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Carbon Dioxide Coordination Chemistry. 3. Vibrational, NMR, and Theoretical Studies of $Ni(CO_2)(PCy_3)_2$

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Complete assignments of FTIR and Raman spectra are proposed for $Ni(CO_2)(PCy_3)_2$ and its $^{13}CO_2$- and $C^{18}O_2$-labeled derivatives. Normal coordinate analysis gives a relevant force-field for side-on complexation at the solid state and shows that the complex can also exist with an "end-on" coordination mode. FTIR study in various solvents at different temperatures allows us to conclude that similar coordination modes are found in solution. Results are compared to that obtained by ^{13}C and ^{31}P NMR (including CPMAS studies) concerning the fluxionality of $Ni(CO_2)(PCy_3)_2$. The paper also deals with CAS–SCF calculations of $Ni(CO_2)L_2$ isomers and shows that the end-on coordination might account for the fluxional behavior of such systems.

Introduction

This is the third paper investigating the vibrational characterization of the CO_2 complexes.[2] The previous ones were concerned with the study of *trans*-$Mo(CO_2)_2(PMe_3)_4$, $Fe(CO_2)(PMe_3)_4$, and $Cp_2Ti(CO_2)(PMe_3)$. This one is devoted to the study of $Ni(CO_2)(PCy_3)_2$[3] and particularly focuses on two points: the establishment of a relevant force-field and the understanding of the fluxionality phenomena encountered in solution[4] for this complex.

Previous studies[2] have allowed us to propose new approaches of FTIR spectra of CO_2 complexes and to correlate structure with spectroscopic properties, especially with the help of isotopic labeling. Our strategy, therefore, has been to use $^{13}CO_2$- and $C^{18}O_2$-labeled compounds to assign infrared spectra and to transfer previous valence force fields to fit the best geometry for $Ni(CO_2)(PCy_3)_2$.

The X-ray structure of $Ni(CO_2)(PCy_3)_2$ is known[5] and shows that the nickel atom lies in a square planar environment defined by the phosphorus atoms, the carbon atom, and one oxygen atom of the CO_2 molecule (CO_2 being η^2-coordinated to the nickel). But, in this complex with only one CO_2 moiety per molecule, two absorptions arising from CO stretching modes are observed in the infrared spectrum. This can be due to different phenomena such as (*i*) *a crystal effect*, (*ii*) *a Fermi resonance effect or a coupling with a* PCy_3 *ligand vibration, and* (*iii*) *the existence of two conformers*. Furthermore, the NMR study, previously performed by Aresta and colleagues,[4c] has shown a fluxional process that was not fully understood. It then appears that several spectroscopic techniques (FTIR, NMR) could be focused onto this dynamic problem, as the time scales are different and allow one to observe fast (ca. 10^{-13} s) and slow (10^{-1}–10^{-9} s) motions.

Concerning the vibrational study,[1a] we propose in the Results the assignment of the observed IR absorptions to fundamentals of each ligand (CO_2, PCy_3) and give the qualitative information directly accessible from the different isotopic data. A summary of the main NMR results[1b] will be given for clarity, but details and full results have been published elsewhere.[4c] In the next section, after discussion of the Fermi resonance effects expected in the IR spectrum, it will be shown that enough vibrations are observed to lead to a normal coordinate analysis for the vibrations of either form and some structural parameters that can thereby be estimated will be discussed more quantitavely.

Finally, the experimental results will be compared with a CAS–SCF study[1c] related to the relative stabilities of $Ni(CO_2)L_2$ fragments with different coordination modes of CO_2.

Experimental Section

$Ni(CO_2)(PCy_3)_2$ was prepared according to the procedure described by Aresta.[3] PCy_3 was obtained from Strem Chemicals 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%) were purchased from CEA-ORIS. Solid samples were handled under argon, and solutions were manipulated at low temperature (between 0 and -20 °C) under a CO_2 atmosphere with the use of Schlenk equipment in conjunction with a vacuum–gas manifold.

FTIR spectra were recorded using a Bruker 113V and a Nicolet 740FT interferometers. Frequencies are accurate to ±1 cm^{-1}. Solid samples were studied as Nujol mulls. Solutions were handled by means of an home-built variable temperature and path length liquid cell described elsewhere.[6] Raman spectra were recorded on a Coderg T800 spectrometer; exciting lines were provided by a Spectra Physics krypton ion laser. Spectra were recorded at 77 K (to avoid thermal decomposition under laser light exposure) on powdered samples in sealed capillary tubes.

The experimental CPMAS NMR is described elsewhere.[4c]

Results

1. FTIR and Raman Studies. 1.1. Solid-State Spectra. The FTIR and Raman spectra of solid $Ni(CO_2)(PCy_3)_2$ are given in Figures 1 and 2, respectively. We shall distinguish two parts in the FTIR spectrum, relative to each ligand: carbon dioxide and tricyclohexylphosphine. When the complex is crystallized from toluene, some solvent remains in the compound. So, a few absorptions related to toluene appear in the spectrum at 1604

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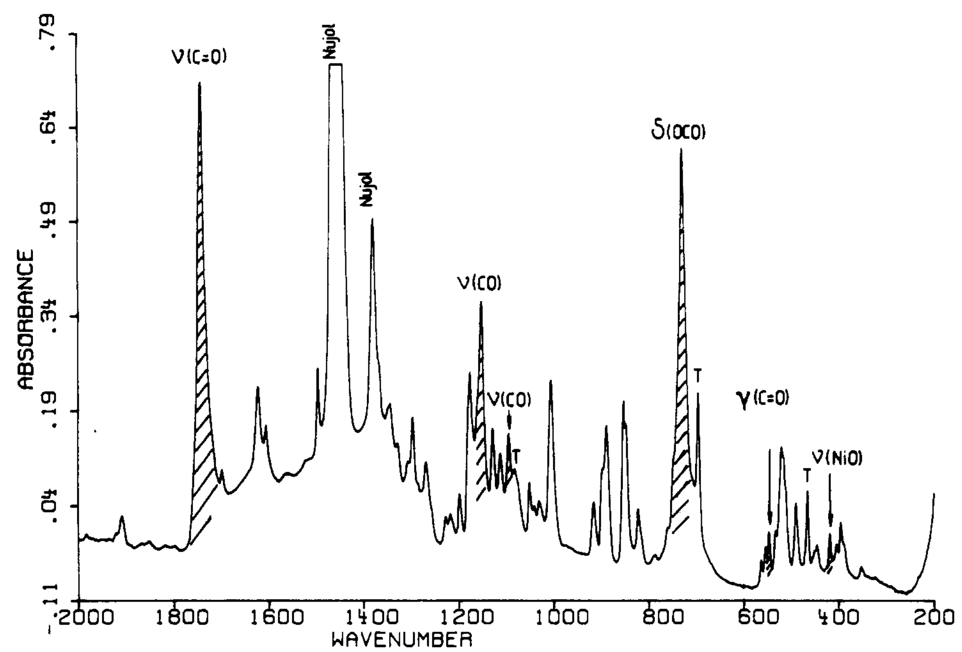

Figure 1. FTIR spectrum (200–2000 cm^{-1}) of solid Ni(CO$_2$)(PCy$_3$)$_2$ (Nujol mull). The shading represents CO$_2$ absorptions. T indicates toluene bands.

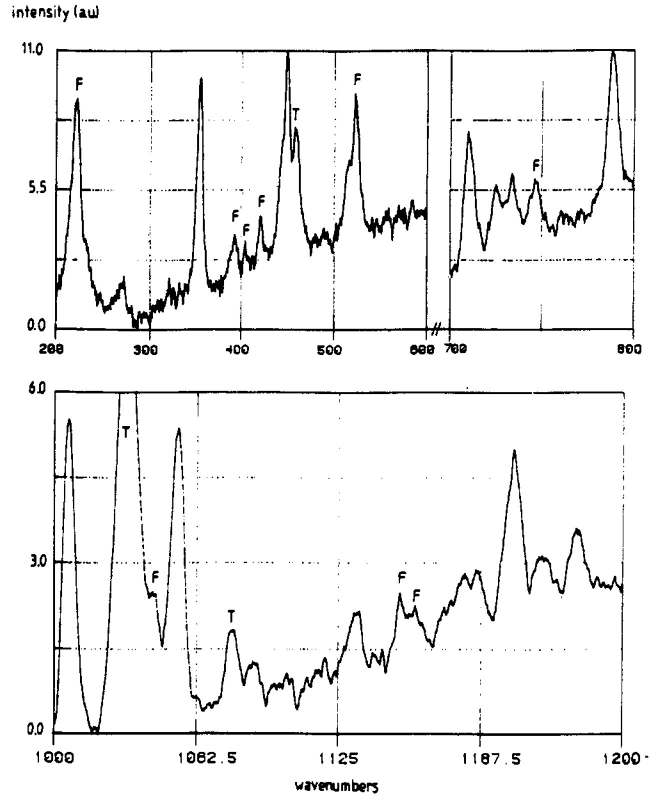

Figure 2. Raman spectrum (200–1250 cm^{-1}) of solid Ni(CO$_2$)(PCy$_3$)$_2$ at 77 K (λ_{exc} = 647.1 nm, 30 mW, resolution 4 cm^{-1}). T indicates toluene and F free PCy$_3$ bands.

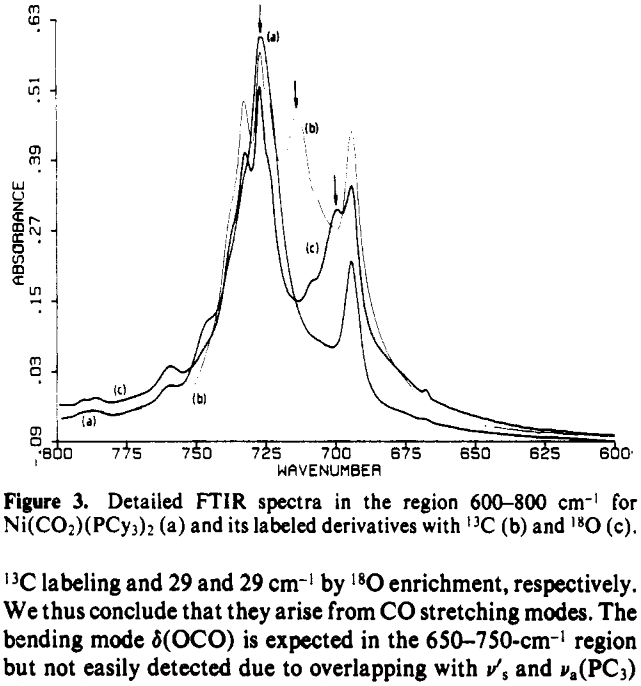

Figure 3. Detailed FTIR spectra in the region 600–800 cm^{-1} for Ni(CO$_2$)(PCy$_3$)$_2$ (a) and its labeled derivatives with ^{13}C (b) and ^{18}O (c).

(vw), 1495 (w), 1460 (sh), 1377 (m), 1084 (sh), 1030 (vw), 726 (vs), 694 (m) and 464 (m) cm^{-1}. (In the Raman spectrum the bands of toluene are observed at 458 (m), 725 (w), 1031 (vs) and 1078 (w) cm^{-1}.)

1.1.1. CO$_2$ Vibrations. Assignments are made with the help of isotopic shifts observed on infrared spectra of labeled compounds Ni(^{13}CO$_2$)(PCy$_3$)$_2$ and Ni(C^{18}O$_2$)(PCy$_3$)$_2$.

The very strong absorption at 1741 cm^{-1}, respectively shifted to 1696 and 1710 cm^{-1} by ^{13}C and ^{18}O labeling, is assigned to the carbonyl stretching ν(C=O). The two sharp bands at 1150 (m) and 1093 (mw) cm^{-1} have isotopic effects of 15 and 20 cm^{-1} by ^{13}C labeling and 29 and 29 cm^{-1} by ^{18}O enrichment, respectively. We thus conclude that they arise from CO stretching modes. The bending mode δ(OCO) is expected in the 650–750-cm^{-1} region but not easily detected due to overlapping with ν'_s and ν_a(PC$_3$) absorptions in the same area. Furthermore, the region is also congested by a strong absorption of toluene at 726 cm^{-1}. Nevertheless, the spectra of the enriched compounds show (see Figure 3) that new bands appear at 713 cm^{-1} for Ni(^{13}CO$_2$)(PCy$_3$)$_2$ and at 699 cm^{-1} for Ni(C^{18}O$_2$)(PCy$_3$)$_2$. Subtractions of IR spectra of Ni(CO$_2$)(PCy$_3$)$_2$ and ^{13}C and ^{18}O labeled compounds allow us to observe the δ(OCO) absorption at 723 cm^{-1}, giving, respectively, isotopic shifts of 10 and 24 cm^{-1}. These values are those generally encountered in similar compounds.[2] The weak absorption located at 554 cm^{-1} is shifted by 16 cm^{-1} due to ^{13}C labeling and not observed in the spectrum of the ^{18}O isotopomer. It is probably hidden by the absorptions of "free" PCy$_3$ located in the same area. As for the δ(OCO) mode, subtraction of Ni(CO$_2$)(PCy$_3$)$_2$ and Ni(C^{18}O$_2$)(PCy$_3$)$_2$ spectra allows us to observe the "missing" band at 551 cm^{-1} (see Figure 4). So, by analogy with previous results,[2] we assign the band at 554 cm^{-1} to the out-of-plane deformation of the C=O vibrator, γ(C=O).

At this point, it is interesting to note that none of the CO$_2$ absorptions described has a coincident band in the Raman

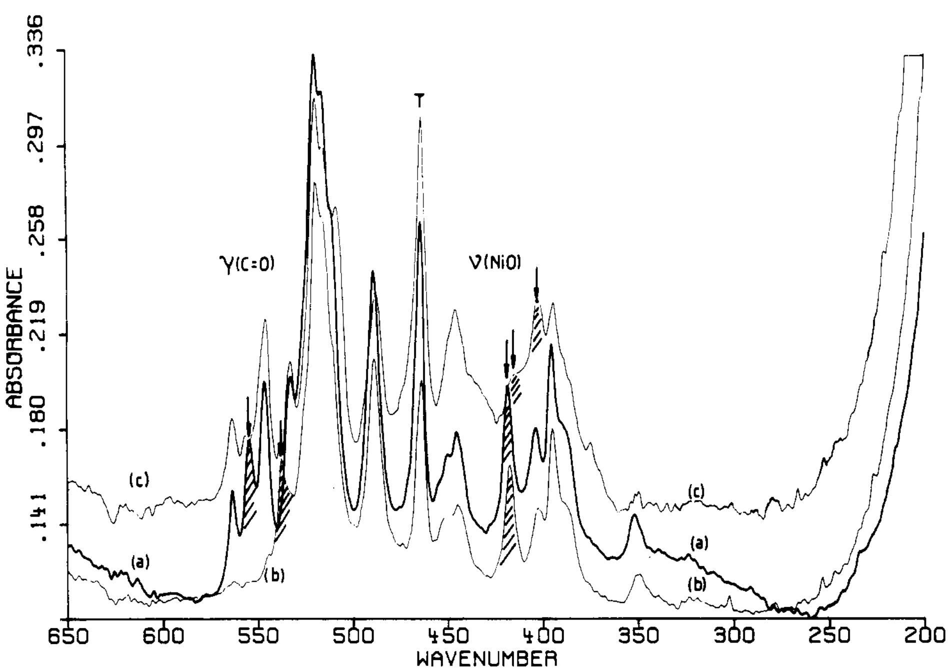

Figure 4. Detailed FTIR spectra in the region 200–650 cm^{-1} for $Ni(CO_2)(PCy_3)_2$ (a) and its labeled derivatives with ^{13}C (b) and ^{18}O (c). T indicates toluene bands.

spectrum. This behavior has already been encountered for trans-$Mo(CO_2)_2(PMe_3)_4$[2a] and is due to the strong polarity of the CO_2 moiety.

Below 500 cm^{-1}, no isotopic shift is observed, except for the band at 418 cm^{-1}, which is shifted for the ^{18}O isotopomer (see Figure 4).

1.1.2. PCy_3 Vibrations. After the study of the FTIR spectrum of solid PCy_3 in suspension in Nujol and comparison with previous vibrational studies on PH_2Cy,[7] we can see that there is no important change in the spectra of free and coordinated PCy_3, except in the region 600–500 cm^{-1}. Concerning the region of importance (2000–200 cm^{-1}), the bending modes of CH_2 are located in the region between 1366 and 1228 cm^{-1} (wagging modes), the counterparts in the Raman spectrum being observed at 1230 (m), 1202 (s), 1185 (w), and 1133 (m) cm^{-1}. The CH_2 rocking modes appear at 1050 (w), 1004 (m), 914 (w) and 894 (sh) cm^{-1}, giving two intense bands in the Raman spectrum at 1054 (s) and 1006 (s) cm^{-1}. Ring modes are observed at 887 (m), 851 (m), 844 (sh, mw), 820 (w) and 789 (vw) cm^{-1}, the latter one being assigned to the ring breathing, observed in the Raman spectrum at 788 (ms) cm^{-1}.

At this point, we must note that the vibrational modes of "free" PCy_3 are only slightly different, and attributed in the FTIR spectra to the very week bands at 1218, 1160, and 1040 cm^{-1} and at 1214, 1158, 1152, and 1043 cm^{-1} on the Raman spectrum. The C–P stretches are located at 757, 746, 721, and 708 cm^{-1} in "free" PCy_3. When PCy_3 is coordinated, these modes are shifted to 731 (ms, sh) in the infrared spectrum, whereas the Raman counterpart is found at 734 (w) cm^{-1} for the asymmetric mode and at 710 (ms) cm^{-1} for the symmetric one, $\nu_s(PC_3)$. At lower wavenumbers, we found the cyclohexyl ring bending modes, which are the ones most shifted by coordination to the metal. Indeed, fairly intense infrared bands are found at 564, 546, and 532 cm^{-1} for "free" PCy_3, which are present with weak intensities in the spectrum of $Ni(CO_2)(PCy_3)_2$ (the complex is prepared in solution with an excess of free phosphine that is not fully eliminated when the compound is isolated). These absorptions are shifted to lower wavenumbers in coordinated PCy_3, at 519 (ms), 515 (sh), 510 (sh), and 488 (m) cm^{-1}, whereas the Raman spectrum shows bands at 522 (ms) and 516 (sh) cm^{-1}. The deformations $\delta(PC_3)$ are expected in the 200–350-cm^{-1} region; assignments will be discussed below with metal–ligand modes $\nu(NiP)$, $\nu(NiO)$, and $\nu(NiC)$, also expected below 500 cm^{-1}.

1.1.3. Metal–Ligand Vibrations. The interpretation of the far-infrared region, between 500 and 200 cm^{-1}, needs a careful comparison of the infrared and Raman spectra of the CO_2 complex with "free" PCy_3 and the precursor compound $NiCl_2(PCy_3)_2$ (see Table I). Weak bands at 449 and 445 cm^{-1} also exist in $NiCl_2(PCy_3)_2$. They are therefore assigned, by analogy to PH_2Cy,[7] to a ring bend mode of PCy_3 ligands. Bands at 418 (m), 403 (w), 395 (m), 389 (sh), and 352 (w) cm^{-1} are found for $Ni(CO_2)(PCy_3)_2$ and the $^{13}CO_2$-labeled complex. Bands at 414 (w), 395 (sh), and 386 (m) cm^{-1} exist in $NiCl_2(PCy_3)_2$. The latter one is assigned to the out-of-phase stretching $\nu_{OPh}(NiCl)$, the in-phase counterpart being observed at 294 (m) cm^{-1} in the Raman spectrum. As well, free PCy_3 presents bands at 427 (m), 406 (m), 387 (w), 373 (m) and 288 (m) cm^{-1}. The spectrum of the enriched ^{18}O nickel complex shows a weaker band at 418 cm^{-1}, whereas the absorption at 403 cm^{-1} rises, with the bands at 395, 389 (sh), and 352 cm^{-1} being unchanged. So, we conclude that some contribution of ring bend modes of PCy_3 ligands may account for the absorptions located at 414 and 403 cm^{-1} and that the band at 418 cm^{-1} can be assigned to the stretching mode $\nu(NiO)$ of the nickel/CO_2 complex. The assignment of the corresponding mode in the ^{18}O isotopomer at 414 or 403 cm^{-1} is not clear.

Assignments of the other bands will be made with help of normal coordinate analysis, but, by analogy with previous results,[2,7] we can propose the following attributions: $\nu(NiP)$ for 395 and 389 cm^{-1} and $\delta_s(PC_3)$ for 352 cm^{-1}, as this mode appears as a strong band in the Raman spectrum.

1.1.4. Conclusion. Table I summarizes the assignment of all the vibrational modes. It then is observed that only the $\nu(CO)$ mode appears as a doublet in the IR spectrum. As already observed for similar compounds,[2] the Raman spectra are quite poor in $NiCO_2$ vibration modes, as only one –$\nu(NiO)$– is observed. So, in order to ascertain the presence of this $\nu(CO)$ doublet at a molecular scale, FTIR spectra have been obtained from solutions of $Ni(CO_2)(PCy_3)_2$.

1.2. Solution Spectra. FTIR spectra have been run for the nickel complex in solution in toluene at –20 °C under a CO_2

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Table I. Observed Vibrational Frequencies (cm^{-1}) and Tentative Assignments for $Ni(CO)_2)(PCy_3)_2$ and its Labeled (^{13}C,^{18}O) Derivatives, $NiCl_2(PCy_3)_2$, and Tricyclohexylphosphine

$Ni(CO_2)(PCy_3)_2$		$Ni(^{13}CO_2)(PCy_3)_2$	$Ni(C^{18}O_2)(PCy_3)_2$	$NiCl_2(PCy_3)_2$		PCy_3		
infrared	Raman	($\Delta\bar{\nu}$)	($\Delta\bar{\nu}$)	Infrared	Raman	Infrared	Raman	assignments
1910 vw								carbonyl (impurity)
1741 vs		1696(45)	1710(31)					ν(C=O)
1696 vw		1672(24)	1665(31)					carbonate (impurity)
1621 w								
1604 vw								toluene
1495 w								toluene
1460 sh								toluene
1377 m								toluene
1366 sh				1366				
1343 w				1341				
1327 vw				1325				
1305 vvw				1306				CH_2 wagging
1295 w				1297		1295 w		
1267 w				1264		1267 w		
1228 vw	1230 m			1230				
1218 vw	1214 w					1221 m		free PCy_3
1196 w	1202 s			1195				
	1180,1185 w			1182				CH_2 twisting
1174 m				1172				
1160 sh	1158,1152 w					1160 ms		free PCy_3
1150 m		1135(15)	1121(29)					ν(CO)
1127 mw	1133 m			1129				
1111 mw				1110		1114		CH_2 twisting
1093 mw		1073(20)	1064(29)					ν(CO)
1084 sh	1078 m							toluene
1050 vw	1054 s			1051				CH_2 rocking
1040 vw	1043 sh,m					1039 w		free PCy_3
1030 vw	1031 vs							toluene
1004 m	1006 s			1001		1003		
914 w				915		913		CH_2 rocking
894 sh				898		894 sh		
887 m				886		887 m		
851 m				848		856, 850 m		ring modes
844 sh, mw				845				
820 w				824, 818		817		
789 vvw	788 m			790			788	ring breathing
757 vw				763		756 m	752	free PCy_3
746 sh	747 w					741 m		free PCy_3
731 sh	734 w			733 s, 723		716 m		ν_a, $\nu'_s(PC_3)$
726 s	725 w							toluene
723		713(10)	699(24)					δ(OCO)
	710 m			708	710,680		698 vs	$\nu_s(PC_3)$
694 m								toluene
564 w						564 w		free PCy_3
554 w		538(16)	551(3)					γ(C=O)
546 w						546 m		free PCy_3
532 w				529		532 m		free PCy_3
519 ms	522 ms							
515 sh	516 sh			516	517		515	ring bend
510 sh				511		510	506	
488 m				489	492	481		
464 m								toluene
	458 m					468	460 m	free PCy_3
449 vw	448 ms			450	448			ring bend
445 vw				440	441	444	445	
418 m	422 w	418(0)	414(4) or 403(15)	428, 414		427	430 m	ν(NiO) + free PCy_3
403 w	405 vw				408	406	390	free PCy_3
395 m	392 w				395			
389 sh				389		373	375 m	ν(NiP) + $\delta(PCy_3)$
				386 s				ν_a(NiCl)
352 w	354 ms				333		320 m	$\delta_s(PC_3)$
					294			ν_s(NiCl)
	272 vw				269	288	264 m	$\delta_s(PC_3)$
	222 ms					231	221	free PCy_3

atmosphere. Figure 5 shows the results obtained. Frequencies and intensities similar to those observed for the solid state were obtained. The ν(C=O) band is slightly shifted from 1741 to 1750 cm^{-1}, whereas the ν(CO) doublet at 1150 and 1093 cm^{-1} is found at 1154 and 1095 cm^{-1}. Furthermore, the γ(C=O) modes is observed at 551 cm^{-1}, instead of 554 cm^{-1} for the solid state.

This result excludes coupling by crystal effects and frequency shifts observed can easily by explained on the basis of solvent effects. Variation of temperature between –20 and +20 °C led to the decomposition of the complex, with a progressive decrease of the ν(C=O) band, together with an increase in the band for free CO_2 at 2340 cm^{-1}. If the CO_2 atmosphere is replaced by argon, decomposition occurs at –20 °C. Surprisingly, decomposition is slower under a N_2 atmosphere, showing that the reactivity of the complex toward electrophiles is more likely due to the existence of a "$(PCy_3)_2Ni$" fragment.

Changing the solvent leads to similar results: small frequency

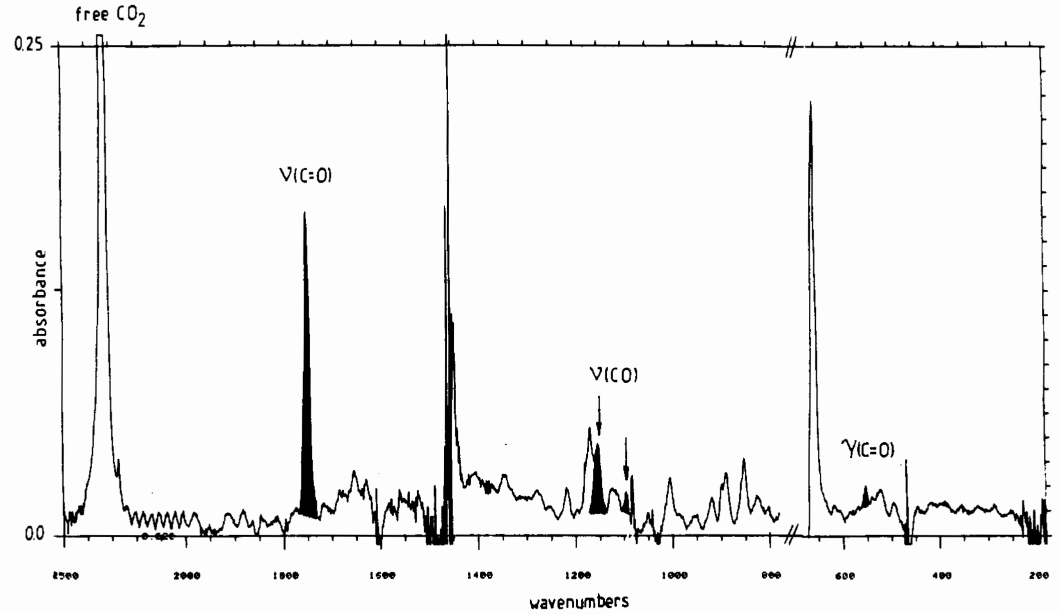


Figure 5. FTIR spectrum of $Ni(CO_2)(PCy_3)_2$ in solution in toluene (solvent absorptions have been substracted).

shifts, due to solvant effects, were observed in the $\nu(C{=}O)$ frequency (i.e. 1742 cm^{-1} in THF and 1717 cm^{-1} in CH_2Cl_2). So the equilibria observed in toluene[4a] for CO_2 complexes

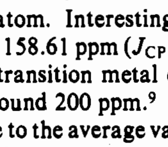
$$Ni(CO_2)L_2 + L \underset{\text{low temp}}{\overset{\text{room temp}}{\rightleftarrows}} Ni(CO_2)L_3$$

with "small" alkyl phosphine ligands (L = PEt_3, $PBu^n{}_3$, PEt_2Ph) do not occur with the tricyclohexylphosphine ligand.

2. NMR Study. In solution, the ^{31}P NMR spectra show a single sharp resonance at 36.1 ppm in the temperature range 197–303 K. The same feature is observed in liquid CO_2.[8] In the solid-state CPMAS ^{31}P NMR of $Ni(CO_2)(PCy_3)_2$, two different isotropic peaks at 45.2 and 22 ppm are observed with a large variation in their chemical shift anisotropy as shown in the spinning sideband pattern, in accordance with the η^2-coordination of carbon dioxide. The phosphorous signal in solution is close to the average value of the two solid-state resonances. CPMAS ^{13}C NMR of a sample of $Ni(CO_2)(PCy_3)_2$ prepared with ^{13}C-enriched CO_2 affords a resonance at 158.4 ppm that represents, to our knowledge, the first solid-state NMR observation of a CO_2 molecule coordinated to a metal atom. Interestingly, this value is close to that found in solution at 158.61 ppm (J_{CP} = 14.8 Hz). This value is unique for the CO_2 transition metal complexes that usually show ^{13}C resonances around 200 ppm.[9] It is interesting to note that this number is close to the average value (162 ppm) between side-on complexes and free linear CO_2 at 124 ppm.

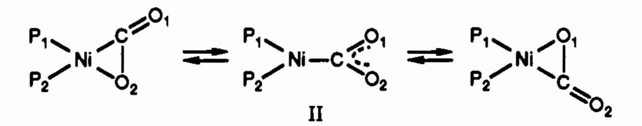
Three different explanations can therefore be suggested.[4c]

(*i*) A η^1-C coordination in solution (diagram I).

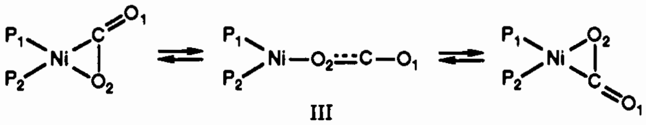


I

(*ii*) A fast dynamic process that averages the two possibilities of η^2-C,O coordination of CO_2 to the metal through a C-coordinated compound (diagram II) or an end-on conformation (diagram III).

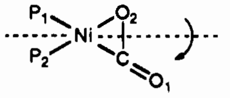


II



III

(*iii*) A fast rotation around the Ni–η^2-C,O bond (diagram IV).



IV

Discussion

We know from solution spectra that (*i*) *the ν(CO) doublet does not arise from an intermolecular coupling (so-called "crystal effect") and (ii) the coordination mode is identical in solution and in the solid state on the infrared time scale.* Indeed, previous results,[2,10] showed that C-coordination of CO_2 induces a smaller split of the CO stretching bands (namely less than 500 cm^{-1}) compared to that induced by η^2-C,O or η^1-O coordination. In our case, the splittings $\nu(C{=}O) - \nu(CO)$ are equal to 591 and 648 cm^{-1}, considering respectively the ν(CO) absorptions at 1150 and 1093 cm^{-1}. Furthermore, a diad would also be observed for the $\nu(C{=}O)$ mode. So, hypotheses 1 and 2 given by the NMR study, involving a (η^1-C) coordination mode, can be ruled out.

So, in order to explain the origin of the ν(CO) doublet, we must now consider the last two hypotheses: a Fermi resonance effect or the existence of two conformers, as suggested in diagrams III and IV by the NMR study.

1. Fermi Resonance Calculations. A Fermi resonance effect is obtained when a combination or an overtone level (ν_c) comes in close proximity to a fundamental (ν_a) belonging to the same symmetry class. It results in an intensity borrowing to the latter, and the degree of mixing between the two resulting levels (ν_+, ν_-)

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will be a function of the closeness of the position of the two original levels ν_a, ν_c. In this case, as the intensity of ν_+ (1150 cm^{-1}) is greater than that of ν_- (1093 cm^{-1}), ν_c is lower than ν_a, from which it borrows intensity. Assuming that the transition moment of ν_c is negligible vs that of ν_a, then the position of unpertubated levels can be deduced from the simple expressions[11]

$$\nu_a = \nu_- + (\nu_+ - \nu_-)/(R + 1)$$

$$\nu_c = \nu_+ - (\nu_+ - \nu_-)/(R + 1)$$

with the intensity ratio $R = I(\nu_-)/I(\nu_+)$. The calculation of ν_a and ν_c for each labeled compound gives the following results: $\nu_a(^{12}C^{16}O) = 1137$ cm^{-1} with $\nu_c = 1106$ cm^{-1}; $\nu_a(^{13}C^{16}O) = 1127$ cm^{-1} with $\nu_c = 1081$ cm^{-1}; $\nu_a(^{12}C^{18}O) = 1104$ cm^{-1} with $\nu_c = 1082$ cm^{-1}. Isotopic shifts of 10 and 33 cm^{-1} are then respectively found for $^{12}C/^{13}C$ and $^{16}O/^{18}O$ labeling for the ν(CO) stretching mode. If the latter one is good, compared to previous results,[2] the first one is too small, as experimental values usually vary between 15 and 32 cm^{-1}.

Considering ν_c as an **overtone**, this calculation locates the corresponding fundamental level at 553 cm^{-1}, which is observed as the γ(C=O) mode (A″). But calculated isotopic shifts (12 cm^{-1} for both ^{13}C and ^{18}O isotopomers) do not fit with experimental results (respectively 16 and 3 cm^{-1}).

Considering now ν_c as a **combination** level, one at least of the involved modes must be related to a CO_2 moiety vibration. The only possibility is therefore a combination with the δ(OCO) mode, observed at 723, 713, and 699 cm^{-1}, respectively, for the nickel/CO_2 complex and its ^{13}C- and ^{18}O-labeled derivatives. Calculated values are then $\nu_c(^{12}C^{16}O) = 1106$ cm^{-1} = 723 + 383 cm^{-1}, $\nu_c(^{13}C^{16}O) = 1081$ cm^{-1} = 713 + 368 cm^{-1}, and $\nu_c(^{12}C^{18}O) = 1082$ cm^{-1} = 699 + 383 cm^{-1}. The far-infrared region of the spectrum shows several bands around 383 cm^{-1} (ν(NiP) at 395 and 389 cm^{-1} and $\delta(PC_3)$ at 352 cm^{-1}) but none of them is shifted by ^{13}C labeling. So, a Fermi resonance effect between ν(CO) and 2γ(C=O) or a combination level with δ(OCO) does not seem likely the cause of the doublet pattern of ν(CO). Furthermore, if we consider the sums of the isotopic shifts measured on each of the ν(CO) band, i.e. 35 and 58 cm^{-1}, respectively, by ^{13}C and ^{18}O labeling, these values are too large to be related to only **one** CO_2 moiety mode.

The last possibility is then a Fermi resonance between ν(CO) and the combination of **two** CO_2 modes. The only solution is therefore the combination δ(OCO) + ν(NiO), as both of them belong to the same symmetry class A′. The simple addition of the experimental wavenumbers gives the following results: ν(CO) = 723 + 418 = 1141 cm^{-1}; $\nu(^{13}CO)$ = 713 + 418 = 1121 cm^{-1}; $\nu(C^{18}O)$ = 699 + 414 = 1113 cm^{-1} or 699 + 403 = 1102 cm^{-1}. These values fit quite well with previous calculated ν_a levels (1137, 1127, and 1104 cm^{-1}) and the splitting ν(C=O) − ν(CO) is equal to 1741 − 1141 = 600 cm^{-1}, which is above 500 cm^{-1}, as encountered in all side-on and end-on CO_2 complexes. An isotopic shift of 20 cm^{-1} is found for ^{13}C labeling which is the usual value observed in CO_2 complexes. The uncertainty comes from the ^{18}O isotopomer. Considering that $\nu(Ni^{18}O)$ is located at 414 cm^{-1}, the ^{18}O shift (28 cm^{-1}) fits the experimental values encountered for side-on complexes. The sums of the isotopic shifts of ν(C=O) and ν(CO) are equal to 65 and 59 cm^{-1}, respectively, for ^{13}C and ^{18}O labeling; these values follow the general relationships that we have found for side-on CO_2 complexes.[2,10] Considering now the value of 403 cm^{-1} for $\nu(Ni^{18}O)$, the ^{18}O shift for ν(CO) is therefore 39 cm^{-1} and the total amount of isotopic shift on both stretching modes is then 70 cm^{-1}, which is the value calculated for end-on CO_2 complexes.[2,10] Finally, considering the transfer of isotopic shifts from δ(OCO) and ν(NiO) to the ν(CO) bands, we find that $\Delta\nu_{calcd}(CO) + \Delta\delta_{obsd}(OCO) + \Delta\nu_{obsd}(NiO)$ is equal to 30 cm^{-1} for ^{13}C labeling and 56 cm^{-1} or 78 cm^{-1} for ^{18}O enrichment, depending on the value considered for $\Delta\nu$(NiO) (4 or 15 cm^{-1}). Comparison of the calculated values to the sums of the experimental isotopic shifts of ν(CO), 35 and 58 cm^{-1}, respectively, by ^{13}C and ^{18}O labeling, leads to the conclusion that a ^{18}O shift of 4 cm^{-1} for ν(NiO) fits better the experimental data.

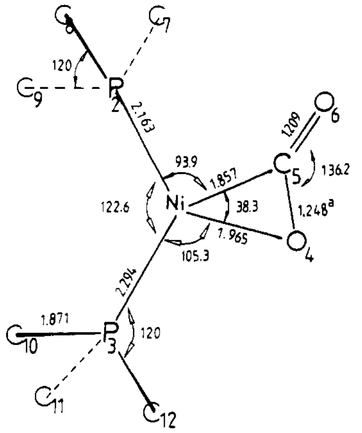

Figure 6. Schematic representation of the structure of $Ni(CO_2)(PCy_3)_2$ used to perform normal coordinate analysis for the side-on arrangement. (a = calculated value, with bond lengths in Å and angles in deg).

At this point, one must keep in mind that (*i*) *an uncertainty exists on the attribution of the $\nu(Ni^{18}O)$ mode and* (*ii*) *the intensities of the ν(CO) bands have not been considered in this calculation.* We cannot therefore conclude without a doubt that a Fermi resonance exists between ν(CO) and a combination of δ(OCO) and ν(NiO). Let us now consider the last possible hypothesis: the existence of two conformers.

2. Normal Coordinate Analysis. 2.1. Definitions. A normal coordinate analysis has been run in order to fit the structural assumptions in III and IV given by the NMR study. Considering the hypothesis in IV (a fast rotation around the axis passing through the metal and the coordinated CO bond), we have considered the two extreme conformations of the motion: the planar side-on C_s form and a "pseudotetrahedral" C_s one (i.e. with the CO_2 moiety perpendicular to the NiP_2 plane, all other structural parameters being identical). Similar planar and perpendicular conformations were also calculated for an end-on form, as suggested in diagram III.

The crystal structure of $Ni(CO_2)(PCy_3)_2$ has been obtained by X-ray diffraction[5] and showed that the environment of the Ni atom is almost planar with a side-on coordination of CO_2. Structural data used to perform the normal coordinate analysis were then those drawn from the X-ray study (see Figure 6). A complete study would have been much too complicated because of the PCy_3 ligands. So, the cyclohexyl rings have been neglected, as no important interactions are expected between vibrators of the cycles (CC, CH) and those of CO_2, and calculations were run for the simplified model compound $Ni(CO_2)(PC_3)_2$. All PC_3 groups were placed in a perfect C_{3v} arrangement with an average PC bond length of 1.871 Å and CPC angles of 120°, the overall symmetry class of the compound being C_s.

The program used to calculate the generalized valence forcefield was similar to Schachtschneider's one.[12] All modes were calculated, but because of the limited experimental data in the low wavenumbers region (14 observed frequencies), the fitting was limited to 170 cm^{-1}, the total number of nonzero interaction force constants being 9. In order to obtain comparable results for both coordination modes, calculations were run by using only

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(11) Fernandez-Bertran, J.; Ballester, L.; Dobrihalova, L.; Sanchez, N.; Arrieta, R. *Spectrochim. Acta* **1968**, *24A*, 1765.

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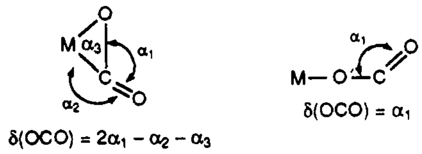
Table II. Assignment of Observed and Calculated Wavenumbers (cm^{-1}) for $Ni(CO_2)(PCy_3)_2$ and its Labeled Derivatives (^{13}C, ^{18}O) with Different Coordination Modes of CO_2

			$\Delta\bar{\nu}(^{13}C)$			$\Delta\bar{\nu}(^{18}O)$			
	calcd wavenumbers			calcd			calcd		
obsd wavenumbers	side-on	end-on	obsd	side-on	end-on	obsd	side-on	end-on	assignments (PED)
1741	1744.4	1742.2	45	47	47	31	30.2	30	$\nu(C{=}O)(70),\nu(CO)(26)$
1150	1139.6		15	23.4		29	29.2		$\nu(CO)(50),\delta(C{=}O)(29),\nu(C{=}O)(26)$
1093		1083.2	20		17	29		36	
	733.1								$\nu_a(PC_3)(72),\nu'_s(PC_3)(23)$
731	731.2								$\nu_a(PC_3)(70),\nu'_s(PC_3)(24)$
	730.3								$\nu'_s(PC_3)(73),\nu_a(PC_3)(24)$
	730.0								$\nu'_s(PC_3)(72),\nu_a(PC_3)(25)$
723	719.2	657.7	10	6.5	7.7	24	30.8	27.2	$\delta(C{=}O)(59),\nu(CO)(18)$
710[a]	709.6								$\nu_s(PC_3)(90)$
	708.2								$\nu_s(PC_3)(90)$
554	556.5	425.9	16	17.4	12.2	3	6	6.7	$\gamma(C{=}O)(99)$
418	420.1	413.6	0	0.3	0.9	4 or 15	9.3	4.3	$\nu(NiO)(47),\nu(NiP_2)(25)$
395	398.8			0.0			3.8		$\nu(NiP_3)(50),\nu(NiO)(13),\nu(NiC)(14)$
389		383.6			0.4			1.9	
352	343.6								$\delta_s(PC_3)(54),\nu(NiP_2)(30)$
no	304.8								$\delta_s(PC_3)(51),\nu(NiC)(28)$
	273.8								$\delta'_s(PC_3)(95)$
272[a]	272.1								$\delta'_s(PC_3)(97)$
	271.4								$\delta_a(PC_3)(98)$
235[a]	247.1								$\delta_s(PC_3)(43),\nu(NiP_2)(16)$
no	200.0								$r_{\parallel}(PC_3)(26),\nu(NiC)(18),\nu(NiP_3)(17)$
no	194.3								$r_{\perp}(PC_3)(98)$
no	179.1								$r_{\parallel}(PC_3)(51),\nu(NiP_3)(15)$
no	174.3								$r_{\parallel}(PC_3)(88)$
no	171.9								$r_{\parallel}(PC_3)(98)$

[a] Raman values; no = not observed; PED = potential energy distribution for the side-on geometry.

internal coordinates of $Ni(CO_2)(PC_3)_2$. For example, the bending mode $\delta(OCO)$ has been defined as an internal coordinate α_1 (and



$\delta(OCO) = 2\alpha_1 - \alpha_2 - \alpha_3$ $\delta(OCO) = \alpha_1$

V

not as a symmetry coordinate $2\alpha_1 - \alpha_2 - \alpha_3$ as previously performed in our calculations[2] because this definition is not valid for the end-on geometry). The main differences between the side-on and end-on forms in coordinates definitions have been the following.

(*i*) *The Absence of the NiC Bond for the End-on Coordination.* In order to avoid large amplitude motion of the C=O bond during the "rotation" of the CO_2 moiety, we have made the hypothesis of a structure where the C=O bond lies along the bisector axis of the PNiP angle. The approach of the OCO moiety with structural parameters taken from the X-ray structure[5] (i.e. OCO = 136.2°) at a distance of 1.965 Å from the $(PC_3)_2Ni$ fragment gives a nickel–carbon distance of 2.67 Å, which is too long to allow the formation of a bond.

(*ii*) *The Definition of the Out-of-Plane Motion of the Carbon Atom of CO_2.* In the side-on geometry, it can be defined as a bending mode $\gamma(CO)$, whereas in the end-on structure, it is replaced by a torsion mode $\tau(CO)$ around the CO axis (we have previously shown[2b] that, in this case, the isotopic frequency shift $^{16}O/^{18}O$ is enhanced compared to that obtained for the side-on geometry).

As previously underlined,[2] the adjustment of the isotopic shifts had priority to that of frequencies themselves in the refinement procedure, because the former are more sensitive to the geometry of the molecule. The initial force field was taken from values previously calculated for $Fe(CO_2)(PMe_3)_4$.[2a]

2.2. Influence of the Rotation Motion. For each coordination mode (side-on or end-on), changing the planar form to the perpendicular one does not induce large shifts on calculated frequencies (namely from 2 to 6 cm^{-1} on all in-plane modes). The isotopic shifts remain unchanged within 2 cm^{-1}, which is the experimental resolution accuracy. In fact, the largest modifications occur for the out-of-plane vibrations such as $\gamma(C{=}O)$ or $\tau(CO)$, for which the frequency is shifted from 20 cm^{-1} toward higher wavenumbers, and in the far infrared region. Indeed, the possibilities of coupling due to the planarity of the molecule—especially between metal–ligand vibrations—are strongly modified when the NiP_2 and $NiCO_2$ entities become perpendicular (see for example our previous studies[2a] on *trans*-$Mo(CO_2)_2(PMe_3)_4$ where the CO_2 moieties are perpendicular to the MoP_4 plane and on $Fe(CO_2)(PMe_3)_4$ where the equatorial plane $Fe(CO_2)P_2$ is similar to that of $Ni(CO_2)P_2$).

As the calculation does not lead to an important shift of the $\nu(CO)$ mode, it can be deduced that, even if a rotation occurs in the complex at the NMR time scale (see diagram IV in Results), this motion does not seem likely to be responsible for the existence of two $\nu(CO)$ modes in the infrared spectrum. We shall then discuss only results concerning the study of the planar forms of the side-on and end-on coordination modes.

2.3. Effects of the Coordination Mode. This calculation has been performed for both structures with the **same** valence force field. Table II summarizes the assignment of the wavenumbers calculated for such geometries. As expected with only **one** CO_2 moiety per molecule, only **one** $\nu(CO)$ mode has been found in each case. If we compare now the frequencies obtained, we can see that the $\nu(C{=}O)$ stretching mode is not modified, whereas, for the end-on geometry, $\nu(CO)$ is shifted towards lower wavenumbers from 57 cm^{-1}, which is actually the observed splitting for $\nu(CO)$ modes of $Ni(CO_2)(PCy_3)_2$. It then appears that the η^1-O coordination induces a lowering of the $\nu(CO)$ stretching mode. The calculated value of $\nu(NiO)$ is almost the same (414 instead of 420 cm^{-1} vs 418 cm^{-1} obsd) but the isotopic shift by $^{16}O/^{18}O$ labeling is divided by two. A careful examination of the spectrum in this area (see Figure 4) shows that there is, besides the band at 403 cm^{-1}, an additional weak band around 414 cm^{-1} on the spectrum of the ^{18}O-labeled compound that could be the $\nu(NiO)$ stretching mode of the end-on form. The uncertainty about the experimental isotopic shift of the $\nu(NiO)$ mode in the

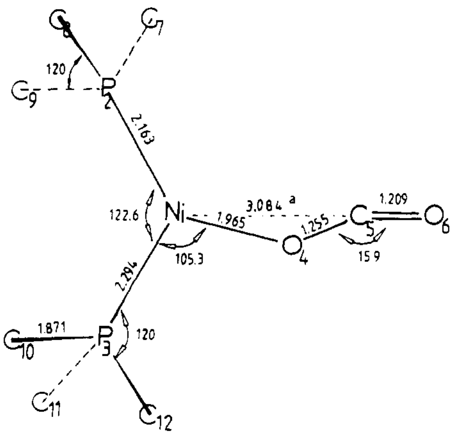


Figure 7. Schematic representation of the structure of $Ni(CO_2)(PCy_3)_2$ used to perform normal coordinate analysis for the end-on arrangement. (a = calculated value, with bond lengths in Å and angles in deg).

^{18}O-labeled compound (4 or 15 cm^{-1}) is found in the calculation, where the smallest shift (4.3 cm^{-1}) better fits the end-on form, whereas the greatest one (9.3 cm^{-1}) is associated with the side-on coordination mode.

Some other important changes occur in $\delta(OCO)$ and $\gamma(C{=}O)$ modes that are also shifted toward lower wavenumbers.

$\gamma(C{=}O)$ is calculated at 556 cm^{-1}, but $\tau(CO)$ (the equivalent mode in the end-on form) is found at 426 cm^{-1}. The isotopic shifts on $^{12}C/^{13}C$ labeling are also modified, and smaller shifts are found (12 cm^{-1} instead of 17 for the side-on form). As observed for experimental spectra, this region is obscured by other absorptions and the expected intensity of $\tau(CO)$ is very weak. So, the calculated value of $\tau(CO)$ might be accurate, but the observation of the spectra does not permit us to verify it. Nevertheless, $\tau(CO)$ can be obtained at the same frequency as $\gamma(C{=}O)$ by adjusting the related force constants (it does not induce modifications on other modes because $\tau(CO)$ and $\gamma(C{=}O)$ are the only ones belonging to the A″ symmetry class in the C_s point group). The force constant value, which is 0.64 mdyn $Å^{-1}$ rad^{-2} for the side-on form, becomes therefore 1.087 mdyn $Å^{-1}$ rad^{-2}. This is a rather high value for a torsion; $\tau(CO)$ is therefore more likely located at lower wavenumbers than $\gamma(C{=}O)$.

The problem is different for $\delta(OCO)$, where (*i*) the calculated value for the end-on form at 658 cm^{-1} is located in a clear part of the FTIR spectrum (we must keep in mind that the corresponding shift, 65 cm^{-1}, is of the same order of magnitude than those observed for the $\nu(CO)$ modes: 57 to 62 cm^{-1}, as $\nu(C\text{-}O)$ and $\delta(OCO)$ are mixed through an interaction force constant of 0.2 mdyn rad^{-1}), and (*ii*) the expected intensity for this mode is of the same order of magnitude as that observed for the corresponding $\nu(CO)$ vibration (i.e. medium weak). But no additional band is observed in this region in IR spectra. Two parameters allow us to obtain a $\delta(OCO)$ mode in the congested region 700–750 cm^{-1}.

(*i*) *The first is the increase of the OCO angle.* This leads to the decreasing of the interaction force constant $f[\nu(CO),\delta(OCO)]$. Without changing the Ni–O distance (i.e. 1.965 Å), this leads to the structure shown in Figure 7, where the Ni–C distance is now 3.084 Å and the OCO angle 159°.

(*ii*) *The second is the modification of the valence force constants for $\delta(OCO)$ and $\nu(CO)$.* As we did not clearly observe weak absorptions associated with the lower $\nu(CO)$ frequency, we could not perform any refinement procedure on a valence force field associated with the end-on form. Nevertheless, it seems clear that an end-on form should lead to a structure with a larger OCO angle (that means a less bent coordinated CO_2 due to less π-back-donation).

Table III. Valence Force Field for $Ni(CO_2)(PC_3)_2$ in a Planar Side-On Arrangement[a]

modes	force constants
$\nu(NiP)$	1.60
$\nu(NiO)$	0.95
$\nu(NiC)$	1.00
$\nu_s(PC_3)$	2.83
$\nu'_s(PC_3),\nu_a(PC_3)$	2.47
$\nu(C{=}O)$	10.00
$\nu(CO)$	6.20
$\delta(C{=}O)$	1.05
$\gamma(C{=}O)$	0.64
$\delta(NiCO),\delta(CNiO),\delta(CONi)$	0.25
$\delta(PNiP)$	0.34
$\delta(PNiC)$	0.28
$\delta(ONiP)$	0.30
$\delta_s(PC_3)$	0.57
$\delta'_s(PC_3),\delta_a(PC_3)$	0.64
$r_{\parallel}(PC_3), r_{\perp}(PC_3)$	0.46
$\tau(NiP),\tau(NiC),\tau(NiO)$	0.0005
$\gamma(NiP)$	0.01
$f[\nu(C{=}O),\nu(CO)]$	0.00
$f[\nu(CO),\delta(C{=}O)]$	0.20
$f[\nu(C{=}O),\delta(C{=}O)]$	0.40
$f[\nu(C{=}O),\delta(NiCO)]$	0.00
$f[\nu(CO),\delta(NiOC)]$	–0.30
$f[\delta(C{=}O),\nu(NiCO)]$	0.10
$f[\nu(C{=}O),\nu(NiC)]$	0.00
$f[\nu(NiP),\delta_s(PC_3)]$	–0.15
$f[\nu(NiP),\nu(NiP)]$	0.00

[a] Force constants are given in mdyn $Å^{-1}$ for bonds, mdyn $Å^{-1}$ rad^{-2} for angles and mdyn rad^{-1} for bond–angle interactions.

2.4. Results for the Side-on Coordination. Considering now the calculation for the planar side-on form, a good agreement between observed and calculated wavenumbers and isotopic shifts allows us to propose a relevant force field for this compound (see Table III). The final values obtained for the CO bonds, 10.0 and 6.2 mdyn $Å^{-1}$, are those encountered for CO bonds with double and single bond character.[13] These values are slightly higher than those obtained for the side-on complex *trans*-$Mo(CO_2)_2(PMe_3)_4$, for which $F[\nu(C{=}O)] = 9.6$ and $F[\nu(CO)] = 5.3$ mdyn $Å^{-1}$ were found. This result indicates that CO_2 is less strongly linked to the metal fragment in the nickel complex than in the molybdenum compound. The C=O bonds therefore most likely keep their "double bond" character, with less Π-back-donation. Actually, the nickel complex is less stable than the molybdenum compound, where reactivity occurs first on PMe_3 ligands instead of on the CO_2 moiety.

In fact, the potential energy distribution shows that the modes $\nu(C{=}O)$, $\nu(CO)$, and $\delta(OCO)$ are mixed even if a zero interaction force constant $f[\nu(C{=}O),\nu(CO)]$ allowed us to fit them. As for *trans*-$Mo(CO_2)_2(PMe_3)_4$, there is no important coupling between CO_2 and phosphine modes. Furthermore, we did not observe any coupling between $\delta(OCO)$ and $\nu_s(P_2C_3)$ vibrations, as for $Fe(CO_2)(PMe_3)_4$, because the frequency of $\nu_s(PC_3)$ is lower in this case (around 710 cm^{-1} in PCy_3 instead of 730 cm^{-1} for PMe_3). As a consequence, the largest $^{16}O/^{18}O$ isotopic shifts are observed at higher wavenumbers and CO_2 modes are quite pure. The adjustment of the $^{12}C/^{13}C$ isotopic shift of $\nu(CO)$ is not very good (23.4 cm^{-1} calculated for 15 observed), but must be compared to that of $\delta(OCO)$ which is calculated to be 6.5 cm^{-1}, instead of the 10 cm^{-1} observed. As these two motions are highly mixed, we must consider the total amount of isotopic shifts on both modes, which is well reproduced (29.9 cm^{-1} calculated vs 25 cm^{-1} observed).

The out-of-plane motion $\gamma(C{=}O)$ is well reproduced too at 556.5 cm^{-1} with a force constant (0.64 mdyn $Å^{-1}$ rad^{-2}) comparable to that of *trans*-$Mo(CO_2)_2(PMe_3)_4$ (0.68 mdyn $Å^{-1}$ rad^{-2}).

Metal-phosphorus force constants $F(NiP_2)$ and $F(NiP_3)$ have been calculated to be equal to 1.6 mdyn $Å^{-1}$, which is the value

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[13] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley Interscience: New York, 1986.

encountered in $Ni(PMe_3)_4$.[14] No difference has been found between the NiP_2 and NiP_3 bonds as no coupling occurs between $\nu(NiP_2)$ and $\delta(OCO)$. The $\nu(NiP_3)$ frequency is calculated at 398.8 cm^{-1} vs 395 cm^{-1} observed, and $\nu(NiP_2)$ is found mixed respectively with $\nu(NiO)$ at higher wavenumbers (420.1 cm^{-1} calculated vs 418 cm^{-1} observed) and with $\delta_s(PC_3)$ at lower wavenumbers (343.6 cm^{-1} vs 352 cm^{-1} observed). It is important to note now that, among the metal–CO_2 modes, only the stretching $\nu(NiO)$ has been found to be quite pure, whereas the $\nu(NiC)$ one is almost completely mixed with $\nu(NiP_3)$ at 398.8 cm^{-1} and with bending and rocking modes of phosphines, $\delta_s(PC_3)$ at 304.8 and $r(PC_3)$ at 200 cm^{-1}. Therefore, no band can be attributed to the $\nu(NiC)$ stretching in the spectrum, and actually, no $^{12}C/^{13}C$ isotopic shift has been experimentally observed. This situation has already been encountered in $Fe(CO_2)(PMe_3)_4$,[2a] where $\nu(NiC)$ has been found, mixed with other modes, at 399, 350, and 324 cm^{-1}. The force constants $F(NiC)$ and $F(NiO)$ are found to be respectively equal to 1.0 and 0.95 mdyn Å^{-1}, but $F(NiC)$ has not been refined due to lack of experimental data for rocking and bending modes of PC_3 in the far-infrared spectrum. Anyway, these values are those encountered in the side-on complex trans-$Mo(CO_2)_2(PMe_3)_4$.[2a]

Below 350 cm^{-1}, no band has been observed in the FTIR spectrum, so the calculation of the bending modes $\delta'_s(PC_3)$ and $\delta_s(PC_3)$ has been fitted with the Raman bands observed respectively at 272 and 235 cm^{-1}. Between 200 and 170 cm^{-1}, we find the rocking modes $r(PC_3)$; their refinement has not been performed because of the lack of experimental data below 200 cm^{-1}.

2.5. Conclusion. The vibrational study does not permit us to distinguish unambiguously between the two possibilities that could explain the presence of the $\nu(CO)$ diad in the FTIR spectrum of $Ni(CO_2)(PCy_3)_2$—(*i*) *a side-on complex with a Fermi resonance effect between* $\nu(CO)$ *and* $\delta(OCO) + \nu(NiO)$ *modes or* (*ii*) *the existence of two isomers, a side-on and an end-on one*—but allows us to exclude the possibility of a C-coordinated intermediate.

3. CAS–SCF Calculations. The occurrence of an η^1-O end-on structure in the fluxional behavior of $Ni(PCy_3)_2(CO_2)$ is in line with our recent theoretical findings on $Ni(NH_3)_2(CO_2)$: preliminary ab-initio CAS–SCF calculations—which we performed in the context of a study of the coupling between CO_2 and C_2H_4 mediated by bis(amine)nickel complexes—showed that the planar η^1-O end on structure has a strong diradical character and is only slightly destabilized with respect to the η^2 side-on ground-state structure.[15] Prompted by the above experimental results we decided therefore to investigate in more detail the fluxionality of $Ni(NH_3)_2(CO_2)$ and carried out ab initio CAS-SCF calculations[16] on structures **1–5** shown in Figure 8. In order to get a closer comparison with the experimental results, calculations were also carried out on the structures **1** and **4** of the bis(phosphine) system $Ni(PH_3)_2(CO_2)$. The CAS–SCF level of theory, which was required to include the near degeneracy correlation effects of these systems (and in particular the strong diradical character of the η^1 isomers)[15] was found to describe adequately this fluxionality. In particular further refinements made by including the dynamical correlation effects did not seem to be highly critical.[17]

The geometrical parameters were set according to related X-ray crystal structures and to other calculations.[20] For the structures **2–5**, where no crystal structure data were available, a partial optimization of the geometry of the Ni–CO_2 unit was carried out. This was also done at the CAS–SCF level, since bond lengths and bond angles of this unit, such as the O–C–O angle, may be sensitive

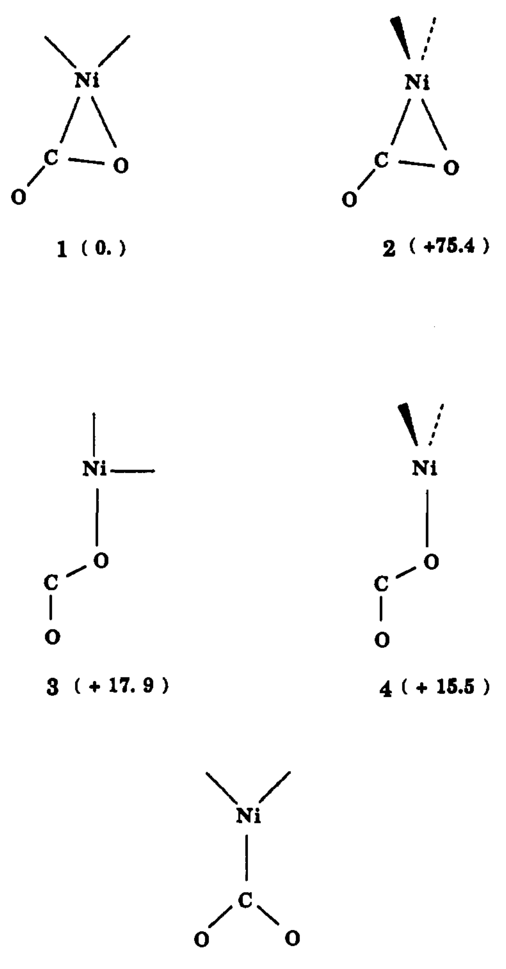

Figure 8. Side-on, end-on and C-coordinated structures of $Ni(NH_3)_2(CO_2)$ which have been studied theoretically (CAS-SCF relative energies—in kJ·mol^{-1}—are given in parentheses).

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(14) Loutellier, A.; Trabelsi, M.; Bigorgne, M. *J. Organomet. Chem.* **1977**, *133*, 20.

(15) Dedieu, A.; Ingold, F. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1694.

(16) (a) Roos, B: O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157. (b) Siegbahn, P. E. M.; Almlöf, J.; Heiberg, A.; Roos, B. O. *J. Chem. Phys.* **1981**, *74*, 2384. (c) Roos, B. O. *Int. J. Quantum. Chem. Symp.* **1980**, *14*, 175.

(17) CI calculations[18] carried out on both **1** and **3** increase the energy difference between these two isomers by 8 kJ·mol^{-1} only. Thus these effects do not seem to be crucial in this kind of conformational analysis.

(18) The CI calculations were multireference contracted CI calculation[19] using as references the configurations which were found to have an expansion coefficient greater than 0.05 in the CAS–SCF wave function. 10 electrons were correlated (the same as in the CAS–SCF wave function) and single and double excitations to all virtual valence orbitals were included.

(19) Siegbahn, P. E. M. *Int. J. Quant. Chem.* **1983**, *23*, 1869.

(20) The geometries were set as follows: in all structures the Ni–N bond of the $Ni(NH_3)_2$ moiety was set at 2.15 Å as in the previous SCF study of Sakaki et al.[21] The N–Ni–N angle was set at 90° in **2** and for the other structures two series of calculations were performed with N–Ni–N = 90 and 120°, respectively. Opening the N–Ni–N angle resulted in some stabilization, and we therefore report only the data corresponding to a N–Ni–N angle of 120° for **1**, **2**, **4**, and **5**. For **1**, the bond lengths of the Ni–CO_2 moiety were taken from the original X-ray crystal structure of $Ni(PCy_3)_2(CO_2)$:[3] Ni–C = 1.84 Å, Ni–O = 1.99 Å, and C–O = 1.22 and 1.17 Å for the bound and unbound C–O bonds, respectively. The CAS–SCF optimum value for the O–C–O angle was computed to be 140°, in fair agreement with the more recent X-ray crystal structure value of Dohring et al.[5] In **2** the same geometry of the Ni–CO_2 unit was used, without reoptimizing the O–C–O angle. This was justified by the fact that in **3** and **4** the O–C–O angle was optimized (at the CAS–SCF level) to 136.5 and 136.0°, respectively. Thus the same value of 136.5° was taken in **3** and **4**. The other geometrical parameters of the $Ni(CO_2)$ unit were also optimized in **4** (at the CAS SCF level) and the corresponding values kept for **3**. This yielded the following values: Ni–O = 2.026 Å; C–O = 1.271 and 1.220 Å for the bound and unbound C–O bonds, respectively; Ni-O-C = 137.0°. Interestingly the optimized Ni–O–C and O–C–O angles yield for the structure **4** a C=O bond parallel to the bisector line of the N–Ni–N angle; see Figure 8. In **5** the optimization of the Ni–CO_2 moiety at the CAS–SCF level yielded the following values: Ni–C = 2.024 Å, C–O = 1.247 Å, and O–C–O = 141°.

(21) Sakaki, S.; Kitaura, K.; Morokuma, K. *Inorg. Chem.* **1982**, *21*, 760.

to the correlation effects.[22] The relative CAS–SCF energies[23,24] obtained for **1**–**5** are given in Figure 8. It is clear from these values that the η^1-O end-on structure, either in its planar (**3**) or in its perpendicular (**4**) conformation is only slightly destabilized with respect to **1**. Another interesting feature is that, among the structures which would have two equivalent ligands in the NMR spectrum, the η^1 end-on structures **4** and **5** are significantly more stable than the perpendicular η^2 side-on structure **2**. Thus structure **2** can be safely discarded from the fluxional pattern. In contrast, on the basis of the calculations carried out for the bis(amine) complex, one cannot rule out the occurrence of the η^1-C structure **5**: this structure is computed to be only 5 kJ/mol above **4**. Yet, bis(phosphine) complexes may behave differently: the careful study of Sakaki et al. on the $Ni(PH_3)_2(CO_2)$ system[22] showed that the η^1-C structure of this model complex is not bound (the separated $Ni(PH_3)_2$ and CO_2 systems being 1.7 kJ/mol more stable). In addition the experimental results reported above exclude the possibility of this isomer. We have determined the CAS–SCF energy difference between **4** and **1**:[25] the computed value of 27.8 kJ/mol is in fairly good agreement with the experimental activation energy, thus giving further support to the occurrence, in the fluxional process, of **4** or of a structure close to it. At this point, one should note however that the geometry which has been optimized for the Ni–CO_2 unit does not correspond exactly to the "experimental" one, which is deduced from the IR measurements (see Figure 7). In particular the C═O bond does not lie along the bisector line of the N–Ni–N angle, but is parallel to it. Interestingly, in this optimized structure, the Ni–C distance amounts to 3.08 Å as in the structure of Figure 7. We have also computed a structure of the $Ni(NH_3)_2(CO_2)$ system with the parameters of the Ni–CO_2 unit taken from Figure 7. It is, from our calculations,[26] destabilized by 78.5 kJ/mol with respect to **4**. We ascribe this destabilization mostly to the deviation of the oxygen atom from the bisector of the N–Ni–N angle, since replacing the optimized C–O and Ni–C bond lengths by the "experimental" (i.e. 1.965, 1.209, and 1.255 Å) in **4** destabilized this structure by 1.6 kJ/mol only[27] (in this structure the value for the Ni–C distance is 3.01 Å, thus again close to the "experimental" value).

Conclusion

As molecular rearrangements usually take much longer than the vibrational spectroscopy time scale,[28] IR spectra give information on the ground state of molecules which are nonrigid on the NMR time scale. Superposition of different forms can be found if there is exchange between isomers, and spectra give thermodynamic information on the relative population of each potential well at a given temperature and the energy difference between the minima. Coalescence is rarely observed in IR experiments, whereas NMR coalescence data give kinetic information about exchange rates and barrier heights between these minima.

Therefore, two interpretations arise from this study, comparing vibrational, NMR, and theoretical results.

(1) $Ni(CO_2)(PCy_3)_2$ exists only in a side-on form in the solid state, and the ν(CO) diad is due to a Fermi resonance effect. Complete assignment of vibrational spectra and valence force-field are now available. In solution, a probable motion could be, by analogy to that observed in *trans*-$Mo(CO_2)_2(PMe_3)_4$ by Carmona[9b,29] and suggested by Hoffmann[30] in $Ni(CO_2)(PH_3)_2$, a rotation of the CO_2 moiety around the axis passing through the metal and the coordinated CO bond. Nevertheless, an important difference between $Ni(CO_2)(PCy_3)_2$ and $Mo(CO_2)_2(PMe_3)_4$ is that the latter is rather stable and that concerted rotation of the CO_2 moieties is obtained by heating a solution of the complex up to 60 °C. The ^{13}C-labeled compound chemical shift is around 200 ppm and no solid-state NMR data are available. In addition, the barriers of rotation which have been computed either in $Ni(CO_2)(PH_3)_2$ (63 kJ·mol^{-1} at the EH level[30] or in $Ni(CO_2)(NH_3)_2$ (75.4 kJ·mol^{-1}, this work) are appreciably higher than experimental value of 39 kJ·mol^{-1} measured for $Ni(CO_2)(PCy_3)_2$. The difference in the ligands (the more bulky PCy_3 ligands instead of PH_3 or NH_3) may account for this feature; however it seems more probable that the rotation of the CO_2 moiety implies an η^1-O coordination, the η^1-C one being ruled out by the vibrational study.

(2) $Ni(CO_2)(PCy_3)_2$ has two conformers: a side-on and an end-on one, the latter being much less stable as shown by relative intensities of the infrared bands ν(CO). In fact, even if the final structure is side-on in CO_2 complexes, the energetically accessible reaction path starts from the end-on structure.[31] The relatively weak destabilization of the planar end-on structure of the bis(amine) complex and the fact that for the non-planar conformer the end-on structure **4** is more stable than the side-on structure **2** by about 60 kJ·mol^{-1} lead us to propose that the planar conformation exists with both a side-on and an end-on coordination mode and that the rotation of the CO_2 moiety implies only an end-on intermediate. The existence of such an "end-on" form could explain the low value of the ^{13}C chemical shift observed both at solid state and in solution. It could also deal with the reactivity of this complex with both an electrophilic terminal oxygen and a nucleophilic carbon.[4b]

Concerning the apparent contradiction between X-ray and spectroscopic analysis, it must be kept in mind that, even if the diffraction pattern represents an average of all possible atomic motions that occur in the crystal, the structure determined is necessarily a representation of the molecule captured in its most stable ground state form (i.e. side-on coordinated). For example, some bis(phosphine)(arene)nickel complexes have also shown such fluxional behavior.[32] Furthermore, a paper appeared on the coordination mode of SO_2 in $Ni(SO_2)(PCy_3)_2$,[33] investigated by means of IR and ^{31}P NMR spectroscopies. Similar fluxionality

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(22) Sakaki, S.; Koga, N.; Morokuma, K. *Inorg. Chem.* **1990**, *29*, 3110.

(23) The active space of the CAS–SCF calculations was made of six active orbitals populated by eight electrons. This space was chosen in order to account for the main bonding interactions as well as for the sd hybridization features. It was also designed to be as coherent as possible for the five structures under investigation. The active orbitals for the structures **1**–**5** were therefore as follows (given the choice of axes shown on the Figure 8): for **1** and **5**, $3d_{z^2}$, $3d_{x^2-y^2}$, $\pi(CO_2)$, $n\pi(CO_2)$, $\pi^*(CO_2)$, and 4s (mixed with $4d_{z^2}$); for **2**, $3d_{z^2}$ (with some $n\pi(CO_2)$ contribution), $3d_{xy}$, $3d_{yz}$, $\pi(CO_2)$, $\pi^*(CO_2)$, and $4d_{yz}$. Note here that starting the calculation with $3d_{xz}/4d_{xz}$ pair of orbitals in order to achieve a better coherency with the other calculations led invariably, through mixing with $3d_{yz}$ and $4d_{yz}$, to a converged wave function having mostly $3d_{yz}/4d_{yz}$ in the set of active orbitals. However the d_{yz} orbitals are not pure and retain some d_{xz} character: for **3** the active orbitals were $3d_{z^2}$, $3d_{xy}$, $\pi(CO_2)$, $n\pi(CO_2)$, $\pi^*(CO_2)$, 4s (mixed with $4d_{z^2}$); for **4** they were $3d_{x^2}$, $3d_{y^2-z^2}$, $\pi(CO_2)$, $n\pi(CO_2)$, $\pi^*(CO_2)$, and 4s (mixed with $4d_{x^2}$).

(24) The corresponding CAS–SCF total energies are as follows: **1**, −1803.7192 au; **2**, −1803.6905 au; **3**, −1803.7124 au; **4**, −1803.7133 au; **5**, −1803.7114 au (1 au = 2625.5 kJ·mol^{-1}).

(25) The geometries used for the $Ni(PH_3)_2(CO_2)$ system were the same as for the $Ni(NH_3)_2(CO_2)$ system except for the phosphine ligands for which the following parameters were used: Ni–P = 2.199 Å, P–H = 1.42 Å, and Ni–P–H = 122.8511°. The total energies, which were computed for the $Ni(PH_3)_2(CO_2) + C_2H_4$ system (again in the context of the $CO_2 + C_2H_4$ coupling reaction), with a noninteracting C_2H_4 at 50 Å distance from the Ni atom, were the following: **1** + C_2H_4, 2453.4012 au; **4** + C_2H_4, 2453.3906 au.

(26) The CAS–SCF total energy is −1803.6834 au.

(27) The CAS–SCF total energy is −1803.7127 au.

(28) Braga, D. *Chem. Rev.* **1992**, *92*, 633.

(29) (a) Carmona, E. *J. Organomet. Chem.* **1988**, *358*, 283. (b) Carmona, E.; Munoz, M. A.; Perez, P. J.; Poveda, M. L. *Organometallics* **1990**, *9*, 1337.

(30) Mealli, C.; Hoffmann, R.; Stockis, A. *Inorg. Chem.* **1984**, *23*, 56.

(31) Sakaki, S. *Stereochemistry of Organometallic and Inorganic Compounds 4*; Elsevier Science Pub.: Amsterdam, 1990.

(32) Benn, R.; Mynott, R.; Topalovic, I.; Scott, F. *Organometallics* **1989**, *8*, 2299.

(33) Hoffmann, T.; Ziemer, B.; Mügge, C.; Bertholdt, U.; Wenschuh, E.; Leibnitz, P. *Z. Anorg. Allg. Chem.* **1991**, *600*, 55.

process was observed but X-ray determination could not confirm the η^2-S,O or η^1-S coordination mode.

It then appears that significant new insights can be obtained, even into previously supposed well-known complexes, when several spectroscopic techniques (FTIR, NMR) are focused onto a single dynamic problem: the existence of an end-on form for the $Ni(CO_2)(PCy_3)_2$ complex seems highly probable from both spectroscopic and theoretical points of view, even if the exact geometry cannot be precisely assessed. Finally, this study illustrates nicely the interplay that can exist between theory and experiment in the field of mechanistic investigations of carbon dioxide activation and reactivity.

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