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A Bonding–Reactivity Relationship for $Ni(PCy_3)_2(CO_2)$: A Comparative Solid-State–Solution Nuclear Magnetic Resonance Study (^{31}P, ^{13}C) as a Diagnostic Tool To Determine the Mode of Bonding of CO_2 to a Metal Center

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^{31}P and ^{13}C nuclear magnetic resonance spectra in the solid state and in solution, at variable temperature, have been used for the first time to determine a direct correlation of the modes of bonding of CO_2 in $Ni(PCy_3)_2(CO_2)$ in the two states. In solution, at 173 K, CO_2 is η^2-CO bonded to nickel and ^{31}P and ^{13}C chemical shifts are almost identical with the value found for the solid complex, while a dynamic process averages, in solution, the two phosphorus atoms ($\Delta G^{\ddagger} = 39.3$ kJ mol^{-1}) at room temperature through an intramolecular motion. The modification of the mode of bonding of CO_2 to a metal center that occurs when a solid sample is dissolved in a solvent may be relevant to the reactivity of CO_2–transition metal complexes, as shown by the reaction of coordinated CO_2 with electrophiles (H^+, Ag^+) and H_2. The temperature can play an important role.

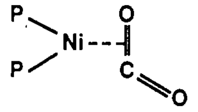
Introduction

The determination of the mode of bonding of carbon dioxide coordinated to metal centers has received considerable attention in the recent past for, among other areas of interest, its relevance to CO_2 reactivity. X-ray diffraction studies have been of great utility in determining how CO_2 is anchored to a metal center in the solid state. This technique has permitted the η^2-CO,[1] η^1-C,[2] μ_2-η^3-CO_2,[3] μ_3-η^3-CO_2,[4] and μ_4-η^3-CO_2[5] modes of bonding to be ascertained. Nevertheless, these data do not furnish information on the reactivity of coordinated CO_2 in solution, as it is questionable whether the metal–CO_2 system maintains the same configuration when dissolved in a solvent.

Quite recently, infrared spectroscopy was demonstrated to be a helpful tool for structure correlation, but since this requires the complete assignment of the vibrations and an analysis of the spectrum structure at variable temperature,[6] it proves to be a quite time-consuming technique.

Several nuclear magnetic resonance studies of CO_2–metal complexes, in solution, are available in the literature. However, most of them give only the value of the ^{13}C resonance of the coordinated CO_2.[1b,d,3,4c,7] Very seldom have more detailed NMR analyses been developed and has information on the fluxionality of CO_2 been obtained.[8] Furthermore, all these investigations were confined to the solution and made no attempt to extend the study to the solid state.

Therefore, it was decided to explore the utilization of solid-state and solution NMR to clarify how the bonding of carbon dioxide to transition metal systems is modified upon dissolution in a solvent. In principle, this approach should furnish precious information in all those cases in which the molecular formula of the compound is such as to permit the use of ^{13}C NMR data in conjunction with those of a second NMR-active heteronucleus. Phosphanes, present as ancillary ligands in several CO_2 complexes, are of great help. We present here the results of our studies on $Ni(PCy_3)_2(CO_2)$, whose solid-state structure is known for both the toluene-solvated[1a] and nonsolvated forms.[9] The nickel atom lies in both cases in a square planar environment defined by the two phosphorus atoms, the carbon atom, and one of the oxygen atoms of the η^2-bonded CO_2:



In addition, we discuss the reactivity of the coordinated CO_2 in relation to the reaction conditions. A satisfactory reactivity–structure correlation has been found.

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Experimental Section

General Procedures. Unless otherwise stated, all reactions and manipulations were conducted under a dinitrogen atmosphere by using vacuum-line techniques. All solvents were dried as described in the literature and stored under dinitrogen. CO_2 ($\geq$99.95%) and H_2 ($\geq$99.999%) were from SIO SpA, carbon-13 dioxide (99% ^{13}C) was from CIL, and AgO_3SCF_3 was an Aldrich product.

IR spectra were obtained with a Perkin-Elmer 883 spectrophotometer.

^{13}C NMR spectra were recorded on a Varian XL-200 instrument operating at 50.5 MHz. ^{31}P NMR spectra were obtained at 109.3 MHz using a JEOL GX 270/89 spectrometer and at 81 MHz with a Varian XL-200 instrument. ^{13}C and ^{31}P chemical shifts were referred to tetramethylsilane (TMS) and 85% H_3PO_4, respectively, using the high-frequency–positive convention.

High-resolution solid-state ^{13}C and ^{31}P NMR spectra were recorded on a JEOL GX 270/89 equipped with a solid-state accessory. Samples were placed in a Delrin rotor (10-mm external diameter) and spun up to 3.5–4.0 kHz by compressed air. Both cross-polarization and single-pulse excitation were performed for the ^{13}C spectra. The ^{31}P spectra were obtained under CPMAS conditions. Quadrature-phase cycling was employed at all times, and in the CP experiments flip-back was used. Chemical shifts in the case of ^{13}C were referenced to external liquid TMS via the secondary reference of the rotor material (Delrin) assumed to be 88.7 ppm. ^{31}P chemical shifts in the solid state were obtained by the replacement of the solid sample with a sample of 85% H_3PO_4. Centerbands were located by varying the spinning speed which was, however, kept deliberately low in some cases in order to observe clearly the larger spinning sideband manifold. The digitized spectra consist of intensities of the individual resonances with a Lorentian shape assumed for each line. Spinning sideband manifolds were analyzed using an iterative computer as previously reported.[10]

The reaction of $Ni(PCy_3)_2(CO_2)$ with Broensted acids was performed as described elsewhere.[7f]

Preparation of $Ni(PCy_3)_2(^{13}CO_2)$. A filtered solution of $[(PCy_3)_2Ni]_2N_2$[1a,7f] (0.200 g, 0.16 mmol) in toluene (20 mL) was allowed to react with 99% $^{13}CO_2$ at 250 K. The orange crystals that separated were filtered off, washed with cold (250 K) toluene, and dried in a CO_2 flow. Anal. Calcd for $C_{37}H_{66}O_2P_2Ni$: C, 67.01; H, 10.00; Ni, 8.83; P, 9.33. Found: C, 67.10; H, 10.07; Ni, 8.73; P, 9.27.

Reaction of $Ni(PCy_3)_2(CO_2)$ with H_2. (a) $Ni(PCy_3)_2(CO_2)$ (0.200 g, 0.3 mmol) was dissolved in toluene (10 mL), and the solution was exposed to 0.103 MPa of H_2 and stirred at room temperature for 12 h. The original orange color disappeared. The solvent was evaporated in vacuo, and the yellow solid, $(H)Ni(PCy_3)_2O(O)CH$,[11] was isolated, washed with cold toluene, and dried in vacuo (0.120 g, 60% yield). IR (Nujol): 1931 [ν(Ni—H)], 1619 [ν(C=O)], 1311 cm^{-1} [ν(C—O)]. ^1H NMR (C_6D_6): δ −27.6 (hydride H), 8.90 (formyl H). Anal. Calcd for $C_{37}H_{68}O_2P_2Ni$: C, 66.70; H, 10.30; Ni, 8.81; P, 9.30. Found: C, 66.75; H, 10.40; Ni, 8.72; P, 9.27.

(b) A similar reaction was performed at 200 K. No change was observed after 24 h using NMR and IR techniques.

Reaction of $Ni(PCy_3)_2(CO_2)$ with AgO_3SCF_3. (a) A 0.200-g sample (0.3 mmol) of $Ni(PCy_3)_2(CO_2)$ was dissolved in THF-d_8 at 250 K under dinitrogen in an NMR tube, and the stoichiometric amount of AgO_3SCF_3 (in THF) was added. The orange solution darkened, and the ^{13}C spectrum was recorded at 250 K. ^{13}C NMR (THF-d_8, 250 K): δ 174.33 (oxalate carbons).

After warming of the reaction mixture to room temperature (293 K), the spectrum was recorded at 300 K. The appearance of other signals was observed. ^{13}C NMR (THF-d_8, 300 K): δ 234.14, 231.89, 216.07, 201.59 (attributed to carbonyl species), 174.33.

(b) A 0.300-g sample (0.45 mmol) of $Ni(PCy_3)_2(CO_2)$ was dissolved in toluene (20 mL), and the stoichiometric amount of AgO_3SCF_3 (0.231 g, 0.90 mmol) was added at 250 K. The precipitate formed was filtered off, washed with pentane, and dried in vacuo. It analyzed for $(COOAg)_2$, 40% yield. IR (Nujol): 1710 cm^{-1} [ν(C=O)], shifted to 1660 cm^{-1} upon ^{13}C labeling.

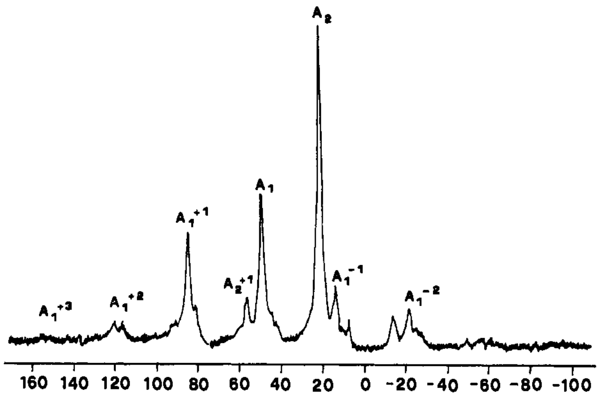

Figure 1. High-resolution solid-state CPMAS ^{31}P NMR spectrum of $Ni(PCy_3)_2(^{13}CO_2)$. The isotropic peaks are denoted as A_1 and A_2.

Results and Discussion

Fluxional Behavior of $Ni(PCy_3)_2(CO_2)$ in Solution. The $^{13}C\{^1H\}$ (50.5 MHz) and $^{31}P\{^1H\}$ (81 MHz) NMR spectra (298 K, $P_{^{13}CO_2} = 0.1$ MPa) of $Ni(PCy_3)_2(^{13}CO_2)$ in C_6D_6/C_7H_8 (1:3 v/v) show, respectively, a triplet at 158.61 ppm ($J_{C-P} = 14.6$ Hz)[7f] and a singlet at 36.15 ppm (see also ref 8a). These features are not those expected for an η^2-CO rigid structure.

The value of the ^{13}C resonance is unique for CO_2 complexes, as it has usually been found around 200 ppm in other metal systems[1b,d,3,4c,7,8] also containing the CO_2 moiety bonded in an η^2-CO mode[1b,d,8b] [the ^{13}C resonance for free CO_2 is encountered at 124.84 ppm in C_6D_6/C_7H_8 (1:3 v/v) at 298 K]. The 160 ppm region is typical for formates,[11] carboxylates,[12] carbamates,[13] and carbonates and hydrogen carbonates.[14] As coordinated CO_2 may very easily either react with water and dioxygen or disproportionate, affording carbonate and carbon monoxide, the unusual chemical shift for the $^{13}CO_2$ signal might leave some doubt concerning the nature of the species in solution. The data reported in this work, however, clearly show that the species in solution is a carbon dioxide complex and provide information on the mode of bonding of CO_2 to the Ni fragment in solution. Moreover, the multiplicity of the coordinated CO_2 ^{13}C resonance and the signal for the phosphorus atoms of the two ligands do not agree with the solid-state structure of $Ni(PCy_3)_2(CO_2)$.

In principle, two different explanations are possible in order to rationalize the structure of the ^{13}C and ^{31}P NMR signals: (a) a change of the mode of bonding of CO_2 to the metal center from η^2-CO to η^1-C or η^1-O coordination; (b) fluxional behavior which makes the two phosphine ligands equivalent.

To increase our knowledge of the Ni system, we studied the high-resolution solid-state ^{31}P and ^{13}C NMR spectra under cross-polarization magic angle spinning conditions (Figure 1 and 2, respectively). To our knowledge, this study represents the first solid-state NMR investigation of a CO_2 molecule coordinated to a metal atom.

The solid-state ^{31}P NMR spectrum shows two main peaks centered at 48.9 and 20.9 ppm, respectively, as expected for a square planar arrangement of ligands around the Ni atom. Each of the peaks presents a different manifold of spinning sidebands, and we were able to determine the position of the central peaks by acquisition of the NMR data at different spinning speeds. The spinning sideband manifolds arise because the rates of rotation available under magic angle conditions are not sufficient to completely remove shift anisotropy associated with the external magnetic field. The intensity of the spinning sidebands, spaced about the central resonance of integral multiples of the spinning speed, can be used for the determination of the chemical shift

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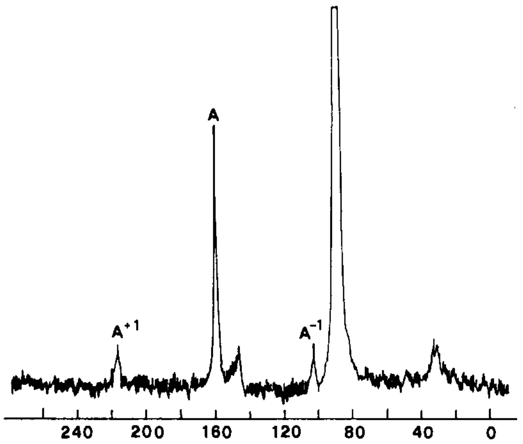

Figure 2. High-resolution solid-state CPMAS ^{13}C NMR spectrum of $Ni(PCy_3)_2(^{13}CO_2)$. The isotropic peak is denoted as A.

tensor components.[15] The chemical shift anisotropy appears to be larger for the signal at 48.9 ppm than for the peak centered at 20.9 ppm. For the former signal, we found a chemical shift anisotropy of 135 ppm, differing greatly from the value of 90 ppm found for the other phosphorus atom. Although there are relatively few CSA data in the literature for M–phosphine derivatives,[16,17] we can postulate that the different values of the chemical shifts and chemical shift anisotropies for the phosphorus atoms depend on the asymmetric interaction of the CO_2 in the η^2-coordination that poses the carbon atom and one of the two oxygen atoms trans to phosphorus.

The CPMAS ^{13}C NMR of a $^{13}CO_2$-enriched sample of $Ni(PCy_3)_2(^{13}CO_2)$ shows the peak of carbon dioxide at 159.28 ppm with a chemical shift anisotropy that can be estimated to be of the order of 100 ppm. This value should be compared with the value found in solution at low temperature (173 K, 159.88 ppm) and that found at room temperature (158.12 ppm) (see below). This confirms, thus, the substantial identity between the solid-state and solution structure for the $Ni–CO_2$ complex and strongly suggests that a fluxional process is responsible for the equivalence of the two phosphine ligands. It would be of interest to ascertain whether the large ^{13}C chemical shift difference found for various $M–CO_2$ complexes is due to the different nature of the metal fragments to which CO_2 is bound or whether it is, rather, related to some change in the coordination of the heterocumulene in solution. Therefore, studies on solid-state–solution structure correlations would help to set unambiguous criteria for correlating the coordinated CO_2 ^{13}C chemical shift to the coordination mode of the heterocumulene.

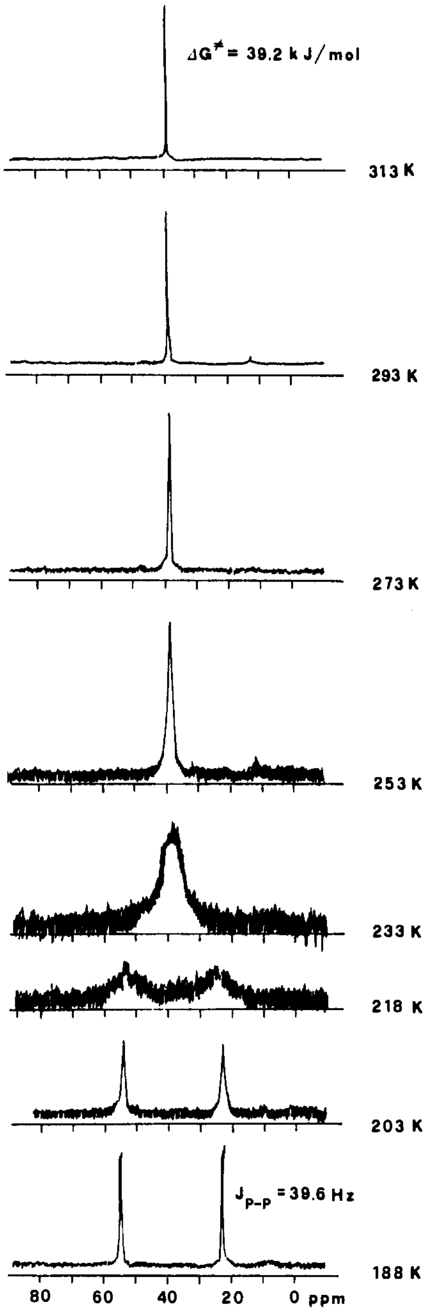

Figure 3. VT $^{31}P\{^1H\}$ NMR (109.3 MHz, C_7D_8) spectra of $Ni(PCy_3)_2(CO_2)$.

In order to demonstrate the fluxionality of $Ni(PCy_3)_2(CO_2)$ in solution and to obtain more information on the nature of the dynamic process, we examined the VT $^{31}P\{^1H\}$ (109.3 MHz) and $^{13}C\{^1H\}$ (50.5 MHz) NMR of $Ni(PCy_3)_2(CO_2)$ in the range 170–313 K (C_7D_8). The ^{31}P low-temperature limiting spectrum at 188 K reveals the presence of two doublets ($^2J_{P-P}$ = 39.6 Hz) at 51.7 and 20.2 ppm, respectively, which agree well with the values observed in the solid state. As the temperature is raised, the two doublets broaden and coalesce (233 K, coalescence temperature) in a single peak at 36.4 ppm (Figure 3) with an estimated value for the free activation energy of the dynamic process (at the coalescence temperature) of 39.3 kJ mol^{-1}.[18] The ^{13}C low-temperature limiting spectrum at 173 K (THF-d_8) of a $^{13}CO_2$-enriched sample of $Ni(PCy_3)_2(CO_2)$ shows a doublet of doublets centered at 159.88 ppm with $^2J_{P-C}$ = 41 Hz and $^2J_{P-C}$ = −10 Hz, respectively [Figure 4 (bottom)]. As the temperature is raised, the CO_2 signal broadens and merges as a triplet (158.12 ppm) at 253 K ($^2J_{P-C}$ = 14.1 Hz) [Figure 4 (top)]. The triplet structure for the coordinated CO_2 ^{13}C resonance, in the fast-exchange regime, allows us to rule out the hypothesis that equilibration of phosphine ligands involves a fast CO_2 decoordination–recoordination mechanism. In fact, if this were the case, spin correlations would be lost and no P–C coupling would be observed in the ^{13}C NMR spectrum, measured under conditions of fast exchange.[19] Therefore, the averaging of phosphine ligand ^{31}P resonances should involve an intramolecular process. The following mechanisms can be envisaged (Scheme I): (i) fast rotation around the Ni–η^2-CO bond; (ii) interconversion of the two equivalent conformations A and B through an η^1-C intermediate; (iii) intercon-

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[18] This value agrees well with that found by Ibers and Mason.[8a]

[19] CO_2 decoordination to generate the "NiP_2" moiety may occur in solution at room temperature, but very slowly on the NMR time scale. This is confirmed by the fact that a toluene solution of $Ni(PCy_3)_2(CO_2)$, equilibrated at room temperature under a dinitrogen atmosphere, shows a band at 2340 cm^{-1} due to free CO_2.

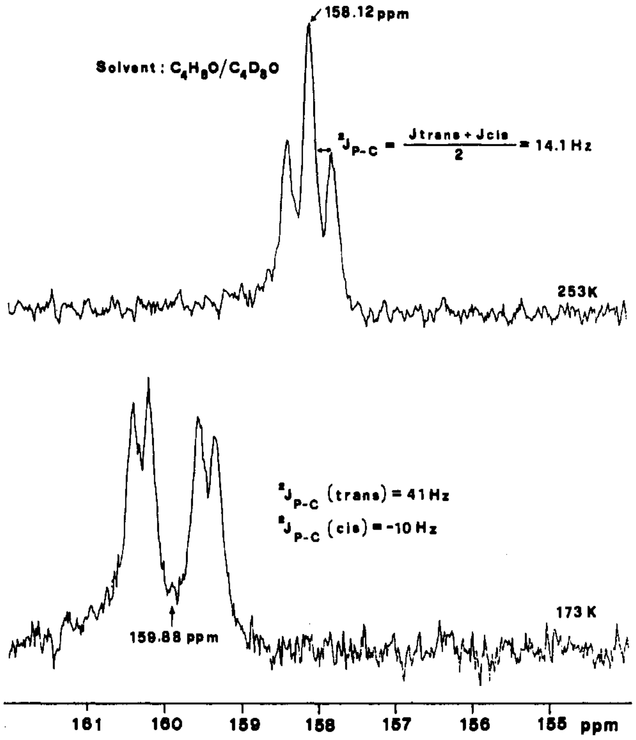
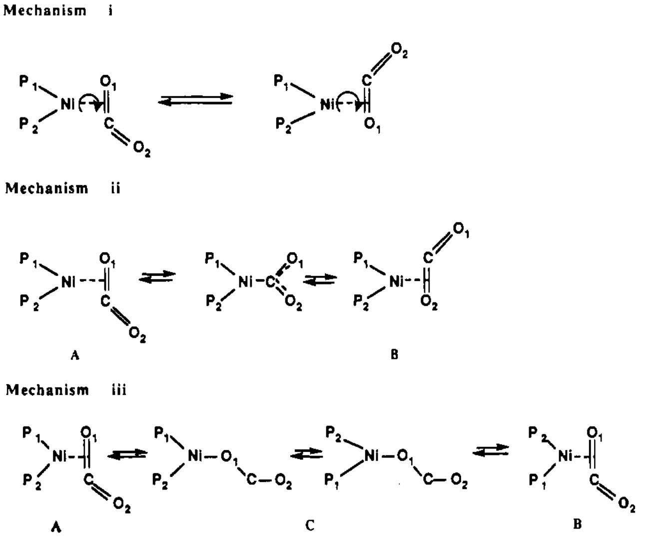


Figure 4. Bottom: Limiting $^{13}C\{^1H\}$ NMR (50.5 MHz, THF-d_8) spectrum of $Ni(PCy_3)_2(^{13}CO_2)$ at 173 K. Top: $^{13}C\{^1H\}$ NMR (50.5 MHz, THF-d_8) spectrum of $Ni(PCy_3)_2(^{13}CO_2)$ at 253 K.

Scheme I. Proposed Mechanisms for the Equilibration of P Ligands in $Ni(PCy_3)_2(CO_2)$[a]



[a] Mechanism i: equilibration of P ligands through fast rotation around the Ni–η^2-CO bond. Mechanism ii: equilibration of P ligands through formation of an η^1-C intermediate. Mechanism iii: equilibration of P ligands through formation of an η^1-O intermediate.

version of the two equivalent conformations A and B through an η^1-O intermediate (C). It is worth noting that mechanism ii implies the equilibration of oxygen atoms in addition to phosphine ligands. Unfortunately, ^{17}O NMR investigation was unsuccessful in differentiating mode ii from modes i and iii, probably owing to the large width of oxygen atom resonances. However, a differentiation among modes i–iii might be possible on the basis of the relevant internal motion energy barrier. Calculated values for the species $Ni(NH_3)_2(CO_2)$ are 85.7, 195.8, and 35.7 kJ mol^{-1}, for modes i–iii, respectively.[20] Exchanging NH_3 for PH_3 ligands is reported to reduce the energy barrier relative to mechanisms i and ii (63[21] and 134 kJ mol^{-1},[22] respectively). However, an ab initio calculation approach suggests that ΔG^* relative to mechanism iii shows a substantially identical value in model compounds $Ni(NH_3)_2(CO_2)$ and $Ni(PH_3)_2(CO_2)$.[23] These data combined with the experimental data apparently point to mechanism iii as the most likely. Further support arises from the IR spectrum of $Ni(PCy_3)_2(CO_2)$ in solution, which shows one ν(C=O) and two ν(C—O) stretching vibrations.[1a,24]

On the basis of these results we propose that, in solution at 173 K, CO_2 is tightly bonded to Ni in an η^2-CO mode, as already ascertained for the solid state. At room temperature, the complex is fluxional with a fast process averaging the two P atoms and loosening the Ni–C bond. The data we have in our hands seem to point to process iii, although the limiting form η^1-O has not yet been detected and characterized, because of either its short lifetime or its low concentration, and this does not allow us to exclude definitely other reaction mechanisms.

Solution Structure versus Reactivity for $Ni(PCy_3)_2(CO_2)$. Very interestingly, we have found that the reaction of $Ni(PCy_3)_2(CO_2)$ with Broensted acids is dependent on the temperature and the nature of the acid. At a low temperature (200 K), the reaction of $Ni(PCy_3)_2(CO_2)$ with Broensted acids (H_2S, PhSH) leads to the protonation of the bound CO_2 and affords bound CO very selectivity (100%), through the formation of [Ni–COOH] species.[7f] The peculiar capability of Ni to catalyze a very selective $CO_2 \rightarrow CO$ conversion under protonating conditions is also confirmed by results obtained using $Ni(cyclam)^{2+}$ as catalyst in electrochemical reduction.[25] The addition of HX (X = Cl, Br, I) to $Ni(PCy_3)_2(CO_2)$ affords bound CO with a yield decreasing with the temperature: $P_2NiH(X)$ is formed with the elimination of CO_2 as the preferential process at room temperature. This result agrees very well with the fact that at low temperature CO_2 is strongly bound to Ni, while at room temperature the adduct is destabilized and the decoordination of CO_2 is a very easy step. These data also suggest that η^2-CO bound CO_2 behaves as good O-nucleophile and can be easily protonated.

Such CO_2 to CO reduction is closely related to the reaction promoted by the enzyme carbon monoxide dehydrogenase (CODH), found in methanogenic bacteria, that catalyzes the reduction of CO_2 to bound CO using active hydrogen [H]. The active center of the enzyme is assumed to be a Ni atom. In order to ascertain whether molecular hydrogen can also afford such a CO_2 reduction to CO, we have studied the reaction of $Ni(PCy_3)_2(CO_2)$ with H_2 under various conditions. We have found that $Ni(CO_2)(PCy_3)_2$ reacts at room temperature with H_2 to afford the hydrido formate species *trans*-$(H)Ni(PCy_3)_2O(O)CH$[11] (see Experimental Section).

This reaction could involve, as a preliminary step, CO_2 decoordination, followed by H_2 oxidative addition to Ni, to give a "$Ni(H)_2$" intermediate,[11] which could then undergo CO_2 insertion into one of the Ni–H bonds to afford $(H)Ni(PCy_3)_2O(O)CH$. Alternatively, the reaction of $Ni(PCy_3)_2(CO_2)$ with H_2 can also be explained in terms of H_2 homolytic or heterolytic cleavage promoted by the η^1-O intermediate (C) (Chart I, pathway a or b), in which the Ni-C bond is loosened. The ^{31}P NMR spectrum of the solution of $Ni(PCy_3)_2(CO_2)$ under H_2 and our experimental conditions does not show the appearance of signals that may suggest that the formation of the Ni–hydrido complexes is the preferential reaction pathway. It is worth noting that the mechanism involving homolytic splitting of dihydrogen seems to be

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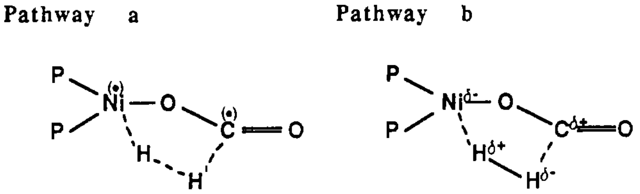
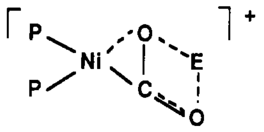
Chart I. Homolytic (Pathway a) or Heterolytic (Pathway b) Addition of H_2 to $Ni(PCy_3)_2(CO_2)$


Pathway a Pathway b

consistent with the results of theoretical calculations,[20] performed for the model compound $Ni(NH_3)_2(CO_2)$, which point to a strong diradical character for this species in the η^1-O form (see intermediate C).

However, whichever of the hypothesized mechanisms may be the correct one, it is of interest to note that $Ni(PCy_3)_2(CO_2)$ does not react readily with H_2 at 200 K. This can be explained by assuming that the formation of formate from $Ni(PCy_3)_2(CO_2)$ and H_2 requires that the C–Ni bond be loosened so that the C atom can present a higher reactivity than it does when it interacts tightly with the metal atom. Moreover, it is worthwhile noting that, under the conditions affording formate, we have observed neither Ni–carbonyl species nor free CO. These results seem to confirm that the interaction of bound CO_2 with an electrophile may lead to the generation of CO, while the formation of formate would require a carbon atom which, not being strongly bonded to the metal center, is ready to react with H atoms or hydride ions.

Of interest is the reaction of $Ni(PCy_3)_2(CO_2)$ with silver triflate, AgO_3SCF_3. According to the reaction conditions, this species behaves as an electrophile toward the oxygen atoms of coordinated CO_2 (250 K) or can oxidize the formal Ni(0) to Ni(II), affording $Ni(PCy_3)_2(O_3SCF_3)_2$. When the reaction is carried out at 250 K, the formation of silver oxalate is observed. This species is scarcely soluble in the organic solvents we used. Nevertheless, if the reaction is carried out in an NMR tube, the signal of the oxalate can be observed at 174.33 ppm. Warming the system causes the appearance of several signals around 200 ppm due to the formation of carbonyl species with loss in selectivity. This feature is very intriguing, as in the electrochemical reduction of CO_2 oxalates are observed only when metal cations are available in the reaction medium but are not observed if protons are the only electrophile species.[25,26] In our reaction conditions it seems likely that an intermediate of the type (where E is Ag^+) can undergo a homolytic Ni–C splitting reaction, affording the radical •COOAg, which can dimerize to afford the oxalate. Conversely, protons might more easily undergo a double-addition reaction to afford CO and water.



Conclusions

In conclusion, coupling solid-state with solution NMR studies, it is possible to gain insight into the behavior of CO_2–transition metal complexes in solution that can help to explain the mode of bonding of CO_2 to a metal center in solution.

On the basis of our studies, we can affirm that in solution at 173 K CO_2 in $Ni(PCy_3)_2(CO_2)$ is bound to nickel in an η^2-CO mode, while at room temperature the CO_2 molecule is fluxional.

The dynamic process is intramolecular and might involve a progressive disanchorage of the carbon atom from Ni to afford an η^1-O intermediate. This behavior is relevant to the understanding of the reactivity of $Ni(PCy_3)_2(CO_2)$ toward dihydrogen, Broensted acids, and AgO_3SCF_3.

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Registry No. $Ni(PCy_3)_2(^{13}CO_2)$, 141997-35-5; $[(PCy_3)_2Ni]_2N_2$, 21729-50-0; $Ni(PCy_3)_2(CO)_2$, 57307-01-4; $(H)Ni(PCy_3)_2O(O)CH$, 111189-75-4; $(COOAg)_2$, 533-51-7.

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