-1}, respectively shifted to 1628 and 1638 cm^{-1} by ^{13}C and ^{18}O labeling, is assigned to the carbonyl stretching $\nu(C{=}O)$. The two sharp intense bands at 1153 and 1102 cm^{-1} have isotopic effects of 29 and 26 cm^{-1} by ^{13}C labeling and 19 and 26 cm^{-1} by ^{18}O enrichment, respectively. We thus conclude that they arise from CO stretching modes.

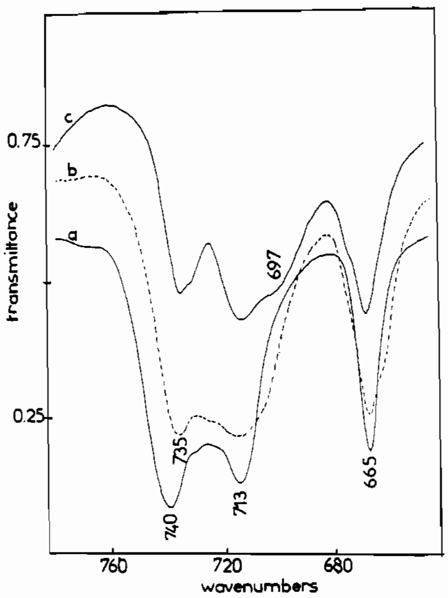

Figure 3. Detailed FTIR spectra in the region 650–750 cm^{-1} for *trans*-$Mo(CO_2)_2(PMe_3)_4$ (a) and labeled derivatives with ^{13}C (b) and ^{18}O (c).

The bending mode $\delta(OCO)$ is expected in the 650–750-cm^{-1} region but not easily detected due to overlapping with ν'_s- and $\nu_a(PC_3)$ absorption in the same area. Nevertheless, the spectra of the enriched compounds show (see Figure 3) that the band at 740 cm^{-1} is no longer present and that a shoulder appears at 697 cm^{-1} in *trans*-$Mo(C^{18}O_2)_2(PMe_3)_4$. This implies that the isotopic shift ^{16}O–^{18}O would be of 43 cm^{-1} for the $\delta(OCO)$ mode, which is too large a value for such a vibration. The question is therefore opened to know if there is only one $\delta(OCO)$ mode [as for $\nu(C{=}O)$] or two [as for $\nu(CO)$]. The two following absorptions at 590 and 542 cm^{-1} have similar isotopic shifts, which are 18 cm^{-1} by ^{13}C labeling and 5 cm^{-1} by ^{18}O enrichment. The large value of

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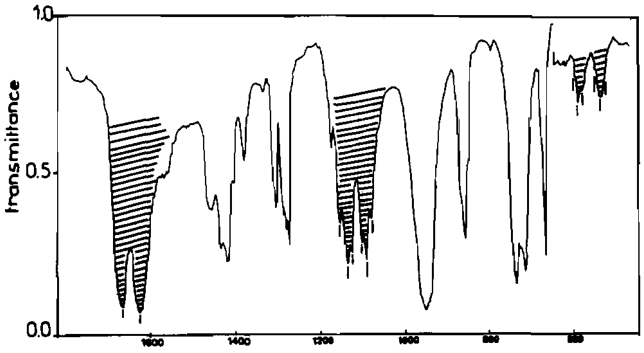

Figure 4. IR spectrum of *trans*-Mo$(CO_2)_2(PMe_3)_4$ enriched with an equimolar mixture of $^{12}CO_2/^{13}CO_2$ (kindly supplied by E. Carmona).

the ^{13}C frequency shift (compared to the ^{18}O one) allows us to assign these absorptions to the out-of-the-plane bendings of the CO bonds γ(C=O), as generally encountered in carboxylic compounds (see for example acetone[25]). At this point, it is interesting to note that none of the CO_2 absorptions previously described has a coincident band in the Raman spectrum. The weak infrared band observed at 450 cm^{-1}, showing a small frequency shift by ^{13}C labeling (3 cm^{-1}) but an important one by ^{18}O enrichment (14 cm^{-1}), is assigned to a stretching mode of the MoO bonds. The medium-intensity band observed in the Raman spectrum at 428 cm^{-1}, shifted to 415 cm^{-1} by ^{18}O labeling, is then thought to be the in-phase mode ν_{ϕ}(MoO), while that observed in the infrared spectrum is thought to be the out-of-phase mode $\nu_{0\phi}$(MoO). Below 400 cm^{-1}, we find several weak bands with isotopic frequency shifts by ^{18}O labeling: 289 (2 cm^{-1}), 182 (3 cm^{-1}), and 150 cm^{-1} (3 cm^{-1}). Assignments will be made with help of normal coordinate analysis.

It then occurs that some modes appear as single frequency [i.e. ν(C=O)] whereas some others present two absorptions [i.e. ν(CO), γ(C=O)]. Furthermore, an infrared spectrum taken by Carmona and colleagues[26] on *trans*-Mo$(CO_2)_2(PMe_3)$ enriched with 50% $^{13}CO_2$ shows that ν(C=O) appears as a doublet at 1668 and 1628 cm^{-1} whereas ν(CO) and γ(C=O) present triplet patterns respectively at 1153–1130–1124, 1102–1087–1076 and 590–580–572, 542–535–525 cm^{-1} (see Figure 4). FTIR spectra taken by us on *trans*-Mo$(CO_2)_2(PMe_3)_4$ enriched with an equimolar mixture of $C^{16}O_2/C^{18}O_2$ show the same pattern, but the triplets of the γ(C=O) modes are not resolved, as the isotopic frequency shifts by ^{18}O labeling are smaller (5 cm^{-1}) than in the ^{13}C case (18 cm^{-1}). So, we can conclude that the two CO_2 moieties are highly coupled through the ν(CO) and γ(C=O) modes (the splitting is about 50 cm^{-1} in each case) but not through the ν(C=O) ones (or the coupling is so small that it cannot be observed as the band at 1668 cm^{-1} is broad). This is a first indication for the nonequivalency of the two CO bonds in CO_2 moieties and thus rules out the possibility of C coordination on the molybdenum atom.

In order to ascertain the intramolecular nature of the observed couplings, FTIR spectra have been obtained from solutions of *trans*-Mo$(CO_2)_2(PMe_3)_4$ in benzene and tetrahydrofuran at different temperatures (from −80 to +45 °C). The FTIR spectra obtained were similar in frequencies and intensities to those observed for the solid state (see Figure 5). So, this result excludes coupling by crystal effect and isomerism. In the same way, infrared spectra[26] of some bis(carbon dioxide)molybdenum complexes with chelating phosphines (i.e. dmpe, dppe) excluding cis isomerism show the same pattern in the ν(CO) region.

Finally, isotopic labeling experiments rule out a Fermi resonance between the first overtone of the mode located at 289 cm^{-1} and γ(C=O) because of the large isotopic shift of γ(C=O) by ^{13}C labeling. In the same way, Fermi resonance between 2γ(C=O) and ν(CO) is excluded by the small isotopic shift of γ(C=O) by ^{18}O enrichment.

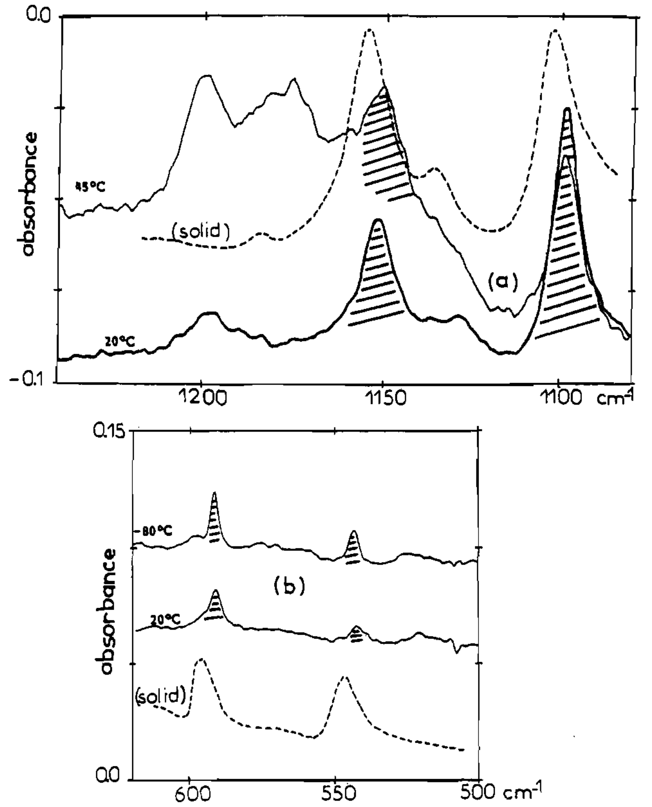

Figure 5. FTIR spectra of Mo$(CO_2)_2(PMe_3)_4$ in solution (a) in benzene, ν(CO) region, and (b) in THF, γ(C=O) region (solvents absorptions subtracted). Dotted lines represent corresponding absorptions of the complex in the solid state at room temperature.

So, we conclude that the splittings of the ν(CO) and γ(C=O) modes in the *trans*-Mo$(CO_2)_2(PMe_3)_4$ infrared spectrum are due to an intramolecular coupling.

Fe$(CO_2)(PMe_3)_4$. There are no structural data on this complex, but a ^{31}P NMR study performed by Karsch[16] has shown that two chemically different methylphosphine ligands are linked to the metal in a cis position, the other two being linked in trans positions. CO_2 is supposed to be side-on coordinated, leading to a trigonal-bipyramidal structure. The overall symmetry is C_1, and 162 vibrations are expected, 144 concerning the trimethylphosphine ligands.

The FTIR spectrum of Fe$(CO_2)(PMe_3)_4$ is shown on Figure 6. It is in agreement with the infrared spectrum previously published by Karsch.[16] Despite several attempts, the Raman spectrum has not been obtained because of the strong fluorescence of this red-brown compound under laser exposure, even with exciting lines at 676 and 647 nm.

As for *trans*-Mo$(CO_2)_2(PMe_3)_4$, the absorptions of trimethylphosphine ligands are easily recognizable at 1300, 1281 cm^{-1} [$\delta_s(CH_3)$], 947, 857 cm^{-1} [$r(CH_3)$], 705 cm^{-1} [ν_a- and ν'_s-(PC_3)], and 660 cm^{-1} [$\nu_s(PC_3)$].

Other bands, that are shifted upon isotopic labeling are assigned to CO_2 moiety vibrations. The strong absorption at 1623 cm^{-1}, which is shifted to 1582 cm^{-1} by ^{13}C labeling and to 1594 cm^{-1} by ^{18}O enrichment is assigned to ν(C=O) stretching. At 1106 cm^{-1}, we find a sharp strong band, with frequency shifts of 16 and 33 cm^{-1} by ^{13}C and ^{18}O labeling, respectively. We therefore conclude that it must be the ν(CO) bond stretching. Figure 7 shows the region 760–620 cm^{-1}, where is expected, besides the PC stretching modes of PMe_3 ligands, the OCO bending mode. In fact, the band at 730 cm^{-1} is shifted to 721 and 717 cm^{-1} by labeling with ^{13}C and ^{18}O, respectively. We therefore assign it to the δ(OCO) deformation mode. A weak band is observed at 610 cm^{-1}; its important frequency shift upon ^{13}C labeling (20 cm^{-1}) compared to the weak one observed by ^{18}O enrichment (5 cm^{-1})

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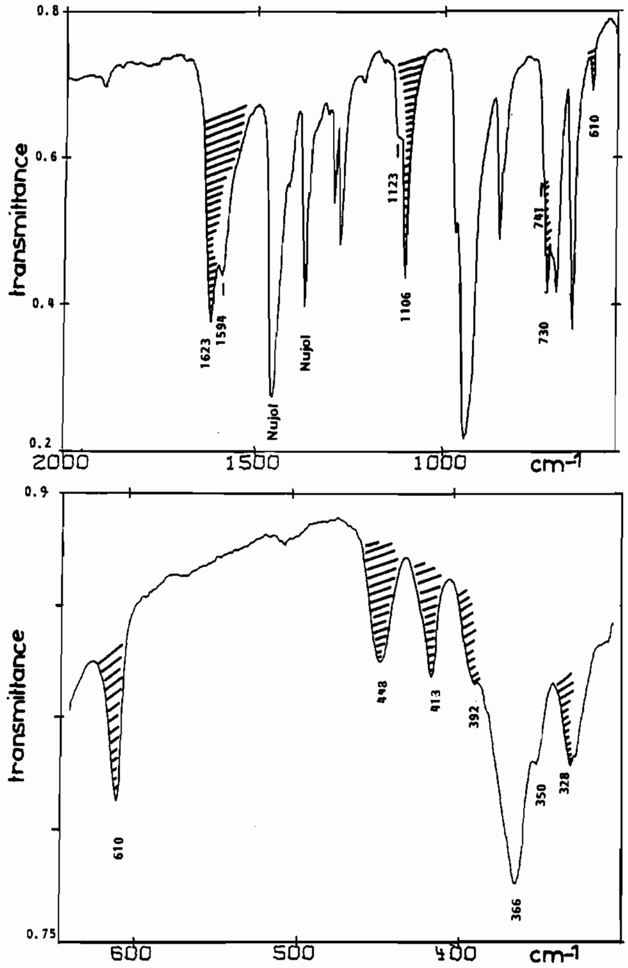

Figure 6. FTIR spectrum (300–2000 cm^{-1}) of $Fe(CO_2)(PMe_3)_4$ (Nujol mull). (The hatching represents CO_2 absorptions.)

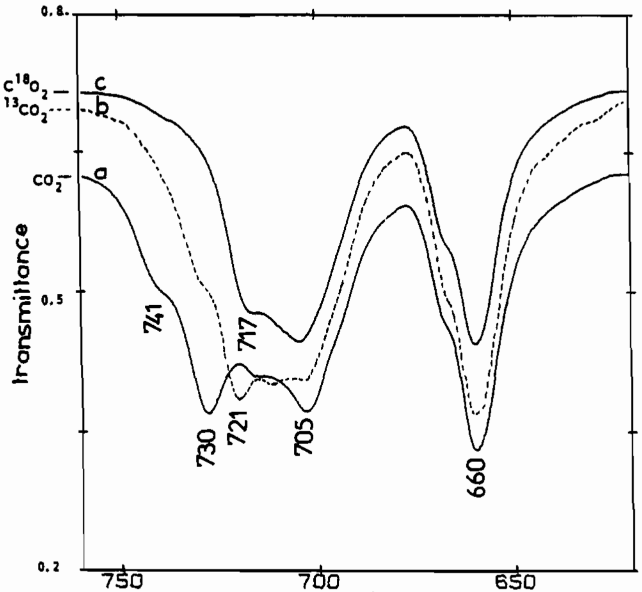

Figure 7. Detailed FTIR spectra in the region 760–620 cm^{-1} for $Fe(CO_2)(PMe_3)_4$ (a) and its $^{13}CO_2$ (b) and $C^{18}O_2$ (c) labeled derivatives.

allows us to assign this frequency to the out-of-the-plane bending of the C=O bond: γ(C=O).

Important isotopic shifts upon ^{18}O labeling are observed on bands at 448 and 413 cm^{-1} (respectively 8 and 3 cm^{-1}). They are probably associated with the Fe–O stretching modes. Some other absorptions are observed under 400 cm^{-1}, 366 and 350 cm^{-1}, that have no isotopic effect and, 392 and 328 cm^{-1}, that are shifted

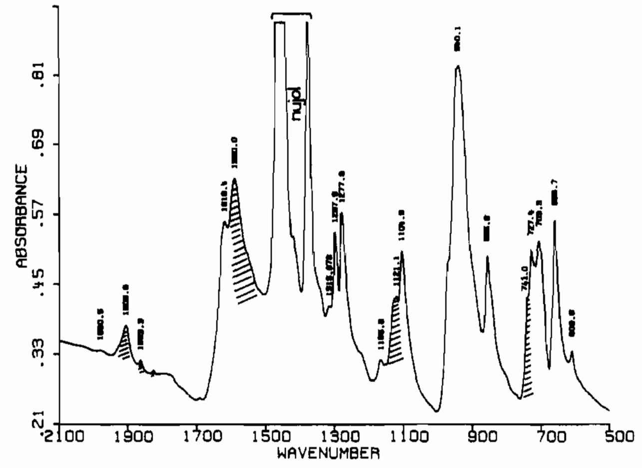

Figure 8. Thermal decomposition of $Fe(CO_2)(PMe_3)_4$.

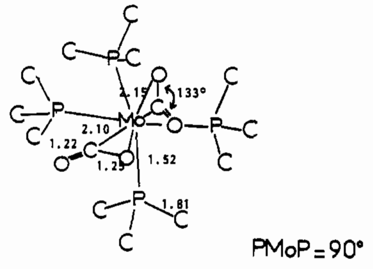

Figure 9. Schematic representation of the structure of *trans*-$Mo(CO_2)_2(PC_3)_4$ used to perform normal coordinate analysis.

to 388 and 324 cm^{-1}, respectively, by ^{18}O labeling. The assignment will be made by means of normal coordinate analysis, but bands at 366 and 350 cm^{-1} probably arise from FeP stretching modes, whereas the importance of ^{18}O effects on all of the low-frequency-region absorptions show that vibrational motions are highly mixed in this compound.

Besides the absorptions described above, one can see on Figure 6 that shoulders exist at 1594, 1123, and 741 cm^{-1}. This set grows after several weeks even if the compound is kept in a sealed flask under argon at −20 °C. Similar behavior is observed for labeled compounds. When the complex is kept at room temperature, thermal decomposition occurs. All the CO_2 absorptions decrease, the shoulders vanishing slower than the main bands. At the same time, absorptions in the 1800–2000-cm^{-1} region grow in, indicating the formation of carbonyls as decomposition products. This has been previously mentioned by Karsh,[16] who described the formation of $Fe(CO)(PMe_3)_4$, $Fe(CO)_2(PMe_3)_3$, and Me_3PO (see Figure 8). This behavior could be indicative of the evolution of the complex in a more stable isomer before decomposition.

Discussion

Bonding and Structure of *trans*-$Mo(CO_2)_2(PMe_3)_4$. There is no structural data on this complex, but the crystal structure of $Mo(CO_2)_2$(iPr-CN)$(PMe_3)_3$[8] indicates that the two CO_2 ligands are mutually perpendicular to each other and eclipsed with respect to the Mo–P bonds and that they are coordinated in a side-on way. The local symmetry of the $Mo(PMe_3)_4$ moiety will then be supposed D_{4h}, but the presence of the staggered CO_2 groups in the trans position lowers the overall symmetry of the molecule to C_1 (see Figure 9). However, for a molecule with such an orientation of the two CO_2 units the CO vibrations can be coupled through the Mo atom. If so, this means that there are both in-phase and out-of-phase combinations of every CO_2 mode. But the question arises of the origin of the magnitude of the splittings, 50 cm^{-1} at 1100 cm^{-1} and 560 cm^{-1}, which are surprisingly high.

We have observed on the infrared spectra the existence of an intramolecular CO_2–CO_2 coupling for the ν(CO) and γ(C=O) modes (and probably for δ(OCO)). In order to assign all the observed frequencies, we have performed normal coordinate analysis for the fragment *trans*-$Mo(CO_2)_2(PC_3)_4$, neglecting H

Table I. Assignments of IR and Raman Observed Wavenumbers of *trans*-$Mo(CO_2)_2(PMe_3)_4$ and Its Labeled Derivatives Compared with Calculated Values[a]

IR, cm^{-1}	Raman, cm^{-1}	calcd wavenumbers, cm^{-1}	assgnts (PED)	$\Delta^{13}C$ obsd	$\Delta^{13}C$ calcd	$\Delta^{18}O$ obsd	$\Delta^{18}O$ calcd
1690 (sh)		1688	$\nu(C{=}O)_{\phi}$ (77)		44.9		30.2
1668 (vs)		1666	$\nu(C{=}O)_{0\phi}$	40	43.8	30	30.7
1580 (w)							
1523 (vw)			carbonate				
	1425, 1433 (w)		δ_a- and $\delta'_s(CH_3)$				
1305 (m)							
1288 (m)			$\delta_s(CH_3)$				
1280 (m)							
1275 (m)							
1183 (sh)							
1153 (s)		1156	$\nu(C\text{-}O)_{\phi}$ (54) + $\delta(C{=}O)$ (33)	29	27.8	19	24
1130 (sh)							
1102 (s)		1103	$\nu(C\text{-}O)_{0\phi}$ (62) + $\delta(C{=}O)$ (40)	26	28.5	26	20.1
950 (vs)			$r(CH_3)$				
855 (ms)							
740 (s)		744	$\delta(C{=}O)_{\phi}$ (42) + $\nu(C\text{-}O)$ (16)	no	4.6	no	36.9
no		730	$\delta(C{=}O)_{0\phi}$ (28) + $\nu'_s(PC_3)$ (28)	no	3.5	no	34.2
735 (s)	735, 720 (m)	739, 738, 737, 734	$\nu'_s(PC_3)$				
713 (s)	710 (w)	735, 733, 733, 732	$\nu_a(PC_3)$				
665 (s)	675 (vs)	678, 676, 676, 676	$\nu_s(PC_3)$				
590 (m)		596	$\gamma(C{=}O)$	18	18.8	5	6
542 (m)		546		17	17.2	5	5.5
450 (vw)		450	$\nu(Mo\text{–}O)_{0\phi}$ (55) + δ_{cycle} (25)	3	0.9	14	16.3
	428 (m)	411	$\nu(Mo\text{–}O)_{\phi}$ (34) + δ_{cycle} (29)	0	1.3	13	13.4
390 (w)	397 (w)	381	$\nu(Mo\text{–}P)$ (71)	no	0.2	no	0.8
360 (vw)	362 (m)	368	$\nu(Mo\text{–}P)$ (60)	0	0.3	no	7.2
	348 (ms)	348	$\nu(MoP)_{\phi}$ (50) + $\delta_s(PC_3)$ (47)	0	0	0	0
339 (m)	337 (s)	336	$\nu(MoP)_{0\phi}$ (52) + $\delta_s(PC_3)$ (52)	0	0	0	0
289 (w)		310	$\nu(Mo\text{–}C)_{0\phi}$ (17) + $\delta_a(PC_3)$ (22)	0	0.7	2	3.8
	295 (w)	298, 296, 296, 291	$\delta_a(PC_3)$				
276 (w)		295, 294, 294, 293	$\delta'_s(PC_3)$	0		0	
	269 (w)	255	$\nu(MoC)_{\phi}$ (25) + $\delta_s(PC_3)$ (42)		0.8		3.8
231 (w)		233	$\delta_s(PC_3)$	0	0.1	0	1.5
	205 (?)	209	$\nu(MoC)_{\phi}$ (34) + $\delta_s(PC_3)$ (20)		1.4		6
	196 (w)	197	$r_{\parallel}(PC_3)$ (40) + $\nu(MoC)_{0\phi}$ (17)	0	0.8	3	3.4
182 (vw)		182, 180, 180	$r_{\parallel}(PC_3)$				
	176 (w)	174, 169, 169, 168	$r_{\perp}(PC_3)$				
		166	$\delta_s(PC_3)$ (51) + $\nu(MoP)_{\phi}$ (35)	0	0		0
		162	$\delta_s(PC_3)$ (46) + $\nu(MoP)_{0\phi}$ (44)		0		0
150 (w)	151 (m)	150	$\delta(PMoO)$ (56)	0	0.1	3	6
		149			0.1		5.9

[a] no = not observed; PED = potential energy distribution.

atoms for simplification. The structural parameters used were those of the *trans*-$Mo(CO_2)_2$(iPr-CN)$(PMe_3)_3$ complex,[8] replacing the iPr-CN ligand by a PC_3 unit in such a way that the structure was symmetric (i.e. all PC_3 groups were in a perfect C_{3v} arrangement and the MoP_4 equatorial plane was supposed D_{4h}).

The initial force field was taken from values calculated by Edwards and colleagues[24] and Loutellier and colleagues[22,23] for the $Mo(PC_3)_4$ fragment and from those established by one of us[14] for the $Mo(CO_2)_2$ moiety. The program used to calculate the generalized valence force field was similar to Schachtschneider's one.[27] Because of the limited vibrational data in the low-frequency region, the fitting was limited to 150 cm^{-1}, but all modes were calculated, the total number of nonzero interaction force constants being 8 for 49 calculated frequencies (29 observed). In the refinement procedure, the adjustment of the isotopic shifts had priority to that of frequencies themselves, because the former are more sensitive to the geometry of the molecule.

Tables I and II summarize the assignment of the vibrational modes and the final results for the valence force field of the $Mo(CO_2)_2(PMe_3)_4$ complex. In our structural hypothesis, the two CO_2 ligands are equivalent and located in perpendicular planes. The calculation then gives two identical frequencies for each mode related to the CO_2 moiety. In order to obtain a splitting of 50 cm^{-1} between the two $\nu(CO)$ modes, we have introduced in the calculation an interaction force constant $f(CO, CO) = 0.44$ mdyn·Å^{-1}, which is lower than one-tenth of the principal force constant $f(CO) = 5.3$ mdyn·Å^{-1}. This interaction induces a splitting of 22 cm^{-1} on $\nu(C{=}O)$ and of 14 cm^{-1} on $\delta(C{=}O)$. These splittings are not detected on our spectra because the $\nu(C{=}O)$ absorption band is very broad ($\Delta\nu_{1/2} = 70$ cm^{-1}) and because the $\delta(C{=}O)$ absorption bands are obscured by the antisymmetric stretching modes of the PC bonds. But we have previously indicated that the assignment of the bands leading to a 43-cm^{-1} shift by ^{18}O labeling seemed not likely for the $\delta(C{=}O)$ vibration. So this could be an indication for the existence of two deformation modes of the OCO angle in this molecule. These can be estimated at 740 cm^{-1} (obsd) and 730 cm^{-1} (calcd). In the same way, the splitting of the $\gamma(C{=}O)$ mode was obtained by means of an interaction force constant $f[\gamma(C{=}O), \gamma(C{=}O)] = 0.065$ mdyn·rad^{-2}, which is without effect on other vibrations as this mode belongs to an other symmetry class (out-of-the-plane bending).

It is generally assumed that interaction force constants must be lower than one-tenth of the main corresponding force constants. The values calculated for *trans*-CO_2/CO_2 coupling constants can then be considered as accurate. In comparison with CO/CO coupling constants in metal carbonyls, the former might appear to be quite large. For example, in $Mo(CO)_6$, Jones and colleagues[28] have calculated the values $f(CO) = 17.15$ mdyn·Å^{-1} and $f(CO,CO) = 0.17$ or 0.01 mdyn·Å^{-1}, depending on whether the

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Table II. Valence Force Field for *trans*-$Mo(CO_2)_2(PMe_3)_4$[a]

force consts	init values	final values
f(Mo–P)	1.62	1.6
f(Mo–O)	2	0.9
f(Mo–C)	2	0.9
f(C–O)	7	5.3
f(C=O)	10	9.6
$f[\nu_s(PC_3)]$	2.75	*b*
$f[\nu'_s(PC_3)]$	2.92	2.42
$f[\nu_a(PC_3)]$	2.92	2.42
f[δ(PMoP) at 90°]	0.34	*b*
f[δ(PMoP) at 180°]	0.68	*b*
$f[\delta(PMoC)]$	0.28	*b*
$f[\delta(PMoO)]$	0.3	0.44
$f[\delta(MoCO)]$	0.35	0.55
$f[\delta(C{=}O)]$	1.0	1.09
$f[\delta(MoOC)]$	0.35	*b*
$f[\delta(CMoO)]$	0.25	*b*
$f[\gamma(C{=}O)]$	0.75	0.68
$f[r_{\parallel}(PC_3)]$	0.46	*b*
$f[r_{\perp}(PC_3)]$	0.46	*b*
$f[\delta'_s(PC_3)]$	0.84	0.64
$f[\delta_a(PC_3)]$	0.84	0.64
$f[\delta_s(PC_3)]$	0.76	0.46
$f[\tau(MoP)]$	0	0.0005
$f[\tau(MoO)]$	0	0.0005
$f[\tau(MoC)]$	0	0.0005
f(C–O, C=O)	0.7	0
f[C–O, δ(C=O)]	0.35	–0.4
f(CO, MoC)	–0.3	*b*
f[C=O, δ(C=O)]	0.65	0
f[C=O, δ(MCO)]	–0.58	0
f(C=O, M–C)	0.68	0
f[δ(C=O), δ(MCO)]	–0.07	0.0
f(Mo–P, Mo–P_{adj})	0.10	0.05
f(Mo–P, Mo–P_{opp})	0.14	0.12
f[MoP, δ(PMoP)]	0.25	0
f[δ(PMoP), δ(PMoP)]	–0.19	0
f[MoP, $\delta_s(PC_3)$]	0.15	–0.09
$f[\delta_s(PC_3), r_{\parallel}(PC_3)]$	0	*b*
f(C–O, C–O)	0	0.44
f[γ(C=O), γ(C=O)]	0	0.065
f[δ(C=O), ν(Mo–C)]	0	–0.2

[a] Force constants are given in mdyn·$Å^{-1}$ for bonds, mydn·Å·rad^{-2} for angles, and mdyn·rad^{-1} for bond–angle interactions. [b] Final value equal to the initial one.

carbonyl ligands are located in a cis (f^c) or trans (f^t) position. But it was shown that (i) the CO/CO interactions arise primarily from dipole–dipole interaction and that changes in π bonding do not enter appreciably and, (ii) inclusion of anharmonic corrections has a significant effect on f^t(CO,CO), which should be twice f^c(CO,CO) if one makes the calculations using the harmonic approximation. So, keeping in mind that (i) distorsion of CO_2 and presence of donor ligands such as phosphines enhances π back-donation, which is a significant contribution to the bonding in CO_2 complexes, and (ii) no anharmonic corrections were used in our calculations, it then seems difficult to offer direct comparison of CO/CO coupling constants between carbonyl and CO_2 complexes.

The good agreement between observed and calculated wavenumbers and isotopic shifts allows us to propose a relevant force field for this compound. The final values obtained for the CO bonds, 9.6 and 5.3 mdyn·$Å^{-1}$, are quite different and show that the CO_2 moieties have two different CO bonds, one with double-bond character (for which force constants are expected to lie in the 8.0–12.0 mdyn·$Å^{-1}$ range) and the other one with single-bond character (where average values of 6 mdyn·$Å^{-1}$ are generally encountered[29]). This is a good indication for the side-on coordination mode in this complex. Furthermore, the ν(MoO) and ν(MoC) frequencies are well reproduced in keeping equal force constants values (0.9 mdyn·$Å^{-1}$), which is a supplementary indication for a side-on coordination.

The MoC and MoO stretches are the only vibrations that show coupling of the two CO_2 units in the complex, as the vibrators have molybdenum as a common atom. As for the ν(MoO) modes, calculated at 450 (IR) and 412 cm^{-1} (R) and described in the previous section, the normal coordinate analysis allows us to assign the infrared absorption at 289 cm^{-1} (calculated at 310 cm^{-1}) to the out-of-the-phase Mo–C stretch, whereas the in-phase vibration is observed at 205 cm^{-1} in Raman spectra and calculated at 209 cm^{-1}. The MoC stretches are also slightly coupled with the δ(C=O) deformation. This confirms the observed small isotopic shifts in these modes by ^{18}O labeling.

Metal–phosphorus force constants are known to be dependent on the nature of the metal and the structure and type of the ligand linked to the phosphorus. For example, in the complexes $Ni(PF_3)_4$, $Pd(PF_3)_4$, and $Pt(PF_3)_4$, M–P force constants are respectively[29] 2.71, 3.17, and 3.82 mdyn·$Å^{-1}$. In the tetrahedral complex $Ni(PMe_3)_4$, the NiP force constant is calculated to be equal to 1.62 mdyn·$Å^{-1}$ by Loutellier and colleagues,[23] which is a lower value than that found for $Ni(PF_4)_4$. In fact, the electroattractive effect of fluorine atoms raises the π back-donation from the metal and then strengthens the M–P bonds. Furthermore, the bonds are expected to be weaker in a D_{4h} planar arrangement than in a T_d geometry. So, with four equivalent coplanar MoP bonds, we find a force constant of 1.6 mdyn·$Å^{-1}$, and the four stretching modes are calculated at 381 (E_u), 368 (E_u), 348 (B_{2g}) and 336 cm^{-1} (A_{1g}) in a D_{4h} symmetry. The former pair is associated with the frequencies observed at 390 and 360 cm^{-1} in infrared spectra and 397 and 362 cm^{-1} in Raman spectra. The mode calculated at 348 cm^{-1} is observed in the Raman spectrum. The last one calculated at 336 cm^{-1} is assigned to frequencies observed at 339 cm^{-1} in infrared spectra and at 337 cm^{-1} in Raman spectra. The lack of exclusion observed in infrared and Raman spectra for Mo–P stretching modes shows that the inversion center is not preserved in the MoP_4 moiety because of the dissymmetry induced by the CO_2 ligand occurring in a trans staggered position.

The potential energy distribution shows that coupling between CO_2 and PMe_3 ligands is weak and that low-frequency modes are relatively pure, probably because the ligands are located in perpendicular planes.

The $\delta(PC_3)$ deformation modes are observed at 295 (δ_a), 276 (δ'_s), and 231 cm^{-1} (δ_s). Contrary to the case for free PMe_3, the symmetric deformation is not observed as the highest frequency[23,24] because the mixture with ν(MoP) induces a splitting of the $\delta_s(PC_3)$ mode at both 339 and 231 cm^{-1}.

Because of the difficulty in observing absorptions below 150 cm^{-1}, the corresponding modes have not been calculated (for example, deformation of the PMoP angles) so the corresponding coupled vibrations (as PC_3 rockings) have not been refined. Anyway, good agreement is obtained between observed and calculated spectra for all the studied compounds (CO_2, $^{13}CO_2$, and $C^{18}O_2$), so we can conclude that CO_2 is side-on coordinated in *trans*-$Mo(CO_2)_2(PMe_3)_4$.

We have previously seen that the coupling between the ν(CO) stretching modes and the γ(C=O) deformation ones was intramolecular. From our structural hypothesis, these vibrators have no shared atom and are quite far from one other. The coupling is authorized (because the motions are not strictly perpendicular), but the observed splitting appears very strong for such a geometry. So, we must consider a large amplitude motion in the molecule that would induce a strong interaction, for example a large amplitude motion where both CO_2's would be eclipsed or would be drawn close to each other.

The question is whether the CO_2 molecule is rigid or rotating around the axis passing through the metal and the coordinated CO bond. In fact, a lot of CO_2 complexes have been found fluxional by NMR studies. This fluxionality is dependent on π back-bonding. When π back-donation is weak, σ donation is preponderant and rotation about a σ bond is generally a low-energy process, since there is no loss of bonding upon rotation. C-coordinated complexes are then expected to have fluxional behavior. When π back-donation is large, the rotational barrier is dependent

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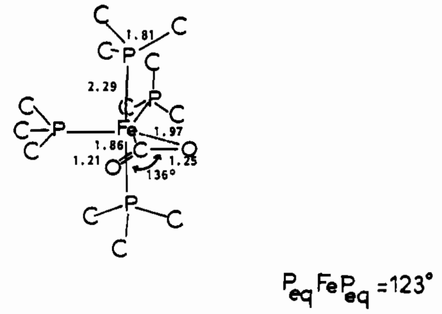

Figure 10. Schematic representation of the structure of $Fe(CO_2)(PC_3)_4$ used to perform normal coordinate analysis.

on the d_π orbitals of the metal. If the metal fragment has perpendicular free d_π orbitals, close in energy and similar in shape, the rotation of CO_2 is not expected to be hindered,[13,30] since there is no loss of bonding upon rotation when the full equivalence of the two orthogonal orbitals is appropriate for back-donation. What can be said about the *trans*-$Mo(CO_2)_2(PMe_3)_4$ complex?

Sanchez-Marcos and colleagues[31] have carried out ab initio calculations and investigated the conformational preferences of the CO_2 ligands in the Mo complex. The most stable conformation has the two CO_2 ligands mutually perpendicular and eclipsing the MoP bonds whereas only 4 kcal mol^{-1} is necessary to have the CO_2 staggered with respect to the MoP bonds. Conformations where the CO_2 would be eclipsed are much higher in energy (~70 kcal mol^{-1}). This suggests a synchronous rotation of the two CO_2 ligands around the carbon dioxide–metal direction rather than their independent rotation. And in fact Carmona and colleagues[15,26,32,33] have shown that a fluxional process, involving synchronous rotation of the CO_2 ligands, is clearly responsible for the temperature dependence of the NMR spectra of the molybdenum complex.

So, a normal coordinate analysis has been performed where the two CO_2 units were eclipsed with respect to one another (and still eclipsed with regard to one of the *trans*-P–Mo–P axes). In this structural configuration, the displacement vectors of the two γ(C=O) vibrations are parallel, leading to a maximum mechanical coupling. But only a gap of 5 cm^{-1} is obtained whereas no splitting is calculated on the ν(CO) vibrators. This calculation shows that the coupling is not a pure mechanical effect but originates almost exclusively from electronic interactions, probably through the electronic delocalization on the $Mo(CO_2)_2$ unit, as observed in spectra by coupling of MoC and MoO stretching modes (with respective splittings of 52 and 22 cm^{-1}). In Raman spectra, only these latter two modes are observed. Their intensity is due to a preresonance effect with the exciting line at 568 nm. (The UV–visible spectra of a THF solution of the Mo complex show absorption at 288 nm, but Raman spectra obtained with 530 and 520 nm were obscured by fluorescence.)

Anyway, a fast motion on the NMR timescale that would strengthen the electronic coupling on the $Mo(CO_2)_2$ skeleton is still possible. A temperature effect on the infrared spectra has been achieved on Nujol mulls between 295 and 80 K and on THF or C_6H_6 solutions between 318 and 193 K. It did not show any variation in the spectra, so that if any motion occurs, it must be very fast on the infrared timescale.

Bonding and Structure of $Fe(CO_2)(PMe_3)_4$. No X-ray structure is available for this complex, so the structural hypothesis was drawn from the known structure of $Fe(CO)_2(CS_2)(PMe_3)(PPh_3)$,[34] replacing CS_2 by CO_2 and all other ligands by PC_3 units. Two PMe_3 are located in the trans position, whereas the other two lie in the same plane as CO_2. As for the molybdenum complex, H atoms have been omitted and all the PC_3 groups were assumed to have C_{3v} symmetry. The CO_2 moiety was initially side-on coordinated, and geometric parameters of $Ni(CO_2)(PCy_3)_2$ have been used for the $M(CO_2)$ unit.[35] All Fe–P distances are equal (see Figure 10).

Table III. Structural Data of $Ni(CO_2)(PCy_3)_2$ (from X-ray Structure Described in Ref 35) and $Fe(CO_2)(PH_3)_4$ (from ab Initio Calculations of Ref 36) Used for Normal Coordinate Analysis of $Fe(CO_2)(PMe_3)_4$

	model compd			model compd	
	$Ni(CO_2)$-$(PCy_3)_2$	$Fe(CO_2)$-$(PH_3)_4$		$Ni(CO_2)$-$(PCy_3)_2$	$Fe(CO_2)$-$(PH_3)_4$
		Bond Lengths (Å)			
M–C	1.857	1.792	C=O	1.211	1.234
M–O	1.967	2.188	$M–P_{eq}$	2.29	2.29
C–O	1.257	1.258	$M–P_{ax}$	2.29	2.21
		Bond Angles (deg)			
OCO	136	137.3	$P_{eq}MP_{eq}$	123	123

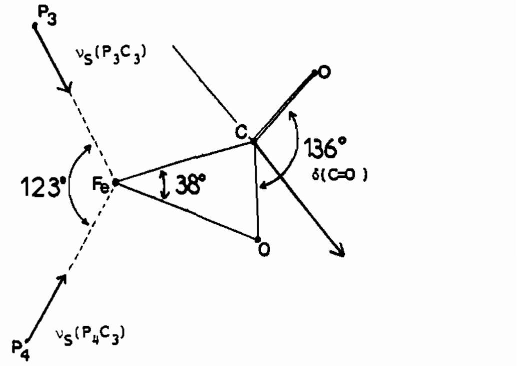

Figure 11. Schematic representation of the equatorial plane of the $Fe(CO_2)(PMe_3)_4$ trigonal-bipyramidal complex.

Another normal coordinate analysis has been performed on the basis of the structure found by Floriani and colleagues from ab initio calculations on $Fe(CO_2)(PH_3)_4$.[36] The main differences in metal–CO_2 and metal–phosphorus bond lengths are described in Table III. Only the first set of structural data (from $Ni(CO_2)(PCy_3)_2$) gave convergent results with experimental spectra.

As for the molybdenum complex, special attention was focused on fitting of the isotopic shifts in the refinement procedure. All the torsions were constrained to zero and calculation was limited to 200 cm^{-1} because of the lack of the corresponding experimental data. The total number of interaction force constants was limited to 9 for 33 calculated and 21 observed frequencies. All interaction force constants without noticeable effect were constrained to zero.

Tables IV and V summarize the assignment of the vibrational modes of the $Fe(CO_2)(PMe_3)_4$ complex and the final results for the valence force field. The good agreement between observed and calculated frequencies allows us to propose a relevant force field and assignments for this compound.

The final force constants $f[\nu(C{=}O)]$ and $f[\nu(CO)]$ are closer than those found for the molybdenum complex. They are respectively 8.7 and 6.3 mdyn·Å^{-1}. Furthermore, the interaction $f[\nu(C{=}O), \nu(CO)]$, without effect in the case of molybdenum, is here equal to 0.6 mdyn·Å^{-1}. Both facts agree to the existence of an important electronic delocalization on the CO_2 unit and then to some kind of "equivalency" of the CO bonds. Isotopic shifts are well reproduced for these two modes, as well as for the out-of-the-plane bending γ(C=O) at 610 cm^{-1}. But we could not reproduce the δ(OCO) mode, and particularly the ^{18}O isotopic effect, by using a valence force field similar to the one found for the molybdenum complex. In fact, with running of the calculation on a simplified molecule $Fe(CO_2)P_4$, the ^{16}O–^{18}O isotopic shift

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Table IV. Assignment of the IR Spectra of $Fe(CO_2)(PMe_3)_4$ and Its Labeled Derivatives[a]

obsd wavenumbers, cm^{-1}	$\Delta^{13}C$		$\Delta^{18}O$		calcd wavenumbers, cm^{-1}	assgnts (PED)
	obsd	calcd	obsd	calcd		
1623	41	45.5	29	25.8	1626	$\nu(C{=}O)$ (67), $\nu(C{-}O)$ (33)
1106	16	15.9	33	36.8	1098	$\nu(C{-}O)$ (51), $\nu(C{=}O)$ (32) $\delta(C{=}O)$ (15)
730	9	2.4	13	12.4	734	$\nu_s(eq)(PC_3)_\phi$ (45), $\delta(C{=}O)$ (17)
					705.4, 704.3, 704.5	$\nu_a(PC_3)$
705					703.2	
					705.9, 705.4, 703.7	$\nu'_s(PC_3)$
					702.5	
					656	$\nu_s(eq)(PC_3)_{0\phi}$
660					654	$\nu_s(ax)(PC_3)_\phi$
					650	$\nu_s(ax)(PC_3)_{0\phi}$
610	20	19.3	4	5.8	613	$\gamma(C{=}O)$ (93)
413	0	1.1	3	6.6	461	$\nu_s(P_3C_3)$ (23), $\delta(C{=}O)$ (21) $\nu(FeP_3)$ (18), $\nu(FeO)$ (17) $\nu(FeP_4)$ (15)
448	2	1.2	8	9.6	448	$\delta(C{=}O)$ (59), $\nu_s(eq)(PC_3)_\phi$ (23) $\nu(FeP_3)$ (18), $\nu(FeO)$ (16)
392	2	2.4	4	4.7	399	$\delta(C{=}O)$ (32), $\nu(FeC)$ (31) $\nu_s(PC_3)$ (19), $\nu(FeO)$ (18) $\nu(FeP_4)$ (17), $\nu(FeP_3)$ (14)
366	0		0		366.5	$\nu_{0\phi}(Fe{-}P_{ax})$ (100) $\delta_s(ax)(PC_3)_{0\phi}$ (23)
350	0	1.6	no	7.5	350.5	$\delta(C{=}O)$ (38), $\nu_s(eq)(PC_3)_\phi$ (29) $\nu(FeC)$ (28), $\nu(FeP_3)$ (19) $\delta_s(P_3C_3)$ (18)
ia	ia		ia		350.2 (ia)	$\delta_s(ax)(PC_3)_\phi$ (60), $\nu_\phi(FeP_{ax})$ (40)
328	0	0.8	4	3.1	324	$\delta_s(P_4C_3)$ (55), $\nu(FeC)$ (19) $\nu(FeP_4)$ (17)

[a] no = not observed; ia = inactive; PED = potential energy distribution.

calculated on the $\delta(OCO)$ mode is found to be 35 cm^{-1}, like for the molybdenum complex. But no mode with such a shift is observed in the iron complex spectrum. So, examination of the eigenvectors in the complete calculation reveals a coupling between the $\delta(OCO)$ and $\nu_s(PC_3)$ modes of the P_3C_3 unit. In fact, if we consider the geometry of the equatorial plane (see Figure 11), we can see that the resulting vectors of the $\delta(OCO)$ and $\nu_s(P_3C_3)$ motions are almost parallel. Their close frequencies joined to a mechanical coupling lead to the splitting of the corresponding wavenumbers, one at high frequency [730 cm^{-1}, which contains 45% $\nu_s(PC_3)$ and only 17% $\delta(C{=}O)$] with a small ^{18}O isotopic effect (13 cm^{-1}) and the second at low frequency [448 cm^{-1}, which contains 59% $\delta(C{=}O)$ and 23% $\nu_s(PC_3)$] with a large ^{18}O isotopic effect (8 cm^{-1}). So in this case, the normal coordinate analysis allowed us to assign correctly the low-frequency region where the large ^{18}O isotopic shifts observed came not only from the Fe–O modes but also from the $\delta(C{=}O)$ contribution in the $\nu_s(PC_3)$ and $\nu(FeC)$ modes (see Table IV). The interaction force constant has been evaluated to 0.45 mdyn·rad^{-1}. On the contrary, none of the vibrations originating from the axial phosphine moieties is coupled with other motions. The asymmetric stretching $\nu_a(FeP_{ax})$ is calculated and observed at 366 cm^{-1} whereas the symmetric counterpart is calculated at 350 cm^{-1} but not observed as forbidden by infrared selection rules.

According to Floriani's ab initio calculations,[36] it has been found that, even if the structure is correctly defined with four identical Fe–P bond lengths, normal coordinate analysis led to the differentiation of the Fe–P bonds, depending on whether the phosphorus is axial or equatorial. Force constants are respectively 1.43 mdyn·Å^{-1} for axial Fe–P bonds, 1.5 mdyn·Å^{-1} for the $Fe{-}P_4$ bond, and 1.9 mdyn·Å^{-1} for the $Fe{-}P_3$ bond, which is coupled with the $\delta(OCO)$ mode.

Furthermore, the force constants $f(FeC)$ and $f(FeO)$ are not found equal as in the molybdenum complex and were found respectively equal to 1.2 and 0.9 mdyn·Å^{-1}. This shows unambiguously that, in the iron complex, even if the CO_2 unit is side-on coordinated, it is preferently linked to the metal by the carbon. This can be related to the Mulliken overlap electronic populations calculated by Floriani and colleagues,[36] which are respectively 0.25 and 0.02 for FeC and FeO bonds and 0.17, 0.15, and 0.08 for the $Fe{-}P_{ax}$, $Fe{-}P_3$, and $Fe{-}P_4$ bonds, and shows that the Fe–C bond is stronger than the Fe–O one. As well, the $Fe{-}P_3$ bond is stronger than the other FeP one in the equatorial plane.

All the low-frequency modes located in the equatorial plane are highly mixed, and refinement has been limited by the fact that in-plane deformations such as $\delta(P_3FeP_4)$, $\delta(P_3FeC)$, and $\delta(P_4FeO)$ have not been observed. An interesting mode is that assigned to the FeC stretching, calculated at 324 cm^{-1} (328 cm^{-1} observed) and showing only ^{18}O isotopic effects because of mixing with the $\delta(C{=}O)$ deformation.

So, in the hypothesis of a D_{3h} bipyramidal structure, we find that the infrared spectra of the complex and of its isotopic labeled derivatives are well reproduced if we suppose CO_2 lying in the equatorial plane with an intermediate coordination between η^2-C,O and η^1-C.

This calculation concerns exclusively the main bands of the infrared spectra and not the shoulders observed by thermal evolution (see previous section) and that could be interpreted as an "isomerization" of the complex. According to Sakaki,[37] $Fe(CO_2)(PH_3)_4$ is a d^8 pentacoordinate complex that tends to exhibit a pseudo-trigonal-bipyramid structure. Orbital energy diagrams of such complexes have been qualitatively given by EH-MO calculations, and the HOMO is a d_π orbital in the equatorial plane. Thus, the CO_2 ligand is expected to coordinate with Fe via a η^2-side-on mode in the equatorial plane. If the CO_2 ligand is perpendicular to the equatorial plane, the CO_2 π^* orbital cannot interact with the HOMO but with the d_π orbital lying lower in energy, and therefore, this conformation is less stable than the in-plane conformation. Of course, the situation is different if the complex has a square-pyramidal structure. In this case, we cannot neglect the possibility of the η^1-C mode like in $Co(R\text{-}Salen)(CO_2)^-$, as the HOMO is now a d_σ orbital.[9] Further studies including ^{13}C and ^{31}P NMR spectra are in progress in order to characterize the structure of the "isomer" detected in the infrared spectra as shoulders of main bands.

Conclusions

For the first time, the metal–CO_2 vibrational modes have been assigned and related force constants evaluated in organometallic

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(37) Sakaki, S. *Stereochemistry of Organometallic and Inorganic Compounds*; Elsevier Science Pub.: Amsterdam, 1990.

Table V. Valence Force Field for $Fe(CO_2)(PMe_3)_4$[a]

vibrational modes	init values	final values
$\nu(FeP)$	1.6	$\nu(FeP_{ax}) = 1.42$ $\nu(FeP_3) = 1.9$ $\nu(FeP_4) = 1.5$
$\nu(FeO)$	0.9	0.9
$\nu(FeC)$	0.9	1.18
$\nu_s(PC_3)$	2.75	2.55
ν_a- and $\nu_s'(PC_3)$	2.42	2.22
$\nu(C-O)$	5.3	6.33
$\nu(C=O)$	9.6	8.7
δ'_s- and $\delta_a(PC_3)$	0.64	*b*
$\delta(CFeO)$	0.25	*b*
$\delta(COFe)$	0.35	*b*
$\delta(OCFe)$	0.35	*b*
$\delta(C=O)$	1.09	0.79
$\delta(PFeP)$	0.34	*b*
$\delta(PFeO)$	0.44	0.30
$\delta(PFeC)$	0.28	*b*
$\gamma(C=O)$	0.68	0.74
$r_{\parallel}(PC_3)$	0.46	*b*
$r_{\perp}(PC_3)$	0.46	*b*
$\delta_s(PC_3)$	0.46	0.57
$\tau(FeP)$	0.0005	0
$\tau(FeO)$	0.0005	0
$\tau(FeC)$	0.0005	0
$\tau(PP)$	0	*b*
$f[\nu(C-O), \delta(C=O)]$	−0.4	0.13
$f[\nu(FeP), \nu(FeP_{opp})]$	0.12	0.33
$f[\nu(FeP), \delta_s(PC_3)]$	−0.09	−0.15
$f[\delta(C=O), \nu(C=O)]$	0.65	0.32
$f[\nu(C-O), \nu(C=O)]$	0	0.6
$f[\nu(FeC), \delta(C=O)]$	−0.2	−0.4
$f[\delta(OCFe), \delta(C=O)]$	0	0.2
$f[\nu(FeO), \delta(C=O)]$	0	*b*
$f[\delta(C=O), \nu_s(PC_3)]$	0	0.45
$f[\delta(C=O), \nu(FeP)]$	0	*b*
$f[\delta(COFe), \delta(C=O)]$	0	0.2

[a] Force constants are given in $mdyn{\cdot}Å^{-1}$ for bonds, $mdyn{\cdot}Å{\cdot}rad^{-2}$ for angles, and $mdyn{\cdot}rad^{-1}$ for bond–angle interactions. [b] Final value equal to the initial one.

complexes. Therefore, the most important part of this paper is devoted to the spectroscopic characterization of the bonding mode of coordination CO_2 by means of FTIR spectroscopy and normal coordinate analysis.

If we compare the $f[\nu(C=O)]$ and $f[\nu(CO)]$ force constants in these complexes, it appears that the gap between both bonds, along with the value of the interaction force constant $f[\nu(C=O), \nu(CO)]$, is indicative of the electronic delocalization on the CO_2 unit and then allows discrimination between true η^2-C,O and η^1-C coordinations. Carbon dioxide has been found to be side-on coordinated in *trans*-$Mo(CO_2)_2(PMe_3)_4$ whereas the bonding is intermediate between η^2-C,O and η^1-C in $Fe(CO_2)(PMe_3)_4$.

It then appears that results obtained by matrix isolation IRTF spectroscopy[14] can be applied to organometallic complexes. But coligands play an important role, as they can modify the spectra when coupling occurs in the molecule by structural effects. Indeed, in the molybdenum complex where the CO_2 lies in a plane perpendicular to other phosphine ligands, no coupling occurs and the CO_2 units present pure vibrational modes. On the contrary, the simultaneous presence of CO_2 and PMe_3 in the equatorial plane of the iron compound leads to a large modification of the $\delta(C=O)$ mode and the expected isotopic shifts. Only normal coordinate analysis has allowed the exact assignment of all the mixed vibrational modes in this complex.

We have also shown that the existence of a mode in the 500–630-cm^{-1} region, with a large ^{13}C isotopic effect (around 20 cm^{-1}), is characteristic of a side-on or C coordination. This mode is easy to characterize because no close frequency appears in the same area and it belongs to a special symmetry class (out-of-the-plane motions) so that it is always pure.

Finally, such descriptions have to be related with the ability of such bonds to give important dynamic effects, which modulate the vibrational motion of the CO_2 ligand.

This paper has been largely devoted to the characterization of the CO_2 bonding mode to the metal in *trans*-$Mo(CO_2)_2(PMe_3)_4$ and $Fe(CO_2)(PMe_3)_4$ and has revealed the important role played by the analysis of isotopic labeling and normal coordinate treatment for this purpose. In the second part, we shall present the study of the CO_2 bonding mode in $Cp_2Ti(CO_2)(PMe_3)$.

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Carbon Dioxide Coordination Chemistry. 2.[1] Synthesis and FTIR Study of $Cp_2Ti(CO_2)(PMe_3)$

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Synthesis and thermal evolution of $Cp_2Ti(CO_2)(PMe_3)$ have been revisited. The FTIR spectra in the solid state and in solution in various solvents of the complex and of its isotopic labeled derivatives ($^{13}CO_2$, $C^{18}O_2$) have been investigated. Normal coordination analysis was performed with different structural hypotheses and led to the conclusion that FTIR spectra indicate that CO_2 is C-coordinated to the titanium in this complex. Complete assignments of FTIR spectra and the valence force field are then proposed. The results of this paper are combined with those of part 1 (preceding paper) to propose an overall scheme for the infrared spectroscopic characterization of CO_2 complexes.

Introduction

This is the second of two papers investigating the infrared characterization of CO_2 complexes. The first one[1] was concerned with the study of *trans*-$Mo(CO_2)_2(PMe_3)_4$ and $Fe(CO_2)(PMe_3)_4$, and we found evidence for a side-on CO_2–metal bonding mode in the molybdenum complex whereas the bonding is intermediate between an η^1-C and a side-on arrangement in the iron compound.

This paper is devoted largely to the study of $Cp_2Ti(CO_2)(PMe_3)$ and focuses, in particular, on the importance of two vibrational modes that are highly sensitive to the CO_2 bonding scheme in the

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