# Solid–Gas Reactions of Molecular Organometallic Complexes. Detection of a Metastable Intermediate in the Carbonylation of a Nickel(0) Complex

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The reaction of the trigonal pyramidal Ni(0) complex [Ni(NP$_3$)] (1) with CO in tetrahydrofuran (THF) solution has been re-investigated [NP$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$]. Depending on the experimental conditions, the reaction gives either the monocarbonyl [Ni($\eta^3$-NP$_3$-*P,P',P''*)(CO)] (2) or the dicarbonyl [Ni($\eta^2$-NP$_3$-*P,P'*)(CO)$_2$] (**3a**). Both products exhibit a distorted tetrahedral coordination geometry; in the monocarbonyl complex, the NP$_3$ ligand uses the three phosphorus atoms to bind the metal center, whereas it uses two phosphorus only in **3a**. Compounds **2** and **3a** have been characterized by IR and $^{31}$P and $^{13}$C NMR spectroscopies in both the solid state and solution. Compound **3a** is thermally stable in the solid state under inert atmosphere even at high temperature whereas, in ambient temperature solutions, it readily converts to **2** *via* CO elimination. The solid–gas reaction between crystals of **1** and CO (1 atm) at room temperature gives a mixture of **2** and of a new species **3b**, which has the same stoichiometry as **3a** but exhibits a different $^{31}$P CPMAS spectrum. On dissolution in THF saturated with CO, **3b** converts to **3a** whereas, under inert atmosphere, it dissolves to give initially **3a** and later **2** and CO. In light of *in situ* DRIFT and $^{31}$P CPMAS spectroscopies, **3b** is suggested to be an ensemble of metastable species in which a phosphine arm from NP$_3$, although unfastened, is located close to the metal center as a consequence of the constraining environment of the crystal lattice. The proximity of the free phosphine arm to nickel makes solid **3b** capable of losing one CO ligand, thus converting to **2**. Unlike in solution, the latter compound undergoes thermal dissociation of CO in the solid state to generate the starting complex **1**.

## Introduction

The ability of coordination compounds to undergo thermal reactions in the solid state has been known for many years. Ligand exchanges and anations, isomerizations of various types (linkage, cis–trans, racemization, structure), polymerizations, and a case of oxidative addition have been reported.[1] Only recently, however, have systematic studies been undertaken to design organometallic complexes capable of reacting in the solid state, at a molecular level, with both inorganic and organic gaseous molecules.[2]

Solid–gas reactions between transition metal complexes and small molecules differ from reactions in solution essentially in the fact that solid-state reactions occur within the constraining environment of the reactant crystal lattice, which can control both the kinetics and the nature of the products.[3] These, therefore, may not necessarily be the thermodynamically most stable products available to the system but may rather be the products of reaction pathways accessible in the environment of the solid. The products are generally amorphous to X-rays due to disruption of the reactant lattice by the product lattice. However, when there is coherence on the molecular level between the two lattices (topotactic reactions), single crystals can be obtained.[2a]

In solid–gas organometallic reactions, the gaseous molecules are required to penetrate the crystals of the solid reactant. Access of the gaseous reagents to as many metal centers as possible in the bulk of the crystal will therefore depend on the physical and chemical nature of both the organometallic compound and the gaseous molecule. In particular, it has been found that the diffusion of small organic molecules into the crystals of a solid reactant is favored when the latter contains an extensive hydrophobic region.[2a–h]

We are developing the solid-state chemistry of transition metal complexes stabilized by tripodal polyphosphines

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(1) Le May, H. E., Jr. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1986; Vol. 7, p 463.

(2) (a) Bianchini, C.; Peruzzini, M.; Zanobini, F. *Organometallics* **1991**, *10*, 3415. (b) Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 3698. (c) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1992**, *114*, 5905. (d) Bianchini, C.; Farnetti, E.; Graziani, M.; Kaspar, J.; Vizza, F. *J. Am. Chem. Soc.* **1993**, *115*, 1753. (e) Siedle, A. R.; Newmark, R. A. *Organometallics* **1989**, *8*, 1442. (f) Siedle, A. R.; Newmark, R. A. *J. Am. Chem. Soc.* **1989**, *111*, 2058. (g) Siedle, A. R.; Newmark, R. A.; Sahyun, M. R. V.; Lyon, P. A.; Hunt, S. L.; Skarjune, R. P. *J. Am. Chem. Soc.* **1989**, *111*, 8346. (h) Siedle, A. R.; Lyon, P. A.; Hunt, S. L.; Skarjune, R. P. *J. Am. Chem. Soc.* **1986**, *108*, 6430. (i) Aubart, M. A.; Pignolet, L. H. *J. Am. Chem. Soc.* **1992**, *114*, 7901. (j) Siedle, A. R.; Markell, C. G.; Lyon, P. A.; Hogdson, K. O.; Roe, A. L. *Inorg. Chem.* **1987**, *26*, 220. (k) Chin, C. S.; Lee, B.; Kim, S. *Organometallics* **1993**, *12*, 1462. (l) Bianchini, C.; Frediani, P.; Graziani, M.; Kaspar, J.; Meli, A.; Peruzzini, M.; Vizza, F. *Organometallics* **1993**, *12*, 2886. (m) Bianchini, C.; Meli, A.; Peruzzini, M.; Frediani, P.; Herrera, V.; Sanchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 2731.

(3) Thomas, J. M.; Morsi, S. E.; Desvergne, J. P. *Adv. Phys. Org. Chem.* **1977**, *15*, 63.

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such as $P(CH_2CH_2PPh_2)_3$ (PP$_3$), $N(CH_2CH_2PPh_2)_3$ (NP$_3$), and $MeC(CH_2PPh_2)_3$.[2a-d,l,m]

Tripodal polyphosphine ligands are well suited to assist solid-state reactions for several reasons. These include the remarkable stability of tripodal polyphosphine metal complexes *vs* thermal decomposition and oxidation reactions and the ease with which small organic molecules can penetrate the crystals of the resulting metal complexes dissolving in the extensive hydrophobic region provided by the carbon backbones of the ligands. Also, access of the gaseous molecules to the metal centers in the crystal lattice appears to be promoted, at relatively high temperatures, either by the motional freedom of the phosphine arms of the tripodal ligands or even by their decoordination.

In spite of the importance of heterogeneous carbonylation reactions,[4] very few studies have been carried out on solid–gas interactions of carbon monoxide with metal complexes.[2a,d,f,k] For this reason, we decided to investigate the solid–gas reaction of CO with a suitable low-valent metal complex such as [Ni(NP$_3$)] (1).[5] Helpful to our study was a re-investigation of the NMR properties of 1 in both the solid state and solution as well as its reaction in solution with CO under different conditions. Valuable information has been provided by the use of *in situ* variable-temperature DRIFT and $^{31}P$ CPMAS NMR spectroscopies.

## Results and Discussion

**Fluid-Solution Reactions.** The starting Ni(0) complex 1 was prepared in the early 1970s by Sacconi *et al.* As shown by a single-crystal X-ray analysis,[5] the compound adopts a trigonal pyramidal structure with the nitrogen donor in the apical position. The very minor differences in the atomic positions of the phosphorus atoms are reflected in the $^{31}P$ CPMAS spectrum, which, in the isotropic region, shows three resonances at 23.9, 23.0, and 19.8 ppm with similar chemical shift anisotropy (CSA) (*ca.* 215 ppm).[6] As expected, in solution the phosphorus nuclei appear magnetically equivalent on the NMR time scale, giving rise to a temperature-invariant A$_3$ spin system (the $^{31}P\{^1H\}$ NMR spectrum in THF-$d_8$ consists of a singlet at 23.01 ppm).

According to the procedure reported by Sacconi *et al.*,[5] the reaction between 1 and CO (<1 atm) in THF at room temperature, followed by addition of ethanol and slow evaporation of the solvent under a stream of nitrogen, quantitatively yields the carbonyl complex $[Ni(\eta^3\text{-}NP_3\text{-}P,P',P'')(CO)]$ (2). The structure of the latter compound[7] consists of discrete molecules in which each nickel center is tetrahedrally surrounded by three phosphorus atoms and a CO group, the bridgehead nitrogen atom being uncoordinated. In line with the solid-state structure, the $^{31}P$ CPMAS spectrum of 2 (Figure 1) in the isotropic region consists of three absorptions of equal intensity at 13.4, 11.8, and 9.8 ppm whose weighted average agrees well with the solution value of 11.9 ppm ($^{31}P\{^1H\}$ NMR A$_3$ spin system, THF-$d_8$ solution). Actually, three resonances in the solid-state spectrum are expected on the basis of the asymmetric unit corresponding to one molecule as found in the X-ray structure determination.[7] The CSA values of the three resonances appear very similar to each other and approach a value of 145 ppm, in the typical range of tertiary phosphines coordinated to a transition metal.[8]

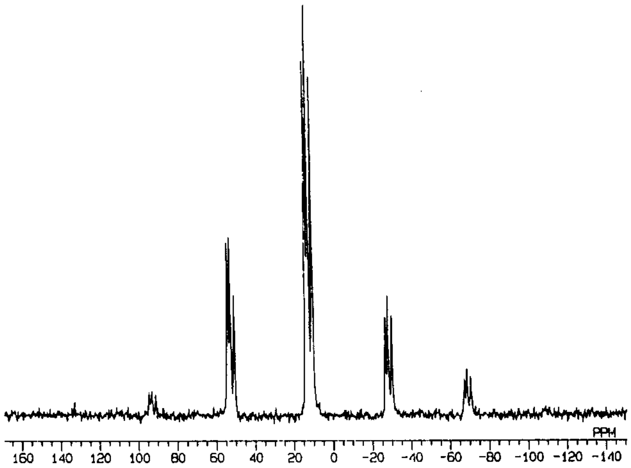

**Figure 1.** $^{31}P$ CPMAS spectrum at ambient temperature of 2 at a spinning speed of 4.0 kHz.

The $^{13}C$ CPMAS spectrum of $[Ni(\eta^3\text{-}NP_3\text{-}P,P',P'')(^{13}CO)]$ (2*) shows a single resonance for the coordinated CO group at 202.7 ppm (no evidence for $^2J_{PC}$ couplings was observed) with the usually large CSA (>400 ppm) of terminally bound carbonyls,[9] a complex absorption in the aromatic region (128–146 ppm) and two resonances in the methylenic carbon region (a broad singlet at 49.0 ppm attributable to the CH$_2$ groups bonded to nitrogen and a doublet at 23.9 ppm with a $J_{PC}$ value of 235 Hz).

The IR spectrum (Nujol mulls) of 2 shows a unique strong absorption in the terminal carbonyl region at 1878 cm$^{-1}$, assigned to $\nu$(Ni–CO). The spectrum contains also a $\nu$(C–H) band at 2800 cm$^{-1}$, which is not present in the spectrum of 1. This absorption is invariably displayed by NP$_3$ complexes in which the tripodal ligand uses only the phosphorus atoms to coordinate the metal centers.[10,11] The appearance of this C–H band is due to formation of eight-membered metalla rings, which are accomplished only when the NP$_3$ nitrogen donor is not bonded to the metal center.

In light of the results of the solid–gas reaction between 1 and CO (see below), we have repeated Sacconi's experiment under 1 atm of CO carefully from the beginning to complete precipitation of almost colorless crystals. This product contains as the largely major component the novel dicarbonyl $[Ni(\eta^2\text{-}NP_3\text{-}P,P')(CO)_2]$ (**3a**), which, depending on the experimental conditions, may be contaminated by variable amounts (5–10%) of the monocarbonyl 2 (Scheme I) and, eventually, by traces of an oxygenated impurity.[12]

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[4] Hunter, D. L.; Moore, S. E.; Dubois, R. A.; Garrou, P. *Appl. Catal.* **1985**, *19*, 275. Hjontkjaer, J.; Chen, Y.; Heinrich, B. *Appl. Catal.* **1991**, *67*, 269.

[5] Sacconi, L.; Ghilardi, C. A.; Mealli, C.; Zanobini, F. *Inorg. Chem.* **1975**, *14*, 1380.

[6] Davies, J. A.; Dutremez, S. *Coord. Chem. Rev.* **1992**, *114*, 61.

[7] Ghilardi, C. A.; Sabatini, A.; Sacconi, L. *Inorg. Chem.* **1976**, *15*, 2763.

[8] (a) Maciel, G. E.; O'Donnell, D. J.; Greeves, R. *Adv. Chem. Series* **1982**, *198*, 389. (b) Aime, S.; Gobetto, R. To be published.

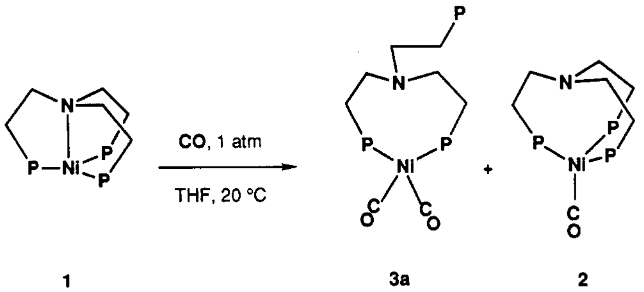
[9] (a) Walter, T. H.; Reven, L.; Oldfield, E. *J. Phys. Chem.* **1989**, *93*, 1320. (b) Hawkes, G. E.; Sales, K. D.; Aime, S.; Gobetto, R.; Lian, L.-Y. *Inorg. Chem.* **1991**, *30*, 1489.

[10] Bianchini, C.; Meli, A.; Scapacci, G. *Organometallics* **1983**, *2*, 1834.

[11] Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*; Methuen: London, 1960; p 17.

[12] The starting complex Ni(0) complex 1 is very sensitive to traces of dioxygen. Also, free phosphine arms of tripodal polyphosphine metal complexes easily undergo oxidation when their solutions are exposed to air (see for example: Bianchini, C.; Meli, A.; Scapacci, G. *Organometallics* **1985**, *3*, 264).

**Scheme I**



However, due to the low solubility in THF/EtOH, analytically pure samples of **3a** can easily be obtained.

Monitoring the CO uptake at room temperature by **1** in THF-$d_8$ solution with the use of $^{31}P\{^1H\}$ NMR spectroscopy, one may readily realize that the first product of the carbonylation reaction is the monocarbonyl **2**, which then undergoes attack by a second CO molecule to give **3a**. The latter product is stable in solution only in the presence of a CO atmosphere and at room temperature. Substitution of CO for $N_2$ or an increase of the temperature (60 °C) rapidly converts **3a** to **2** *via* CO elimination. This explains why **3a** may often be contaminated by variable amounts of **2**, depending on the workup conditions. Unlike in solution, the dicarbonyl **3a** is stable in the solid state at room temperature, undergoing a limited conversion to **2** (2–5%) when heated at 90 °C under nitrogen for 3 h (based on $^{31}P$ CPMAS NMR (see below) and IR spectroscopies).

The IR spectrum of **3a** (Nujol mulls) contains two $\nu$(CO) bands, both of them at higher energy (1928 and 1991 cm$^{-1}$) than the one of the monocarbonyl **2**.

At room temperature, the $^{13}C\{^1H\}$ NMR spectrum of $[Ni(\eta^2\text{-}NP_3\text{-}P,P')(^{13}CO)_2]$ (**3a***) in THF-$d_8$ shows a single absorption at 200.5 ppm in the terminal carbonyl region. On decreasing the temperature, this resonance broadens and then splits into two signals of the same intensity at 201.3 and 196.6 ppm, respectively (Figure 2). The calculated free energy of activation for this exchange process is 37.5 kJ mol$^{-1}$ (coalescence point measurement).

The $^{31}P\{^1H\}$ NMR spectrum of **3a** in $CD_2Cl_2$ at room temperature consists of two resonances at 21.2 and −19.2 ppm in the relative intensity ratio 2:1. The high-field resonance can readily be assigned to an uncoordinated phosphorus atom of $NP_3$.[13] As the temperature is decreased (Figure 3), the signal at 21.2 ppm broadens, collapses at −90 °C, and then, at lower temperature, separates into two resonances of equal areas at 31.5 and 16.1 ppm, respectively, whereas the signal of the uncoordinated phosphorus remains sharp over the whole temperature range. Comparable fluxional behavior is exhibited by **3a** in acetone-$d_6$ and THF-$d_8$. Since in the latter solvent the free energy of activation calculated from the variable-temperature $^{31}P\{^1H\}$ NMR spectra matches the value obtained from the $^{13}C$ NMR spectra, a single mechanism most likely accomplishes both site-exchange processes. The dynamic process affecting **3a** may thus be interpreted in terms of a slowing-down of the exchange process over the pseudotetrahedral surface of the Ni(0) center. To our knowledge, this is the first example in which phosphine/CO exchange around a tetrahedral Ni(0) center is frozen out. The chemical shift separation between the two coordinated phosphorus atoms in the slow-exchange regime is remarkable and reflects large effects on the $^{31}P$ chemical shifts associated with changes in the chelate ring conformations. The larger line width of the low-field phosphorus resonance may tentatively be explained in terms of a different degree of "freezing-out" of the dynamic process; likely, this phosphorus lies in a coordination position which has much room for large-amplitude oscillations to result in a wide dispersion of chemical shifts.

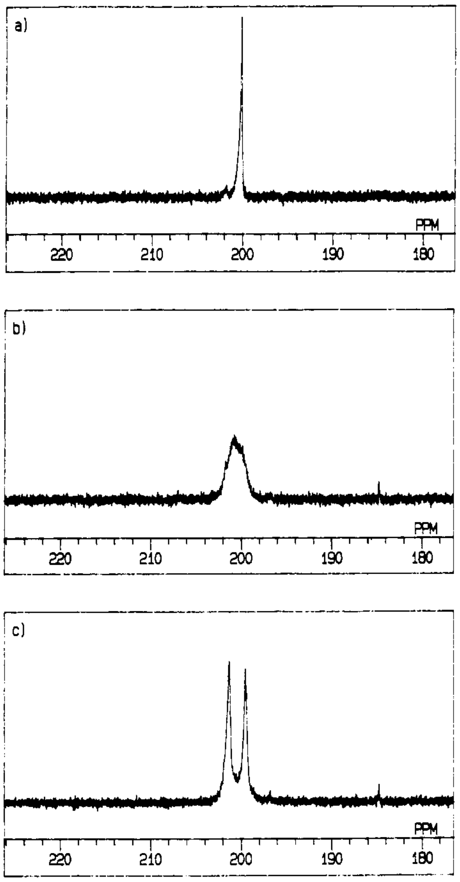


**Figure 2.** VT $^{13}C\{^1H\}$ NMR spectra of **3a*** in $CD_2Cl_2$ at 100.4 MHz: (a) 298 K; (b) 196 K; (c) 181 K.

The $^{31}P$ CPMAS spectrum of **3a** (Figure 4) is only in part consistent with the solution spectrum in the slow-exchange regime. In fact, one observes two resonances for coordinated phosphorus atoms at 23.4 and 11.6 ppm, respectively, and an ensemble of three resonances of different intensities for uncoordinated phosphorus at −17, −26, and −28 ppm, respectively. These resonances collectively account for the expected integrated area of 1:2 with respect to the coordinated phosphorus signal. Several $^{31}P$ CPMAS spectra were recorded on samples obtained from different reaction runs, and it was observed that large variations may occur in the relative intensities of the resonances assigned to the uncoordinated phosphorus. Thus, it appears that the layout of the free arm may differ somewhat from sample to sample, resulting in sizable differences in the observed $^{31}P$ chemical shifts.

The significant difference between the chemical shifts observed in the solid state and those measured in solution outlines either a remarkable solvent effect of THF not noted in case of **1** or **2** or a different conformation of the chelate ligands in the two phases, which may affect the phosphorus chemical shifts.

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[13] (a) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1984**, *23*, 2731. (b) Bianchini, C.; Meli, A.; Scapacci, G. *Organometallics* **1985**, *3*, 264.

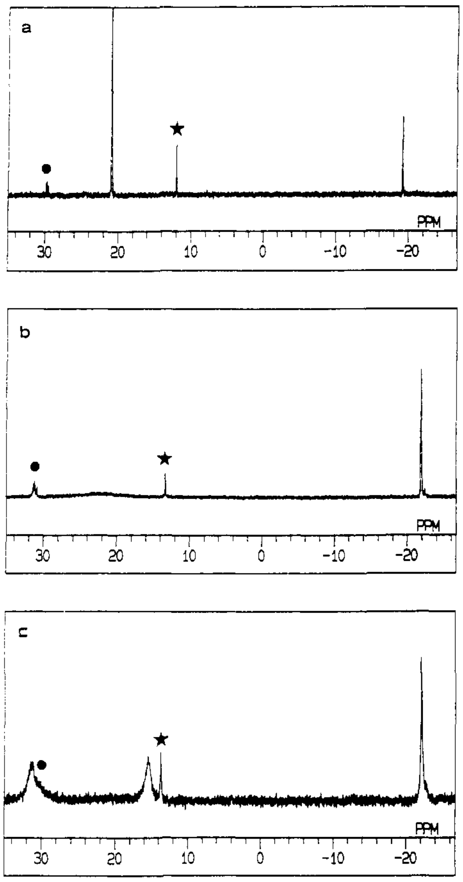


**Figure 3.** VT $^{31}P\{^{1}H\}$ NMR spectra of **3a** in $CD_2Cl_2$ at 161.8 MHz: (a) 298 K; (b) 196 K; (c) 181 K; ★, impurity of **2**; ●, impurity of oxygenated products.

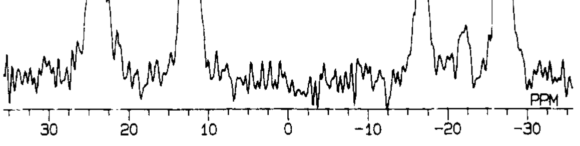
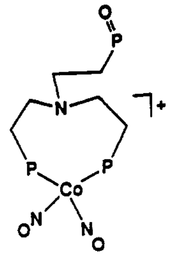


**Figure 4.** $^{31}P$ CPMAS spectrum at ambient temperature of **3a** at a spinning speed of 7.0 kHz.

It is therefore reasonable to conclude that, in both the solid state and low-temperature solution, **3a** is a dicarbonyl complex in which the nickel(0) center adopts a distorted tetrahedral coordination geometry that differs from the one of the monocarbonyl **2** as shown in Scheme I. A similar $\eta^2$-*P,P* bonding mode of $NP_3$ has been authenticated in the complex cation $[(NP_3O)Co(NO)_2]^+$ (**I**).[14] It is worth noting that the free arm of $NP_3$ (in this case phosphine oxide due to oxidation of the free phosphine) lies far away from the metal center.



**I**

**Solid–Gas Reactions.** When red crystals of **1** (*ca.* 100 mg) are exposed to a steady stream of CO at room temperature, a reaction takes place as shown by a color change to yellow. The solid–gas reactions are complete in times that increase with increasing the crystal size (from 0.03 to 0.05(1) mm$^3$). In all cases, however, a reaction time of 8 h is sufficient to completely transform **1**. Even though there is no fragmentation of the starting crystals of **1**, the carbonyl products are amorphous to X-rays. Notably, however, the absence of fragmentation indicates that the reactions do not proceed by interaction of CO with the surface of **1**, followed by breaking-up the crystal structure to facilitate further migration and reaction. In other words, there is convincing evidence that the solid–gas reactions occur in the bulk of the crystals.

The reactions can be monitored *in situ* with the use of DRIFT spectroscopy by means of the apparatus described in the Experimental Section. As an example, Figure 5 illustrates the changes observed in the $\nu$(CO) region in the course of a solid–gas reaction between **1** and CO carried out at room temperature. After 10 min, DRIFT bands at 1992, 1925, and 1885 cm$^{-1}$ were observed (Figure 5a). Monitoring the kinetics of carbonylation, one may readily infer that the first Ni complex to form is **2** (band at 1885 cm$^{-1}$). The concentration of the dicarbonyl compound (bands at 1992 and 1925 cm$^{-1}$), hereafter **3b**, increases as the reaction proceeds. After 90 min, **3b** prevails over **2** as shown in Figure 5d. A further 4 h of exposure to CO at room temperature did not produce any relevant change in the intensity ratio, suggesting the termination of the carbonylation process. In a similar way, in the $\nu(CH_2)$ region, after appearance of the band due to **2**, additional bands appear, giving rise to a broad, indented absorption centered at *ca.* 2800 cm$^{-1}$, which indicates that, in the solid-state, different strained rings are formed by the chelating $NP_3$ ligand.[11] IR spectra (Nujol mulls) on samples withdrawn at different stages of the reaction are in excellent correlation with the DRIFT spectra and, thus, show that the solid–gas reaction indeed occurs in the bulk of the crystals.

We have examined the thermal stability of the solid mixture of **2** and **3b** from room temperature to 70 °C in a flow of nitrogen (Figure 6). As is evident from inspection of the DRIFT spectra, the dicarbonyl complex **3b**, unlike the congener **3a**, loses one CO ligand and transforms into the monocarbonyl **2**. Such a process, even though slow, occurs even at room temperature and is rather rapid at 70 °C.

Under comparable reaction conditions, $^{31}P$ CPMAS spectroscopy provides valuable and intriguing information on the structure of **3b**. As the solid–gas reaction proceeds, we clearly note (Figure 7, traces a–d) the progressive decrease of the signals due to the parent compound **1** with concomitant formation of **2** and the upsurge of two broad absorptions centered at 0 and −23 ppm, respectively. Since

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[14] Ghilardi, C. A.; Sacconi, L. *Cryst. Struct. Commun.* **1975**, *4*, 687.

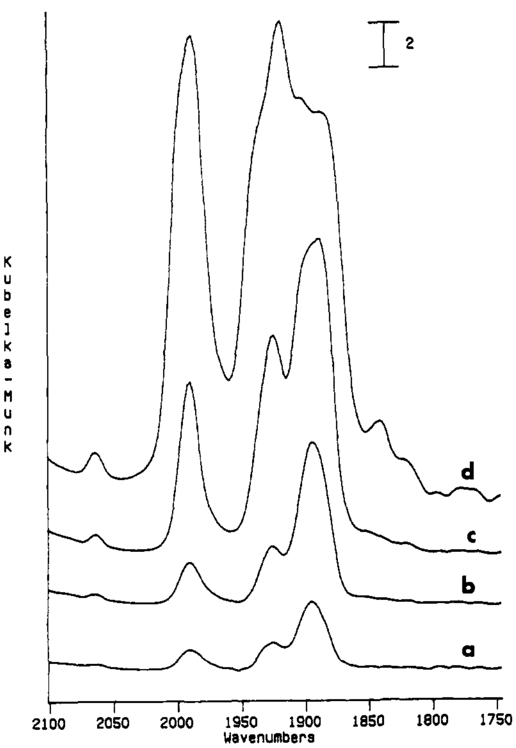


**Figure 5.** DRIFT spectra in the $\nu$(CO) region of [Ni(NP$_3$)] in a flow of CO at room temperature: (a) 10 min; (b) 20 min; (c) 30 min; (d) 90 min.

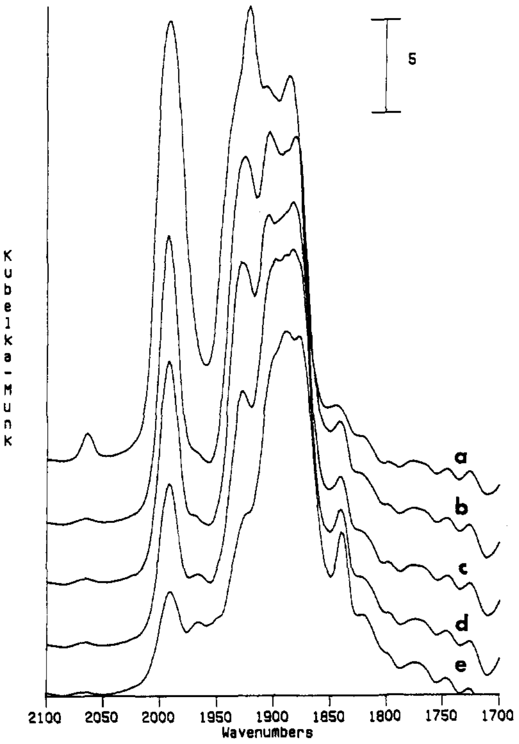


**Figure 6.** DRIFT spectra in the $\nu$(CO) region of a solid mixture of **2** and **3b** in a flow of N$_2$: (a) initial, room temperature; (b) 50 °C for 6 h; (c) 50 °C for 12 h; (d) 70 °C for 8 h; (e) 70 °C for 17 h.

the corresponding set of DRIFT (and IR) spectra unambiguously reveal the presence of a species with two terminal carbonyl ligands in addition to **2**, we conclude that **3b** is characterized by the two broad high-field absorptions and by another absorption masked by the broadened resonance of **2** at *ca.* 12 ppm.

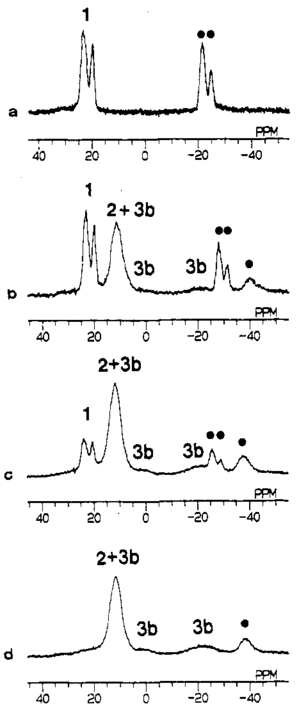
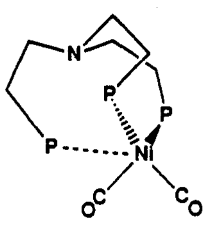


**Figure 7.** $^{31}$P CPMAS spectra of the product of a solid–gas reaction between **1** and CO (1 atm) at different reaction times: (a) 0; (b) 2 h; (c) 5 h; (d) 20 h. ● indicates the spinning sidebands flanking the isotropic peaks.

When the flow of CO is stopped, we first note the disappearance of **3b**, and only after *ca.* 12 h, does **2** release CO and transform into the parent complex **1**.

The significant differences in both the $^{31}$P NMR patterns and the overall stability between **3b** and **3a**, as well as the similarity of their IR and DRIFT spectra, strongly suggest that **3b** represents a metastable or activated species (not observable in solution) in the CO addition reaction which converts **2** to **3a** in solution. Our view is that **3b** corresponds to an ensemble of closely related structures of the type proposed in sketch **II** with a free phosphorus atom exhibiting different degrees of unfastening from the metal center. This ensemble results in a large dispersion of the $^{31}$P chemical shifts as shown by the broad absorptions observed in its $^{31}$P CPMAS spectrum.



II

In light of the experimental evidence, one may readily conclude that the addition of one CO to **1** to form **2** can occur in the solid state with small rearrangements around the metal center, *i.e.* without an extensive alteration of the overall crystal lattice. In contrast, the further transformation of **2** to **3a**, in which the free phosphine arm is expected to lie far away from the metal,[15] would produce

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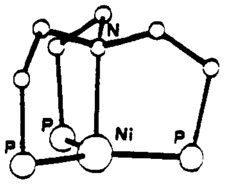
[15] Bianchini, C.; Mealli, C.; Midollini, S.; Sacconi, L. *Inorg. Chim. Acta* **1978**, *31*, L433. Bianchini, C.; Mealli, C.; Meli, A.; Sacconi, L. *Inorg. Chim. Acta* **1980**, *43*, 223. Tau, K. D.; Uriarte, R.; Mazanek, T. J.; Meek, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 6614. Balch, A. L.; Fung, E. Y. *Inorg. Chem.* **1990**, *29*, 4764.

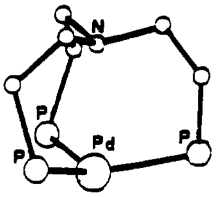
changes not tolerable in the solid. Indeed, the formation of the thermodynamically more stable **3a** form in the solid state would cause an increase in the volume of the crystals, which in fact is not expected for a solid–gas reaction, as elegantly shown by Siedle through BET nitrogen physisorption experiments.[2e]

In conclusion, the reaction between solid 1 and CO stops at the stage containing two CO's bound to the nickel atom but the internal pressure in the solid does not allow the phosphine arms to move too far away from the coordination sphere of the metal. This stage is likely characterized by large-amplitude oscillations around the equilibrium positions, and this, in turn, may be responsible for the extensive broadening observed for the $^{31}P$ resonances of **3b**. This compound dissolves in THF under a CO atmosphere, converting to **3a**, or, in the solid state, thermally releases CO to give 2 and then 1. The latter reaction path does not occur in solution, where the monocarbonyl 2 is thermally stable. Again, the internal pressure in the solid may be a driving force for the elimination of CO and formation of the smaller parent complex 1.

The various bonding capabilities of the $NP_3$ ligand have been the subject of a recent review.[16] Only two diamagnetic complexes of the formula $[M(NP_3)]$ are known, namely 1 and $[Pd(NP_3)]$.[17] The two compounds exhibit different structures in the solid state (see sketches **III** and **IV**), the Pd complex being, in fact, trigonally elongated (TE). However, the energy barrier, calculated at the EHMO level, between trigonal pyramidal (TP) and TE structures of the nickel and palladium compounds is very low.[18] Actually, the TP and TE isomers can be in equilibrium in solution and the preferential TE structure of Pd may be due to a solid-state effect. Thus, it is not surprising that facile unfastening of the bridgehead nitrogen atom in 1 can also take place in the solid state, provided a small amount of thermal energy is added. In contrast, it is quite surprising to have found that even the decoordination of a phosphine arm is a feasible pathway in the solid state.



III



IV

As a final consideration, we wish to highlight the fact that solid–gas interactions of gaseous small molecules with transition metal complexes may lead to formation of species not observable in analogous fluid-solution reactions.[2c,d,1] This suggests that continued work on solid–gas organometallic reactions might lead not only to further rapid development of new synthetic techniques[2,19] but also to important mechanistic breakthroughs. Indeed, the solid-state kinetic control over the distribution and nature of the products evidently implies that increasing information on the reaction mechanisms may be learned, particularly in case of solid–gas reactions occurring at relatively low temperature, as they offer the advantage that structural elements can be preserved in the transformation from reactant to product. In this way, new structure types, some of which are metastable, may be arrived at through a series of mechanistically well-understood steps.[2]

## Experimental Section

**General Procedure.** Tetrahydrofuran was distilled over $LiAlH_4$. All solvents were stored over molecular sieves and purged with nitrogen prior to use. $^{13}CO$ (99% enriched) was purchased from Isotec. All other chemicals were commercial products and were used as received without further purifications. Literature methods were used for the preparation of 1 and 2.[5] The solid complexes were collected on sintered-glass frits and washed with appropriate solvents before being dried in a stream of nitrogen or of CO. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer using samples mulled in Nujol between KBr plates. *In situ* solid-state IR measurements were performed by diffuse reflectance infrared spectroscopy (DRIFTS) on an FTS-40 Digilab spectrophotometer equipped with a Harrick DRA-2CI diffuse reflectance attachment and a Harrick HVC cell, which allows one to record the spectra of a solid sample under controlled temperature and gas flow. DRIFT measurements under CO were carried out at atmospheric pressure at room temperature. The thermal stability of the solid products was investigated in a flow of $N_2$ in the temperature range from 20 to 70 °C. All DRIFT spectra were recorded at $4\text{-cm}^{-1}$ resolution with coaddition of 100 scans per spectrum. Raw spectra were converted to the Kubelka–Munk reflectance form by using the initial spectrum of 1 as reference. NMR measurements in solution were carried out on a JEOL EX 400 spectrometer where the $^{13}C$ and $^{31}P$ nuclei resonate at 100.4 and 161.8 MHz, respectively. Chemical shifts ($\delta$ scale, high-frequency positive) were referenced to external $H_3PO_4$ 85% or neat TMS, respectively. Deuterated solvents for NMR measurements were dried over molecular sieves. High-resolution solid-state $^{31}P$ and $^{13}C$ NMR spectra were recorded at 109.7 and 67.8 MHz, respectively, on a JEOL GSE 270 spectrometer under conditions of cross polarization, proton decoupling, and magic angle spinning. Typical CPMAS conditions: contact time, 3.5 ms; recycle time, 12 s. Samples (typically 100–150 mg) were positioned in rotors of zirconia and spun at spinning rates in the range from 4.0 to 7.0 kHz. Chemical shift anisotropies were calculated from the shielding tensor components derived by graphical analysis (Herzfeld–Berger method)[20] of the spinning sidebands using an iterative computer program based on the equations given by the Levenberg–Marquardt method.[21]

**Reaction of 1 with CO in THF Solution. (A) Preparative Scale.** Air was evacuated from a 100-mL autoclave; then a THF (20 mL) solution of 1 (0.5 mmol, 325 mg) prepared in a Schlenk tube was introduced by suction. The system was evacuated and refilled with CO (1 atm) six times. The solution in the autoclave was stirred at 20 °C. After 1 h, the yellow solution was collected under CO and cold absolute ethanol (25 mL) saturated with CO was added. A steady stream of CO was maintained until off-white crystals precipitated. The product was filtered off, washed with ethanol, and dried in a stream of CO. Recrystallization from THF/EtOH (1:1, v/v) under a CO atmosphere gave **3a** in 85% yield. Anal. Calcd for $C_{44}H_{42}O_2NiP_3$: C, 70.05; H, 5.61; Ni, 7.78; P, 12.32. Found: C, 69.95; H, 5.58; Ni, 8.01; P, 12.45.

**(B) NMR Studies.** A sample of 1 (*ca.* 0.03 mmol) was dissolved in THF-$d_8$ (0.7 mL) in a 5-mm NMR tube under

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nitrogen. After a couple of freeze/pump/thaw cycles at −196 °C, the solution was frozen and pumped on. After addition of CO (*ca.* 20 equiv), the frozen tube was sealed and then introduced into an NMR spectrometer. The reaction was followed by $^{31}P\{^1H\}$ NMR spectroscopy. A reaction between **1** and CO rapidly occurred to give **2**. With time, **2** slowly disappeared. Formed in its place was **3a**. When the solution was allowed to stand at 20 °C for 1 h, almost complete conversion of **2** to **3a** was observed.

**Solid–Gas Reactions.** Reactions of **1** with CO were carried out either in a glass apparatus previously described[2a,d] or directly on samples positioned into DRIFT and NMR spectrometers. In the first case, after placement of the complex (100 mg), the glass container was evacuated to $<10^{-4}$ Torr. The reaction vessel was carefully back-filled with CO (1 atm). After evacuation of CO, the solid product was collected and immediately characterized. When necessary, the products were stored under a CO atmosphere in Schlenk tubes.

Identification of the products was made, in the solid state, both by IR (Nujol mulls, KBr, DRIFTS, elemental analyses) and by $^{31}P$ and $^{13}C$ CPMAS NMR spectroscopies or, in solution, by multinuclear NMR spectroscopy in THF-$d_8$, $CD_2Cl_2$, or acetone-$d_6$ solutions.

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