Incorporation and Deoxygenation of Carbon Dioxide: A Metal-Assisted Facile Conversion of Carbon Dioxide and Primary Amines to Isocyanates

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Metal *N*-alkylcarbamato complexes $[M(O_2CNHR)_n]$ ($M = Na$, $n = 1$; $M = Mn, Co$, $n = 2$) were prepared by treating CO_2 with a primary amine RNH_2 ($R = Ph, Cy, Pr$) and various complex precursors. For $M = Mn$ or Co and $R = Cy$, MCl_2 can be used as starting material. These complexes were readily decomposed by acyl halides $R'COCl$ ($R' = Ph, Me$), and two reaction pathways were observed. One led to decarboxylation and formation of amides $RNHC(O)R'$, while the other afforded isocyanate RNCO and carboxylic acid ($M = Na$) or carboxylic anhydride ($M. = Mn, Co$). Analysis of the reaction products showed that the metal plays a major rôle in the formation of the isocyanate, intercepting one of the reaction products. A mechanistic rationalization is proposed.

Einbau und Desoxygenierung von Kohlendioxid: Eine Metall-katalysierte einfache Umwandlung von Kohlendioxid und primären Aminen in Isocyanate

Metall–*N*-Alkylcarbamato-Komplexe $[M(O_2CNHR)_n]$ ($M = Na$, $n = 1$; $M = Mn, Co$, $n = 2$) wurden durch Reaktion von CO_2, einem primären Amin RNH_2 ($R = Ph, Cy, Pr$) und verschiedenen Komplex-Vorstufen dargestellt. Für den Fall $M = Mn, Co$ und $R = Cy$ kann MCl_2 als Edukt eingesetzt werden. Diese Komplexe werden von Acylhalogeniden $R'COCl$ ($R' = Ph, Me$) rasch auf zwei Wegen zersetzt. Einer führte zur Decarboxylierung und Bildung von Amiden $RNHC(O)R'$, während der andere Isocyanat RNCO und Carbonsäure ($M = Na$) oder Carbonsäureanhydrid ($M = Mn, Co$) lieferte. Eine Analyse der Reaktionsprodukte ergab, daß das Metall eine wichtige Rolle bei der Entstehung des Isocyanates spielt, indem es eines der Reaktionsprodukte abfängt. Ein Reaktionsmechanismus wird vorgeschlagen.

The effective utilization of the carbon dioxide molecule may follow two different routes, i. e. reduction and incorporation[1]. Reduction of CO_2 implies its conversion to other C_1 molecules (such as CO, HCOOH, CH_3OH or CH_4), by reaction with high-energy reductants such as metal hydrides[2] or hydrogen[3]; or by reduction with external energy sources such as electrochemical potential[4] or light[5], usually in the presence of transition metal complexes as electron transfer agents. Most frequently the products of both electrochemical or light-driven reductions are formates and/or CO, and a common mechanistic feature is the proposed[4a,b,c;5a,b] formation of an intermediate MCOOH. This requires the formation of a metal–carbon bond between an electron-rich metal centre and CO_2, reminiscent of the coordination of carbon dioxide to nucleophilic metal complexes[6].

Incorporation of carbon dioxide, on the other hand, deals with the formation of $C-CO_2$, $N-CO_2$, or $O-CO_2$ bonds. These reactions are consistent with the ready reactivity of CO_2 towards nucleophiles, and in some cases can be used in catalytic processes[7,8,9]. As the formation of a carbon–element bond between the carbon atom of CO_2 and the substrate is required, it is not surprising that this chemistry does not make much use of the coordination chemistry of CO_2[6]. The use of metal systems may nevertheless constitute an important stage in the stoichiometric CO_2 incorporation processes. The formation of a metal–oxygen bond is, for example, involved in the stoichiometric $C-C$ coupling of CO_2 with olefins[10] and with organometallic compounds[11].

In $N-CO_2$ adducts, the presence of a metal may help to stabilize the carbamato anion obtained from the interaction of a secondary amine with carbon dioxide[12a], and this led us to the synthesis and characterization of transition metal *N,N*-dialkylcarbamato complexes of the general formula $[M(O_2CNR_2)_n]_m$[12]. The literature reports several examples of carbamates used as precursors in the preparation of urethanes from CO_2[13], and we have shown that metal-assisted electrophilic reactions may be performed on the oxygen atoms of the CO_2 moiety of metal carbamates[14], thus providing, for example, a facile synthesis of mixed carbamato-carboxylato anhydrides [see equation (1)].

$$M(O_2CNR_2)_n + n\,R'COCl \rightarrow MCl_n + n\,R_2NC(O)OC(O)R' \qquad (1)$$
$$M = Na^+, Ti(III), V(III), Mn(II), Co(II), Cu(II)$$

Examination of reaction (1) suggested that monosubstituted *N*-alkylcarbamates could be precursors of the unstable[15] *N*-alkylanhydrides, and their decomposition could eventually result in the formation of isocyanates[16].

In this paper we report the synthesis of *N*-alkylcarbamato complexes of manganese(II) and cobalt(II), and describe their reactions with acyl halides, reactions that result in the overall conversion of CO_2 and a primary amine to an isocyanate.

Syntheses of $[M(O_2CNHR)_2]_n$

Our general synthetic method for the preparation of transition metal *N,N*-dialkylcarbamato complexes[12] can be applied also to primary amines. By this route we prepared the manganese(II) and cobalt(II) *N*-cyclohexylcarbamato complexes [see equation (2)].

$$n\,MCl_2 + 2n\,[CyNH_3]^+\,[O_2CNHCy]^- \rightarrow [M(O_2CNHCy)_2]_n + 2n\,CyNH_3Cl \qquad (2)$$
$$M = Mn, Co$$

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Other amines led to difficulties in separating the products, but we have recently found that $MnCp_2$ ($Cp = \eta^5\text{-}C_5H_5$) is an appropriate starting material[12b], and we report here its use for the preparation of various monoalkyl derivatives [see equation (3)].

$$n\,MnCp_2 + 2n\,CO_2 + 2n\,RNH_2 \rightarrow [Mn(O_2CNHR)_2]_n + 2n\,CpH \qquad (3)$$
$$R = Ph, Pr, Cy$$

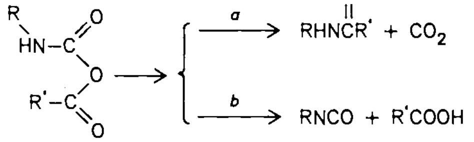
Although the solid-state structures of these compounds have not been determined, their low solubility and the fact that the corresponding dialkylcarbamato complexes (where no hydrogen bond can be present) were found to be hexanuclear[12a,b], precludes a monomeric formulation. The sodium *N*-propylcarbamate $[Na(O_2CNHPr)]_n$ was prepared by treating the corresponding ammonium carbamate with sodium sand[17].

Reaction with R'COCl and Formation of Isocyanates

When a suspension of the metal carbamate in a hydrocarbon medium was treated with a stoichiometric amount of acyl halide R'COCl (R' = Ph, Me), we observed the formation of the corresponding isocyanate RNCO (see Table, entries 1 – 8). Isotopic labelling of the starting complex with $^{13}CO_2$ confirmed that the carbonyl group was derived from CO_2 [$\tilde{\nu}(N^{13}CO) = 2209\ cm^{-1}$ vs. $2260\ cm^{-1}$ for $\tilde{\nu}(N^{12}CO)$]. To ascertain the influence of the cation, we conducted some experiments with ammonium carbamates (see entries 9 – 11).

These reactions occurred at room temperature or lower, and were usually complete within a few hours. No unreacted carbamate was present at the end of the reaction, but the low yields of isocyanate are accounted for by the fact that its formation is always accompanied by evolution of CO_2 and formation of amide RNHC(O)R'. In some cases, the latter was the only product. By assuming that *N*-alkylcarbamato complexes react similarly to *N,N*-dialkylcarbamato ones [see reaction (1)], these observations could be explained by assuming two possible decomposition pathways starting from the mixed anhydride, as shown in Scheme 1. Both paths *a*[15] and *b*[16] have been reported in the literature.

Scheme 1



Several facts, however, were at odds with the intermediacy of the mixed anhydride. The results obtained for different cations (see Table) cannot be ascribed to the decomposition of a common organic intermediate[18]. Scheme 1 also implies that carboxylic acid should be observed among the products; however, for Mn and Co carbamato derivatives (i. e. when the isocyanate yield is higher), we observed the carboxylic anhydride instead. A third, and perhaps the major inadequacy of the Scheme comes from the consideration that pathway *b* represents a thermodynamically forbidden transformation, as follows from the subsequent discussion.

Table. Major products[a)] observed in the reaction[b)] of $M(O_2CNHR)_n$ with R'COCl

Run	M	R	R'	*n*	Solvent	RNCO[c)]	$\mathrm{RNH\overset{O}{\overset{\|}{C}}R'}$[d)]	$\mathrm{R'\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R'}$
1	Mn	Ph	Ph	2	toluene	2	1	f)
2	Mn	Ph	Me	2	*n*-pentane	7	e)	f)
3	Mn	Pr	Ph	2	toluene	3	e)	f)
4	Mn	Pr	Me	2	*n*-pentane	40[g)]	e)	e)
5	Mn	Cy	Me	2	*n*-pentane	40	52	12
6	Co	Cy	Me	2	*n*-pentane	42	41	23
7	Na	Pr	Ph	1	toluene	2	e)	f)
8	Na	Pr	Me	1	*n*-pentane	16	e)	f)
9	$PrNH_3$	Pr	Ph	1	toluene	0	50	f)
10	$PrNH_3$	Pr	Me	1	*n*-pentane	0	e)	f)
11	$CyNH_3$	Cy	Me	1	*n*-pentane	2	e)	f)

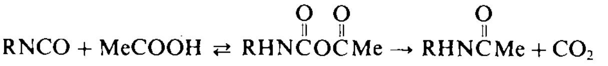
a) Other compounds were observed in lower amounts (see Experimental). – b) For reaction conditions, see Experimental. – c) Yields, determined spectroscopically. – d) Isolated product. – e) Yield not determined. – f) Not detected. – g) In toluene as solvent, the yield dropped to 10%.

Decomposition of Mixed Anhydrides

Disubstituted *N,N*-dialkyl anhydrides of the type $R_2NC(O)OC(O)R'$ may lose CO_2 with formation of amides $R_2NC(O)R'$[19]. As far as *N*-monosubstituted anhydrides are concerned, they can be obtained by the reaction of carboxylic acids with isocyanates[15], but they can be isolated only in a limited number of cases[15c]. They usually decompose thermally to give amides and CO_2 or to give ureas and carboxylic anhydrides, depending on the nature of R and R' and on the reaction conditions[15b].

We checked this reactivity in the following cases *A* and *B*.

A) Acetic acid reacts smoothly at room temperature with both phenyl and *n*-propyl isocyanates, to give only amide and CO_2 [reaction (4)]. In the latter case the intermediacy of the mixed anhydride could be inferred from the IR spectra (see Experimental), but in both cases the consumption of isocyanate was complete.



$$RNCO + MeCOOH \rightleftarrows RHN\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}Me \rightarrow RHN\overset{O}{\overset{\|}{C}}Me + CO_2 \qquad (4)$$

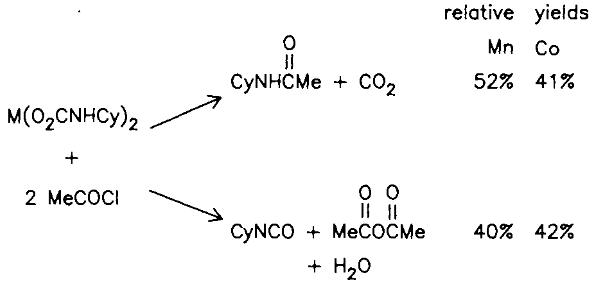
Thus, on thermodynamic grounds, isocyanate and carboxylic acid formation by decomposition of the anhydride should not take place[20].

B) The reaction between benzoic acid and *n*-propyl isocyanate showed different behaviour: the mixed anhydride was found to exist in equilibrium with the starting reagents. Rather than formation of the amide, thermal decomposition to isocyanate and acid was observed. Similar situations have already been reported for the interaction of acyl[16b] or phenyl[16a] isocyanates with benzoic acid. The relative stability of the Ph/Pr combination for the anhydride accounts for its observation in run 3 (two strong absorptions at 1780 and 1730 cm^{-1} were evident in the IR spectrum of the reaction mixture, see Experimental).

Mechanism of Formation of Alkyl Isocyanate

For both $[Mn(O_2CNHCy)_2]_n$ and $[Co(O_2CNHCy)_2]_n$ as starting materials, we identified all the reaction products, and determined the relative yields; the results are shown in Scheme 2. The metal was recovered as the metal chloride complexed to one or more of the reaction products.

Scheme 2

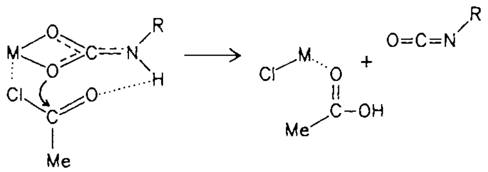


No other product (for example *sym*-dialkylurea[15b,c]) could be detected, and these data show that two parallel reaction pathways are followed.

The formation of the *N*-alkylamide can be ascribed, a) to the decomposition of the mixed anhydride obtained by addition of the acyl chloride to the oxygen atom of the carbamate, or b) to the direct reaction of acetyl chloride with the nitrogen atom. At the present time no clearcut distinction between the two possibilities can be made.

On the other hand, we can envisage a possible interaction giving rise to alkyl isocyanate (see Scheme 3).

Scheme 3



Two acetic acid groups, bound to the same or to different metal centres, would then be dehydrated, and acetic anhydride released into solution, while water remains bound to the metal. The formation of a mixed carbamato – carboxylato anhydride is no longer required, and coordination of one of the products to the metal drives the system towards the otherwise unfavourable transformation. Formation of water has two distinct advantages for the successful isolation of isocyanates. The hydration enthalpy of the metal halide contributes favourably to the free-energy balance, and the presence of acetic anhydride, rather than acetic acid, in solution with the alkyl isocyanate, results in a stable system[21]. The reaction of $Na(O_2CNHPr)$ with MeCOCl may represent a special case, probably because of the large difference between the ΔH^0_{hydr} of Na^+ (-95 kcal/mol[23]) and those of both Mn^{2+} and Co^{2+} (-438 and -490 kcal/mol, respectively[23]). This easily accounts for the failure to observe dehydration, acetic acid being only physically adsorbed on sodium chloride.

In addition to these thermodynamic considerations, we must consider a kinetic effect, by which the incipient formation of a chloride – metal bond would direct the attack of the acyl group on the carbamato oxygen. Also on the basis of earlier results[17] with MeI, it is to be noted that *O*-attack by electrophiles should be regarded as a kinetically controlled reaction.

The overall process from CO_2 to alkyl isocyanates corresponds to the deoxygenation of carbon dioxide [see equation (5 – 7)].

$$2CO_2 + 4RNH_2 + MCl_2 \rightarrow M(O_2CNHR)_2 + 2RNH_3Cl \quad (5)$$

$$M(O_2CNHR)_2 + 2MeCOCl \rightarrow 2RNCO + MeC(O)OC(O)Me + H_2O + MCl_2 \quad (6)$$

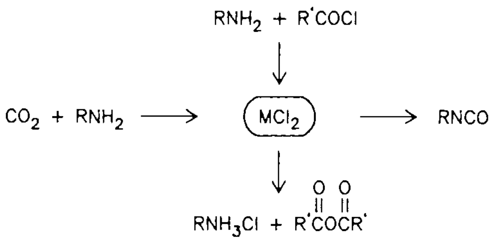
$$2CO_2 + 4RNH_2 + 2MeCOCl \rightarrow 2RNCO + MeC(O)OC(O)Me + 2RNH_3Cl + H_2O \quad (7)$$

Deoxygenation of CO_2 to CO is a well-established process. It requires an oxygen sink, and reported examples include the CO_2 itself[24], a metal[25] or a phosphorus[26] atom or, in some cases, the carbon atom of a metal-bonded isocyanide[27].

The present reaction shows that it is also possible to achieve an effective functionalization of an organic molecule. Isocyanates are valuable organic intermediates[28], and non-phosgene routes to their synthesis may have significant applications.

From equation (7) it follows that the metal chloride is not involved in the mass balance, so that the total transformation may be described as a metal-assisted reaction. In a pictorial way, Scheme 4 shows that the thermodynamically forbidden[29] conversion of CO_2 and RNH_2 to RNCO and H_2O, has been accomplished by the simultaneous conversion of amine and acyl chloride to ammonium salt and carboxylic anhydride.

Scheme 4



The formation and reactivity of metal – oxygen bonds are the keypoints in this scheme, and this seems to be a general clue for the extension of synthetic uses of carbon dioxide.

This reaction can be compared with the reported[31] syntheses of symmetric dialkylureas from amines and CO_2, which also represent a productive deoxygenation of the CO_2 group mediated by carbamate formation. As far as the synthesis of isocyanates is concerned, two examples of the use of CO_2 for this purpose can be found in the literature: the high temperature decomposition of the adduct obtained from CO_2 and a phosphoramidate anion[32], and the reaction of an alkyl halide with a copper(I) isocyanate complex, obtained by a copper(I) silylamide and CO_2[33].

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Experimental

All of the operations were carried out under an inert atmosphere of prepurified nitrogen or argon. Solvents were dried by conventional methods. $PhNH_2$ was distilled from NaOH, while $PrNH_2$ and $CyNH_2$ were distilled from sodium – potassium alloy and kept over sodium sand. The acyl halides MeCOCl and PhCOCl were distilled and kept under nitrogen. Labelled $^{13}CO_2$ was prepared by decomposing $Ba^{13}CO_3$ (CEA, 90% enrichment) with concentrated sulphuric acid. Infrared spectra were measured with a Perkin-Elmer 283 spectrophotometer and the ^{1}H-NMR spectra with a Varian T 60 spectrometer. GC-MS analyses were run on a Dani 3800 gas chromatograph coupled to a Hewlett-Packard 5970 mass spectrometer. The CO_2 content of the carbamates was determined by gasvolumetric measurements after decomposition with 20% H_2SO_4; manganese and cobalt were determined by standard complexometric titration with EDTA. Bis(cyclopentadienyl)manganese(II), $MnCp_2$, was prepared according to the literature[34]. The organic products obtained in the subsequent reactions were identified by comparison (IR, ^{1}H-NMR) with pure samples, which were obtained commercially or prepared by straightforward routes (amides), i. e. from the appropriate amine and acyl chloride. The isocyanates were also identified by GC-MS analysis of the corresponding solutions.

Synthesis of $[Mn(O_2CNHPh)_2]_n$ (**1**): To a suspension of $PhNH_2$ (1.377 g, 14.79 mmol) in 30 ml of *n*-heptane, 1.359 g of $MnCp_2$ (7.34 mmol) was added, and the mixture was stirred for 3 d under atmospheric pressure of CO_2. A light yellow, insoluble solid was obtained, which was collected by filtration, washed with small volumes of *n*-heptane and toluene and dried in vacuo (2.388 g, 94% yield). – IR (nujol mull): 3320 m, 2980 – 2880 vs, 1600 s, 1580 s, 1530 s, 1500 sh, 1460 s, 1440 s, 1380 s, 1340 s, 1240 ms, 1180 w, 1150 w, 1080 w, 1050 w, 1030 mw, 990 w, 950 vw, 890 w, 870 vw, 795 m, 745 ms, 685 ms, 630 m, 500 m cm^{-1}. – Although the CO_2/Mn ratio in this compound was close to the theoretical value of 2 (average value, 1.89 for two determinations), satisfactory elemental analyses could not be obtained, and the low solubility of the material prevented its recrystallization. It was therefore used as such for the subsequent reactions.

Synthesis of $[Mn(O_2CNHPr)_2]_n$ (**2**): A solution of $PrNH_2$ (0.179 g, 3.03 mmol) in *n*-heptane (20 ml), was treated with $MnCp_2$ (0.286 g, 1.54 mmol). After 5 h, the manganocene had been totally transformed into a colourless solid; the mixture was stirred for about 12 h under atmospheric pressure of CO_2. This solid was then filtered, washed with 10 ml of toluene and dried in vacuo (288 mg, 72% yield). – IR (nujol mull): 3350 m, 2980 – 2880 vs, 1640 ms, 1570 vs, 1530 sh, 1460 s, 1440 s, 1370 s, 1360 sh, 1340 m, 1290 w, 1250 ms, 1140 w, 1060 mw, 1050 w, 970 vw, 870 vw, 805 m, 760 vw, 750 vw, 720 mw, 630 w, 590 w cm^{-1}.

$C_8H_{16}MnN_2O_4$ (259.2) Calcd. CO_2 34.0 Mn 21.2
Found CO_2 33.1 Mn 20.7
(CO_2/Mn, 2.00)

Synthesis of $[Mn(O_2{}^{13}CNHPr)_2]_n$: A Schlenk tube containing *n*-pentane (10 ml), $MnCp_2$ (463 mg, 2.5 mmol) and $PrNH_2$ (294 mg, 5.0 mmol) was prepared under argon, connected by a three-way stopcock to a flask charged under argon, with 1.390 g of $Ba^{13}CO_3$ (corresponding to 5.0 mmol of $^{13}CO_2$) and closed with a serum cap. The Schlenk tube was cooled to about –80°C and evacuated; concentrated sulphuric acid was then added by syringe through the serum cap, and when pressure buildup was evident, the three-way stopcock was opened and the gas from the flask allowed to diffuse into the Schlenk tube. After 1 h the Schlenk tube was warmed to room temperature, and $^{12}CO_2$ was introduced in order to be sure that all manganocene had reacted. When no more gas uptake was visible (3 h), a yellowish solid was present. The IR spectrum (nujol) measured on a small portion of this solid was identical with that of compound **2**, except for a shift to lower wavenumbers (20 – 30 cm^{-1}) of the bands at 1570, 1530, 1340, and 805 cm^{-1}. The *n*-pentane suspension was used directly for the reaction with MeCOCl (vide infra).

Synthesis of $[Mn(O_2CNHCy)_2]_n$ (**3**): A solution of $CyNH_2$ (9.537 g, 96.17 mmol) in THF (75 ml) was cooled to 0°C and saturated with CO_2. A thick, colourless solid formed after a few minutes, so that the solution became a single solid phase. Anhydrous $MnCl_2$ (2.950 g, 23.45 mmol) was added, and the mixture was gently warmed at about 50°C in a water bath. A liquid phase reappeared, and when no more gas uptake was observed (3 h) the colourless solid was filtered off (it was spectroscopically identical with a sample of pure cyclohexylammonium chloride; 5.407 g, 85% yield) and a clear orange solution was obtained. The latter was concentrated to half of its volume under reduced pressure, and 60 ml of *n*-heptane was added. A colourless, gelatinous solid precipitated out, which was filtered off and dried in vacuo for several hours (6.454 g, 81% yield). – IR (nujol mull): 3310 m, 2980 – 2880 vs, 1570 vs, 1520 s, 1460 s, 1380 ms, 1340 ms, 1280 mw, 1260 mw, 1240 sh, 1150 w, 1050 mw, 880 w, 800 mw, 720 mw, 640 w, 500 w cm^{-1}.

$C_{14}H_{24}MnN_2O_4$ (339.3) Calcd. CO_2 25.9 Mn 16.2
Found CO_2 25.0 Mn 15.4
(CO_2/Mn, 2.03)

Synthesis of $[Co(O_2CNHCy)_2]_n$ (**4**): A solution of $CyNH_2$ (7.803 g, 78.68 mmol) in toluene (50 ml) was saturated with CO_2 to give a colourless solid. After the addition of anhydrous $CoCl_2$ (2.500 g, 19.23 mmol), a blue liquid phase appeared. The mixture was stirred for about 12 h under atmospheric pressure of CO_2, and the solid was then filtered off. The blue solution was evaporated to dryness to give a blue microcrystalline solid (5.235 g, 79% yield). – IR (nujol mull): 3310 m, 2980 – 2880 vs, 1570 vs, 1520 vs, 1460 vs, 1380 s, 1340 s, 1280 mw, 1260 mw, 1240 sh, 1150 w, 1050 m, 960 w, 885 mw, 800 m, 720 m, 640 w, 580 w, 460 w, 440 w cm^{-1}.

$C_{14}H_{24}CoN_2O_4$ (343.3) Calcd. CO_2 25.6 Co 17.2
Found CO_2 25.0 Co 16.8
(CO_2/Co, 2.00)

Synthesis of $Na(O_2CNHPr)$ (**5**): A suspension of compound **6** (2.609 g, 16.08 mmol) in THF (30 ml) was treated with a stoichiometric amount of sodium sand (0.400 g, 17.39 mmol) under a nitrogen atmosphere. Rapid hydrogen evolution was observed; however, the suspension soon reverted to a colourless foam that was impossible to stir. Addition of 50 ml of THF and 50 ml of *n*-heptane, followed by warming of the reaction flask at about 60°C in a water bath, yielded a grey suspension. This was stirred until no more metallic sodium was present (30 h). Filtration and drying afforded 1.681 g of the colourless sodium derivative (84% yield). – IR (nujol mull): 3450 sh, 3330 m, 2980–2880 vs, 1590 vs, 1460 vs, 1380 s, 1340 ms, 1320 m, 1240 w, 1160 m, 1150 m, 1110 w, 1030 w, 970 vw, 880 w, 820 sh, 810 ms, 760 w, 740 sh, 715 m, 600 mw, 560 w, 450 w cm^{-1}.

$C_4H_8NNaO_2$ (125.1) Calcd. CO_2 35.2
Found CO_2 35.2

Synthesis of $(PrNH_3)(O_2CNHPr)$ (**6**): A solution of $PrNH_2$ (10 ml, 121.3 mmol) in 100 ml of *n*-heptane was saturated with CO_2. When gas uptake was over, the colourless solid present was filtered off and dried in vacuo (4.958 g, 50% yield). – IR (nujol mull): 3320 m, 2980–2880 vs, 2210 m, 1670 sh, 1600 s, 1550 s, 1520 sh, 1490 vs, 1460 vs, 1380 s, 1350 s, 1330 sh, 1290 s, 1240 ms, 1200 ms, 1185 m, 1160 m, 1140 ms, 1080 m, 1045 ms, 960 m, 895 w, 870 w, 830 sh, 810 s, 760 ms, 740 ms, 710 ms, 650 ms, 610 sh, 580 w, 460 m cm^{-1}.

$C_7H_{18}N_2O_2$ (162.2) Calcd. CO_2 27.1
Found CO_2 26.7

Synthesis of $(CyNH_3)(O_2CNHCy)$ (**7**): This compound was synthesized in a manner analogous to the previous one. Starting from 1.730 g of $CyNH_2$ (17.4 mmol) in 100 ml of *n*-heptane, 1.416 g of the colourless **7** was obtained (67% yield). – IR (nujol mull): 3400 mw, 3300 m, 2980–2880 vs, 2780–2500 s (broad, multiple absorption), 2200 mw, 1625 s, 1590 vs, 1545 s, 1460 vs, 1380 s, 1340 s, 1325 s, 1280 m, 1250 m, 1235 m, 1180 w, 1160 m, 1140 mw, 1080 w, 1060 w, 1050 m, 1035 sh, 960 mw, 920 vw, 885 m, 890 w, 820 sh, 810 ms, 800 m, 780 vw, 705 ms, 685 m, 550 w, 500 mw, 460 mw, 450 mw, 400 w cm^{-1}.

$C_{13}H_{26}N_2O_2$ (242.4) Calcd. CO_2 18.2
Found CO_2 17.9

Reaction of **1** *with PhCOCl:* To a toluene (50 ml) suspension of **1** (1.366 g, 4.18 mmol), 0.97 ml of PhCOCl (1.176 g, 8.36 mmol) was added, and the mixture was stirred for 24 h at room temperature. After this time, a pink solid was present, while the liquid phase was virtually colourless and its IR spectrum showed two weak absorptions due to CO_2 (2320 cm^{-1}) and PhNCO (2250 cm^{-1}) in addition to a third weak band at 1680 cm^{-1}. On filtration and cooling to –80°C, colourless crystals precipitated out, which were collected and identified as PhC(O)NHPh [IR (KBr): $\tilde{\nu}_{CO}$ 1660 cm^{-1}]. The mother liquor was evaporated to dryness; a few drops of an oily substance were left, whose IR spectrum was the sum of those recorded for pure samples of PhCOCl and PhNCO.

Reaction of **1** *with MeCOCl:* A suspension of **1** (0.320 g, 0.98 mmol) in *n*-pentane (15 ml) was treated with MeCOCl (0.154 g, 1.97 mmol) to give a light pink solid suspended in a colourless solution, whose IR spectrum showed only two weak absorptions due to CO_2 and PhNCO. After 20 h, the solid was filtered off and extracted with 5 ml of toluene. Evaporation of the extract left an oily residue, which was heated at 70°C under reduced pressure (0.1 Torr). A small amount of a colourless solid was collected on a cold finger and identified as MeC(O)NHPh.

Reaction of **2** *with PhCOCl:* Compound **2** (0.707 g, 2.73 mmol) was suspended in toluene (25 ml) and treated with PhCOCl (0.788 g, 5.60 mmol) at room temperature. After 6 d, the IR spectrum of the liquid phase did not show any further change, and showed absorptions in the CO stretching region at 2320 mw [CO_2], 2260 m [PrNCO], 1780 m, 1730 m, 1670 m + 1510 w [PrNHC(O)Ph] cm^{-1}. The solid was filtered off and the solution distilled at atmospheric pressure. The first fraction collected (b. p. 84–86°C) was composed of PrNCO and toluene. The second fraction was mainly toluene. A residual brown oil remained, whose IR spectrum showed, in addition to the absorptions due to PhCOCl, PhC(O)NHPr, and toluene, strong bands at 1780 and 1730 cm^{-1}. These bands were still present in the case of the colourless oil collected on a cold finger after heating the residue to 200°C at 0.05 Torr.

Reaction of **2** *with MeCOCl:* A suspension of **2** (2.568 g, 9.90 mmol) in 50 ml of *n*-pentane was treated with MeCOCl (1.54 g, 19.6 mmol), while the flask was cooled in an ice bath. The reaction was followed by IR. The disappearance of MeCOCl was paralleled by the appearance of a band at 2260 vs cm^{-1}, due to PrNCO, and of additional bands, of lower intensity, at 1840 m, 1770 m and 1130 s cm^{-1}, due to acetic anhydride. After 22 h the reaction was over. A colourless solid was present, which was filtered off and heated to 150°C at 0.05 Torr. A colourless liquid [PrNHC(O)Me] was collected on a finger cooled to 15°C, while a few drops of a colourless liquid [MeCOOH] condensed in a trap cooled to about –80°C. The mother liquor was distilled at atmospheric pressure to give a mixture of *n*-pentane and PrNCO (b. p. 40°C). The residue was distilled under reduced pressure (20°C/1 Torr), and 258 mg of a colourless liquid was collected at about –80°C, containing a mixture of PrNCO and acetic anhydride.

When a stoichiometric amount of MeCOCl was added to the *n*-pentane suspension of $[Mn(O_2{}^{13}CNHPr)_2]_n$ at –30°C, an analogous reaction was observed, and IR monitoring showed the presence, in addition to the bands observed in the previous case, of a strong absorption at 2209 cm^{-1}, attributed to $PrN^{13}CO$ [calculated value for $\tilde{\nu}(N^{13}CO)$ = 2211 cm^{-1}].

Reaction of **3** *with MeCOCl:* Compound **3** (2.060 g, 6.07 mmol) was suspended in 25 ml of *n*-pentane and treated with 0.95 g of MeCOCl (12.10 mmol) at room temperature. After 24 h, all of the acetyl chloride had reacted, and no further change was observed (IR of the mixture). The IR spectrum showed absorptions at 2320 m (CO_2), 2260 vs (CyNCO), and 1840 m + 1770 m (Ac_2O) cm^{-1}. From the intensity of the absorption bands at 2260 and 1840 cm^{-1}, the concentrations of the corresponding species could be measured (ε_{2260} = 1500 M^{-1} cm^{-1}; ε_{1840} = 500 M^{-1} cm^{-1}); 4.8 mmol of CyNCO and 1.4 mmol of Ac_2O were found. The isocyanate could not be easily purified by routine distillation, and after three consecutive distillations a 7% yield of product was obtained, whose IR spectrum still showed the absorption pattern of acetic anhydride. A colourless solid was present in the reaction mixture, and it was collected by filtration and dried briefly in a stream of nitrogen (1.697 g). A part of it was extracted with Et_2O; the IR spectrum of the solution showed absorptions due to Ac_2O and CyNHC(O)Me. This solid (368 mg) was heated up to 300°C under reduced pressure (0.05 Torr), and the volatile fractions collected at 20 and –80°C. The cold finger at 20°C was covered with a colourless solid, identified by IR as pure CyNHC(O)Me (194 mg); the trap at about –80°C contained a few drops of a colourless liquid, found to be a mixture of H_2O and MeCOOH. The solid left as residue after this treatment (131 mg) was analyzed and found to contain Cl (53.4%) and Mn (40.6%; Cl/Mn ratio 2.04), corresponding to at least 95% pure $MnCl_2$ (calcd. Cl 56.3; Mn 43.6). Its IR spectrum of a nujol mull (prepared under prepurified nitrogen) showed only absorptions at 3500 w, 3450 w and 1605 w cm^{-1}, due to lattice water.

Reaction of **4** *with MeCOCl:* A blue suspension of **4** (2.224 g, 6.54 mmol) in *n*-pentane (50 ml) was allowed to react with MeCOCl (1.02 g, 13.09 mmol) for 3 h. A sky blue solid was formed, and the

IR spectrum of the colourless liquid phase in the CO stretching region showed only absorptions at 2320 w (CO_2), 2260 vs (CyNCO), and 1840 m + 1770 m (Ac_2O) cm^{-1}. As in the preceding reaction, the concentrations of the organic products were measured by IR, and found to correspond to 5.5 mmol of CyNCO and 3.0 mmol of Ac_2O. The solid was filtered off and dried briefly in vacuo (1.469 g); its IR spectrum as a nujol mull showed the bands corresponding to CyNHC(O)Me, but the $\tilde{\nu}_{CO}$ value was shifted to 1600 cm^{-1} (1640 cm^{-1} in the pure compound), thus indicating coordination to the cobalt cation. A portion (1.197 g) of the solid was heated up to 300°C under reduced pressure (0.5 Torr), and the volatile fractions were collected as before. On the cold finger, pure CyNHC(O)Me was collected (623 mg), while in the cold trap a few drops of a colourless liquid condensed, identified as a mixture of H_2O and AcOH. The sublimation left a blue residue (353 mg), whose IR spectrum of a nujol mull (prepared as described above) showed only weak absorptions due to lattice water. Analysis of the blue solid residue gave the following values: Cl 53.1; Co 43.6; Cl/Co 2.02; corresponding to $CoCl_2$ (calcd. Cl 54.6; Co 45.4) with a purity of about 97%.

Reaction of **5** *with PhCOCl:* To a toluene (30 ml) suspension of **5** (0.506 g, 4.04 mmol), 0.545 g of PhCOCl (3.88 mmol) was added, and the mixture stirred at room temperature. After 1 h the reaction was complete, and the IR spectrum of the liquid phase showed the presence of CO_2 (2320 s cm^{-1}), PrNCO (2260 w cm^{-1}), and PrNHC(O)Ph (1670 s + 1510 m cm^{-1}). A colourless solid was present, which was collected by filtration, washed with acetone, oven-dried, and identified as NaCl (210 mg, 89% yield).

Reaction of **5** *with MeCOCl:* Compound **5** (0.311 g, 2.48 mmol) was suspended in 15 ml of *n*-pentane, and MeCOCl (0.194 g, 2.46 mmol) was added. The starting colourless solid was converted slowly to a grey, gummy solid. After 5 h, all of the acetyl chloride had reacted, and the IR spectrum of the liquid phase showed absorptions at 2260 s (PrNCO), 1720 w (AcOH), 1655 m and 1550 vw (PrNHC(O)Me) cm^{-1}. No absorption due to acetic anhydride could be detected. The gummy solid was separated by filtration and extracted with diethyl ether (10 ml). A colourless powder was left, identified as NaCl (92 mg, 64% yield). The ether solution was evaporated to yield a small amount of a colourless liquid, whose IR and ^{1}H-NMR spectra were the sum of those due to MeCOOH and PrNHC(O)Me.

Reaction of **6** *with PhCOCl:* Compound **6** (0.549 g, 3.38 mmol) was suspended in toluene (30 ml) and stirred for about 12 h with PhCOCl (0.473 g, 3.36 mmol). The IR spectrum of the final reaction mixture showed only absorptions due to CO_2 and PrNHC(O)Ph. A colourless solid was present, which was filtered off and dried, and whose IR spectrum of a nujol mull was identical with that of an authentic sample of $PrNH_3Cl$ (242 mg, 75% yield). The mother liquor was concentrated to half of its volume and cooled to −30°C. After 10 days, 264 mg of PrNHC(O)Ph (50% yield) was obtained after filtration of the cold solution.

Reaction of **6** *with MeCOCl:* An *n*-pentane (15 ml) suspension of **6** (0.170 g, 1.05 mmol) was cooled to 0°C, and MeCOCl (82 mg, 1.04 mmol) was added. After 2 h, all of the acetyl chloride had reacted, as shown by the IR spectrum of the liquid phase, which did not display any absorption in the 2500−1000 cm^{-1} region. A colourless solid was present, whose IR spectrum of a nujol mull was the sum of those of $PrNH_3Cl$ and PrNHC(O)Me. These could be separated by extraction of the amide with toluene.

Reaction of **7** *with MeCOCl:* To an *n*-pentane (50 ml) suspension of **7** (1.06 g, 4.48 mmol), MeCOCl (0.351 g, 4.48 mmol) was added. After 3 h, all of the acetyl chloride had reacted, and the IR spectrum of the liquid phase in the carbonyl stretching region showed absorptions at 2260 w (CyNCO) and 1720 vw (MeCOOH) cm^{-1} only. A colourless solid was present, which was collected by filtration (1.057 g), and whose IR spectrum of a nujol mull was the sum of those of $CyNH_3Cl$ and CyNHC(O)Me.

Interaction between PhNCO and MeCOOH: Equimolar amounts of PhNCO and MeCOOH were allowed to react in a toluene solution, without stirring. Periodic analysis of the IR spectrum of this solution in the 2500−1000 cm^{-1} region showed only a steady decrease of the absorptions due to the starting compounds, while colourless needles began to separate out shortly after mixing. After 24 h, no more isocyanate was detected in the solution; the solid was separated by filtration, washed with *n*-pentane, and identified as PhNHC(O)Me by its IR and ^{1}H-NMR spectra.

Interaction between PrNCO and MeCOOH: This reaction was followed by IR monitoring (4000−1000 cm^{-1}) of an equimolar mixture of the two compounds, either without solvent or in concentrated toluene solution. In both cases, new bands appeared at 3330 m, 1780 s, 1730 vs, 1530 m, 1370 m, 1250 m, 1170 ms cm^{-1} shortly after mixing. After 1 h, a new band at 1660 cm^{-1} appeared, whose intensity increased steadily with time, while the former bands decreased. After 24 h, only absorptions at 3300 m, 1660 vs, 1550 ms, 1360 w, 1250 m cm^{-1} were present, corresponding to pure PrNHC(O)Me. When the reaction was carried out in *n*-pentane, no intermediate compound was observed by IR spectroscopy, and after 24 h, almost total conversion to PrNHC(O)Me had taken place.

Interaction between PrNCO and PhCOOH: When equimolar amounts of benzoic acid and isocyanate were stirred together, slow dissolution of the acid was observed, accompanied by the conversion of the liquid to a jelly-like syrup. After 1 h, nearly all of the solid had dissolved, and the IR spectrum (KBr windows) of the syrup showed, among others, strong absorptions at 1770, 1730, 1215, 1085, 1055, 1020, and 705 cm^{-1}. No absorption due to PhCOOH was detected, while a weak band at 2270 cm^{-1} (PhNCO) was still present. When this syrup was dissolved in toluene, a dramatic change in the IR spectrum was observed; the absorptions due to benzoic acid and to isocyanate were the most intense ones, while weak bands at 1780 and 1730 cm^{-1} were present. This spectrum displayed the same overall pattern and the same relative intensity of the absorptions as that obtained after mixing the pure compounds in toluene solution, and it did not change after prolonged standing at room temperature or after a short period at reflux. A portion of the preceding syrup was heated to 100°C under reduced pressure (2 Torr) for 10 minutes. It reverted totally to a colourless solid (PhCOOH), while a colourless liquid condensed in a trap cooled at about −80°C (PrNCO). No other compound seemed to be produced by this treatment.

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