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Carbon dioxide–transition metal complexes
IV. New Ni(0)–CO_2 complexes with chelating diphosphines: influence of P–Ni–P angle on complex stabilities

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Abstract

The reaction between Ni(0) complexes (dp) (dp = 1,2-bis(dicyclohexylphosphino)ethane, 1,3-bis(dicyclohexylphosphino)propane, 1,4-bis(dicyclohexylphosphino)butane; dcpe, dcpp, dcpb, respectively) and carbon dioxide is described. The influence of the P–Ni–P bond angle on the stability of the corresponding adducts is discussed. The reactions of Ni(dcpp)CO_2 and Ni(dcpb)CO_2 with dioxygen are also described.

Introduction

In recent years numerous examples of CO_2 insertion reactions into M–X bonds (X = C, H, O or N) have been reported. On the contrary, only a few catalytic reactions involving CO_2 giving rise to carbon–carbon bond formation have been described [1, 2].

Coordination to a transition metal is a powerful way to activate [1, 3] the carbon dioxide molecule and it is considered significant [3b] in most reactions concerning the CO_2 molecule.

Since the first crystallographically characterized CO_2 complex, $Ni(PCy_3)_2CO_2$ [4], was reported, many carbon dioxide–transition metal complexes have been described in the literature [5].

Although many CO_2 complexes have been spectroscopically and chemically identified, only a few of them have also been structurally characterized.

Among the many papers dedicated to the coordination chemistry of CO_2 [1–5] we wish to mention a number of theoretical studies aimed at defining the nature of the CO_2 metal bond [6].

Some of these studies dealt specifically with the complexes $Ni(PH_3)_2(CO_2)$ [6a, b], $\{Co(alcn)_2(CO_2)\}^-$ [6d], *trans*-$Mo(CO_2)(PH_3)_4$ and *trans,mer*-$Mo(CO_2)_2(CNH)(PH_3)_3$ [6c] intended to be models of the really well characterized complexes $Ni(PCy_3)_2(CO_2)$ [4], Co(R-salen)(CO_2) [7], *trans*-$Mo(CO_2)_2(PMe_3)_4$ and *trans,mer*-$Mo(CO_2)(CNPr^i)(PMe)_3$ [5a].

In our work on nickel–carbon dioxide complexes [4] it became evident that their stability is related to the basicity of the phosphines and to the P–Ni–P bond angle. For instance taking into account the nature of the Ni–CO_2 bond, the unsuccessful formation of the complex Ni(dppe)(CO_2) (dppe = 1,2-bis(diphenylphosphino)ethane) was ascribed [4b] to the fact that the P–Ni–P bond angle in the distorted square-planar geometry of the putative complex Ni(dppe)(CO_2) is expected to be less than 120° owing to the geometric requirements of the diphosphine. Moreover it was calculated [6b] that the total energy for the complex $Ni(PH_3)_2(CO_2)$ is a function of the P–Ni–P angle, being the most favourable one when this angle is just 120°.

We show now that the lack of any interaction, in solution or in the solid state, between carbon dioxide and bis{1,2-bis(diphenylphosphino)ethane}nickel(0) has to be ascribed to the insufficient basicity of the diphosphine and not to its chelating geometry. Indeed, the Ni(0) complexes with the more basic chelating diphosphines $Cy_2P–(CH_2)_n–PCy_2$ (Cy = cyclohexyl; $n = 2$, 3, 4: dp = dcpe, dcpp and dcpb, respectively) do react with CO_2 and afford the CO_2–nickel(0) adducts Ni(dp)CO_2. The complex in which the P–Ni–P angle is about 90° ($n = 2$) is unstable and cannot be isolated in the solid state owing to a rapid disproportionation into a carbonate complex of nickel(II) and a not isolable

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monocarbonyl complex of nickel(0). On the contrary those for which a higher P–Ni–P angle ($n=3$, 4) is expected, are stable and isolable in the solid state.

Experimental

All reactions were carried out in anhydrous solvents which were distilled and stored under inert atmosphere. Ni(dp) and $Ni(dcpe)_2$ complexes were prepared as described by us [8]; $Ni(dcpe)Cl_2$ and $Ni(dcpe)(CO)_2$ were prepared as described in refs. 9 and 10. Samples for decomposition point measurements were sealed in capillary tubes under nitrogen.

NMR solvents were dried over activated 5 Å molecular sieves and deoxygenated by repeated freezing–pumping cycles. NMR spectra were recorded with a Varian XL200 spectrometer operating in FT mode. ^{13}C NMR spectra were referenced by using the ^{13}C resonance of the solvent as an internal standard but are reported with respect to TMS. The IR spectra were recorded with a Perkin-Elmer 883 spectrophotometer.

The analyses of gas (H_2, CO_2) were performed with a Carlo Erba chromatograph, model CAT_2 Fractovap (equipped with a column filled with Chromosorb 102) connected to a Varian 4270 integrator using the conditions standardized in our previous report for carbon dioxide [4b].

Reaction of Ni(dcpe) with gaseous CO_2

A solution of Ni(dcpe) (0.50 g) in toluene (10 ml) was stirred under carbon dioxide for a few minutes at room temperature and atmospheric pressure. The IR spectrum of the solution showed the 1898, 1660, 1630 cm^{-1} strong absorption bands attributable to a mixture of Ni(dcpe)(CO) and $Ni(dcpe)(CO_3)$. After 10 h a yellow solid precipitated which was characterized as $Ni(dcpe)(CO_3)$ by elemental analysis, IR, NMR and chromatographic analysis of the gases released upon treating the solid complex with H_2SO_4 (see below).

Reaction of Ni(dcpe) with gaseous $^{13}CO_2$

A solution of Ni(dcpe) (0.50 g) in C_7D_8 (10 ml) was stirred under $^{13}CO_2$ for a few minutes at room temperature and atmospheric pressure and used to record NMR and IR spectra. IR: 1852, 1605, 1580 cm^{-1}. $\delta(^{13}C\{^1H\})$ in C_7H_8: 166.2(s), 204.1(t, $J=4$ Hz) ppm.

After 6 h the carbonate complex precipitated, which was recovered by filtration. IR (nujol mull): 1604, 1576 cm^{-1}. $\delta(^{13}C\{^1H\})$ in CD_2Cl_2: 168.6(s) ppm.

The ^{13}C spectrum of the solution recorded after filtration of $Ni(dcpe)^{13}CO_3$ showed the triplet at 204.1 ppm but no signal near 166 ppm.

Reaction of $Ni(dcpe)_2$ with gaseous CO_2

A solution of $Ni(dcpe)_2$ (0.18 g) in toluene (5 ml) was stirred under carbon dioxide for a few minutes. Immediately a sequence of IR spectra was recorded which is reported in Fig. 1. After 6 h a yellow solid precipitated from the solution which was identified as $Ni(dcpe)(CO_3)$.

Reaction of Ni(dcpe) and $Ni(dcpe)(CO)_2$

$Ni(dcpe)(CO)_2$ (0.4 mmol) and Ni(dcpe) (0.4 mmol) were heated in toluene (10 ml) under nitrogen at 50 °C for 10 min. The spectrum of the cooled solution showed, besides the 1924 and 1986 cm^{-1} bands initially present and due to $\{Ni(dcpe)(CO)_2\}$, a band at 1898 cm^{-1}.

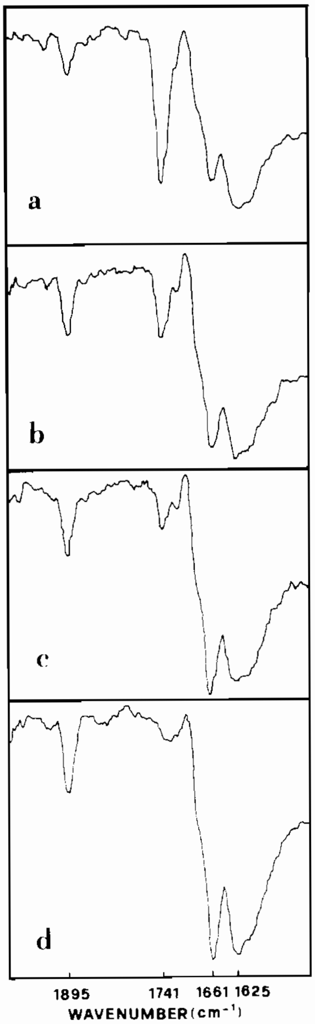


Fig. 1. Sequence of IR spectra of a toluene solution of $Ni(dcpe)_2$ under CO_2 recorded at different times: (a) immediately; (b) after 5 min; (c) after 10 min; (d) after 15 min.

1,2-Bis(dicyclohexylphosphino)ethanenickelcarbonate, Ni(dcpe)CO$_3$

1.0 g (0.91 mmol) of Ni(dcpe)Cl$_2$ dissolved in CH$_2$Cl$_2$ (10 ml) was added to 10 ml of a saturated aqueous solution of Na$_2$CO$_3$ to give a biphasic system. In a few minutes the organic phase became yellow and was separated from the aqueous one. By evaporating the CH$_2$Cl$_2$ a yellow solid was collected which was dried *in vacuo*. Yield 0.92 g. m.p. = 204 °C.

Anal. Calc. for $C_{27}H_{48}NiP_2O_3$: C, 59.91; H, 8.94; Ni, 10.84; P, 11.84. Found: C, 59.63; H, 8.97; Ni, 10.78; P, 11.42%. $\delta(^{13}C\{^1H\})$ in CD$_2$Cl$_2$: 168.6(s) ppm. IR (nujol mull): 1657, 1622 cm^{-1}.

By treating the solid with sulfuric acid, a 1CO$_2$/1Ni gas evolution was revealed by chromatographic analysis.

Reaction of Ni(dcpp) with gaseous CO$_2$

A solution of Ni(dcpp) (0.20 g) in toluene (5 ml) was stirred under carbon dioxide for 10 min at room temperature and atmospheric pressure. The IR spectrum showed a strong absorption at 1740 cm^{-1} with a shoulder at 1733 cm^{-1}. On cooling to -20 °C a yellow solid precipitated which was washed with cold heptane and dried *in vacuo*.

IR (nujol mull): 1730(s) cm^{-1}. *Anal.* Calc. for $C_{27}H_{50}NiP_2CO_2$: Ni, 10.88; P, 11.49. Found: Ni, 10.81; P, 11.38%.

By treating the solid complex with sulfuric acid, 1CO$_2$/1Ni and 1H$_2$/1Ni gas evolution was revealed by chromatographic analysis.

Reaction of Ni(dcpp) with gaseous ^{13}CO$_2$

A solution of Ni(dcpp) (0.30 g) in toluene (10 ml) was stirred under ^{13}CO$_2$ for 5 min at room temperature and atmospheric pressure and used to record ^{13}C NMR and IR spectra:

IR: 1693(s) cm^{-1}. $\delta(^{13}C\{^1H\})$ in C$_7$H$_8$: 164.2(d, J = 45 Hz) ppm.

Reaction of Ni(dcpb) with gaseous CO$_2$

A solution of Ni(dcpb) (0.18 g) in toluene (5 ml) was stirred under carbon dioxide for 10 min at room temperature and atmospheric pressure. The IR spectrum showed a strong absorption at 1742 cm^{-1}. After evaporation of the solvent *in vacuo* and addition of n-heptane (3 ml), a yellow solid precipitated which was washed with cold n-heptane and dried *in vacuo*.

IR (nujol mull): 1720 cm^{-1}. *Anal.* Calc. for $C_{28}H_{52}NiP_2CO_2$: Ni, 10.61; P, 11.19. Found: Ni, 10.55; P, 11.00%.

Treatment of the solid with sulfuric acid gave a 1CO$_2$/1Ni and 1H$_2$/1Ni gas evolution which was revealed by chromatographic analysis.

Reaction of Ni(dcpb) with gaseous ^{13}CO$_2$

A solution of Ni(dcpb) (0.30 g) in toluene (10 ml) was stirred under ^{13}CO$_2$ for a few minutes at room temperature and atmospheric pressure and used to record ^{13}C NMR and IR spectra. IR: 1712 cm^{-1}. $\delta(^{13}C\{^1H\})$ in C$_7$D$_8$: 162.0(d, J = 37 Hz) ppm.

(Peroxocarbonato)1,3-bis(dicyclohexylphosphino)-propanenickel(II), Ni(dcpp)CO$_4$

Finely powdered Ni(dcpp)CO$_2$ (50–70 mg) was exposed to dry oxygen at room temperature and atmospheric pressure until the solid turned to yellow–orange and showed IR bands at 1658, 1627 and 745 cm^{-1}.

(Peroxocarbonate)1,4-bis(dicyclohexylphosphino)-butanenickel(II), Ni(dcpb)CO$_4$

Finely powdered Ni(dcpb)CO$_2$ (50–70 mg) was exposed to dry oxygen at room temperature and atmospheric pressure until the solid turned to orange and showed IR bands at 1670, 1632 and 740 cm^{-1}.

Results and discussion

The reaction of Ni(dcpe) with CO$_2$ at room temperature in toluene leads to a solution which exhibits IR bands at 1898, 1660 and 1630 cm^{-1} (for this and the other IR absorptions, see Table 1). From this solution a yellow solid precipitates which exhibits IR bands (nujol mull) at 1657 and 1622 cm^{-1}.

The solution resulting after precipitation shows only the 1898 cm^{-1} band, which can be ascribed to a monocarbonyl species. Attempts made to isolate such a compound have been unsuccessful. To verify this hypothesis we carried out a reaction between Ni(dcpe) and Ni(dcpe)(CO)$_2$ in toluene and we noticed the appearance in the IR spectrum of the solution of a band at 1898 cm^{-1} together with the bands of the dicarbonyl complex at 1924 and 1986 cm^{-1}. This agrees with the establishment in solution of the equilibrium:

$$\mathrm{Ni(dcpe)(CO)_2 + Ni(dcpe) \rightleftharpoons 2Ni(dcpe)(CO)}$$

Also in this case attempts to isolate the monocarbonyl species were unsuccessful.

The isolated yellow solid (IR = 1657, 1622 cm^{-1}) develops CO$_2$(CO$_2$/Ni = 1), but no hydrogen, when treated with sulfuric acid. Its elemental analyses are consistent with a compound of formula Ni(dcpe)CO$_3$. Moreover, the compound, dissolved in CD$_2$Cl$_2$, shows a ^{13}C NMR signal at δ = 168.6(s) ppm which is identical to that given by the complex, characterized as Ni(dcpe)CO$_3$, prepared by the reaction of Ni(dcpe)Cl$_2$ with Na$_2$CO$_3$ in a two-phase system.

Therefore, the reaction between Ni(dcpe) (in which the P–Ni–P angle is about 90° [8]) and gaseous CO$_2$

TABLE 1. IR absorptions (cm^{-1}) of some functional groups in products derived from the reaction of Ni(dp) complexes with CO_2 and of Ni(dp)CO_2 with molecular O_2

Complex		νCO	νCO_2	νCO_3	νCO_4	νO–O
Ni(dcpe)CO	toluene	1898				
Ni(dcpe)^{13}CO	toluene	1852				
Ni(dcpe)CO_3	nujol			1657, 1622		
Ni(dcpe)CO_3	toluene			1660, 1630		
Ni(dcpe)$^{13}CO_3$	toluene			1605, 1580		
Ni(dcpe)$^{13}CO_3$	nujol			1604, 1576		
Ni(dcpp)CO_2	toluene		1740, 1733(sh)			
Ni(dcpp)CO_2	nujol		1730			
Ni(dcpp)$^{13}CO_2$	toluene		1693			
Ni(dcpb)CO_2	toluene		1742			
Ni(dcpb)CO_2	nujol		1720			
Ni(dcpb)$^{13}CO_2$	toluene		1712			
Ni(dcpp)CO_4	nujol				1658, 1627	745
Ni(dcpb)CO_4	nujol				1670, 1632	740

can be summarized as:

$$2Ni(dcpe) + 2CO_2 \longrightarrow Ni(dcpe)CO + Ni(dcpe)CO_3$$

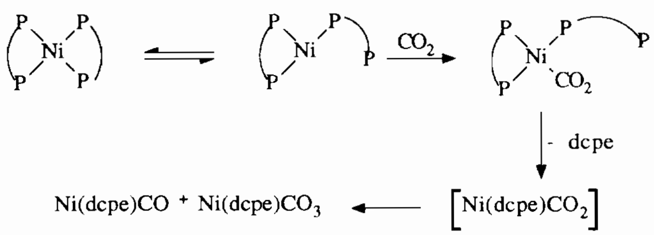
Cases of interaction of CO_2 with transition metal complexes leading to a disproportionation into carbonato and carbonyl complexes are known in the literature [11] and a monocarbonyl complex of Ni(0) was isolated [12] showing a 1895 cm^{-1} band in the IR spectrum.

We have evidence that the first species formed in the reaction between Ni(dcpe) and CO_2 is a CO_2 adduct which rapidly disproportionates into carbonyl and carbonate complexes according to the sequence:

$$2Ni(dcpe) + 2CO_2 \longrightarrow 2[Ni(dcpe)CO_2] \longrightarrow Ni(dcpe)CO + Ni(dcpe)CO_3$$

In fact, on allowing a Ni(dcpe)$_2$ toluene solution to react with gaseous CO_2 and immediately recording the IR spectrum, we noticed a strong band at 1741 cm^{-1}, together with a weak band at 1898 cm^{-1} and two bands at 1660 and 1630 cm^{-1}. Rapid recording of the IR spectra of the solution (Fig. 1) reveals the progressive weakening of the 1741 cm^{-1} band and the increase of the 1660 and 1898 cm^{-1} bands.

This behaviour can be explained on the basis of Scheme 1.



Scheme 1.

In contrast with Ni(dcpe)$_2$, Ni(depe)$_2$ (depe = 1,2-bis(diethylphosphino)ethane), does not react with CO_2. We have shown [8] that both these complexes are prevalently tetracoordinate in solution. However, the ability of Ni(dcpe)$_2$ to react with CO_2 suggests that this complex is somewhat dissociated in solution. In fact this different behaviour can be ascribed to the very different steric bulkiness of the two diphosphines of comparable basicity.

The ^{13}C NMR spectrum of a C_7D_8 solution of Ni(dcpe) under $^{13}CO_2$ showed signals at 166.2 (s) and 204.1 (*t*, $J = 4$ Hz) ppm (Table 2). The singlet at 166.2 (C_7D_8) ppm is consistent with that of Ni(dcpe)CO_3 (168.6 ppm, CD_2Cl_2); the 204.1 ppm triplet must be assigned to the monocarbonyl species Ni(dcpe)(^{13}CO) and not to a Ni–CO_2 adduct, albeit in the literature 190–210 ppm has been proposed as the region in which the $^{13}CO_2$ resonance of carbon dioxide adducts falls [5a, b, e, 13]. Although this might be true when the transition metal belongs to the second row of the Periodic Table*, we can now demonstrate that this is not valid for Ni–CO_2 adducts. In fact we have recorded the NMR spectrum of Ni(PCy_3)$_2CO_2$ in C_7D_8 and the obtained value 157.3(t)

TABLE 2. ^{13}C data (ppm) in C_7D_8

Complex	δ	*J* (Hz)
Ni(PCy_3)$_2$$^{13}CO_2$	157.3	14
Ni(dcpe)^{13}CO	204.1(t)	4
Ni(dcpe)$^{13}CO_3$	166.2(s)	
Ni(dcpp)$^{13}CO_2$	164.2(d)	45
Ni(dcpb)$^{13}CO_2$	162.0(d)	37

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*^{13}C NMR CO_2 signals are: 200.5 ppm for [Nb(η-C_5H_4Me)$_2$(CH_2SiMe_3)(η^2-CO_2)], 206.1 ppm for *trans*-Mo(CO_2)$_2$(PMe_3)$_4$, 193 ppm for (COD)$_2Rh_2OsH_2$(CO_2)(PMe_2Ph)$_3$ and 203.8 ppm for Mo(dmpe)$_2$(CO_2)(OCHO)H_3.

ppm supports our assignment of the 204.1 ppm signal to the monocarbonyl complex.

The ^{13}C NMR spectrum of a solution of Ni(dcpe)$_2$ under ^{13}CO$_2$ did not show any peak besides those attributable to Ni(dcpe)CO and Ni(dcpe)CO$_3$, evidently because it was not possible to record the spectrum immediately after the uptake of carbon dioxide.

The reactions of Ni(dcpp) and Ni(dcpb) with gaseous CO$_2$ in toluene lead to solutions which possess strong IR absorptions at 1740 (with a shoulder at 1730 cm^{-1}) and 1742 cm^{-1} and which afford crystalline solids with bands at 1730 and 1720 cm^{-1} (nujol mull), respectively. Both the compounds, treated with sulfuric acid, develop one mole of CO$_2$ and H$_2$ per mole of nickel and analyze as Ni(dp)CO$_2$ (dp = dcpp, dcpb).

The ^{13}C NMR spectra of solutions of Ni(dcpp) and Ni(dcpb) under ^{13}CO$_2$ show doublets at 164.2 ($J = 45$ Hz) and 162.0 ($J = 37$ Hz) ppm, respectively.

The presence of a doublet with the chelating diphosphines dcpp and dcpb suggests that in solution the CO$_2$ ligand is η^2-bonded to the nickel atom so that the carbon atom couples with the *trans* phosphorus atom; no coupling is observed between the CO$_2$ carbon atom and the *cis* phosphorus atom as predictable for this mutual steric situation [14]. On the contrary, the presence of a triplet with the monodentate PCy$_3$ can be explained by admitting that, in the prevalent form of Ni(PCy$_3$)$_2$CO$_2$ in solution, the CO$_2$ moiety is η^1-C bonded to the nickel atom. In the case of bulky chelating phosphines, it is probable that CO$_2$ cannot rotate around to the Ni–C bond and it is 'locked' in an η^2-coordination.

Ni(dp)CO$_2$ complexes (dp = dcpp, dcpb) are found to react with oxygen at atmospheric pressure at room temperature in the solid state to give nickel(II) peroxocarbonate species via insertion of O$_2$ into the Ni–C bond:

$$\mathrm{Ni(dp)CO_2 + O_2 \longrightarrow Ni(dp)CO_4}$$

Their IR absorptions (see Table 1) are in accordance with those reported for analogue complexes of Ni [4a], Pd and Pt [15].

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