Converting Carbon Dioxide into Carbamato Derivatives[†]

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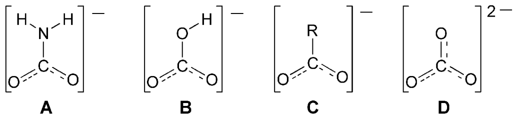
Contents

1. Introduction

This review article covers compounds containing the monoanionic *N*,*N*-dialkylcarbamato ligand, of formula $O_2CNR_2^{(-)}$, R being H, an alkyl-, or an aryl group. Due to their relatively recent appearance in the literature, the metal-containing compounds of this class are believed to be covered exhaustively by this review. On the other hand, the R_2NH/CO_2 system, which is the basis for the subsequent development of this chemistry, has attracted the earlier interest of researchers since the beginning of last century, especially in connection with industrially relevant processes. Therefore, section 2 will be dedicated to a discussion of the available scientific information on the interaction of carbon dioxide with ammonia, and with primary and secondary amines.

The $O_2CNR_2^{(-)}$ ligand carries a single negative charge in ionic compounds, for example, in the dialkylammonium derivatives $[NH_2R_2][O_2CNR_2]$, and contributes by one unit to the oxidation state in metal-containing covalent combinations. Compounds containing this function are called "carbamates", and they are formulated as $[M(O_2CNR_2)_n]_m$, *n* and *m* being the oxidation number of the central atom M and the nuclearity of the system, respectively. These compounds are named after considering that they are formally derivatives of carbamic acid H_2NCO_2H. This compound shares with carbonic acid $HOCO_2H$ the important property to be reluctant to isolation, whereas the corresponding anions $H_2NCO_2^-$ (**A**) and $HOCO_2^-$ (**B**) are well established, vide infra (Scheme 1).

Scheme 1



Other anionic species containing a "CO_2" fragment occupy a central role in chemistry and are well established, namely, the carboxylato (**C**) and the carbonato (**D**) anions, all formally deriving from carbon dioxide. The first clear evidence of the chemical relation between carbonates and carbon dioxide probably goes back to experiments carried out at the

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[†] Dedicated to the memory of Professor Salvatore (Turi) Castellano, who rewarded us with his friendship, in recognition of his outstanding scientific contributions.

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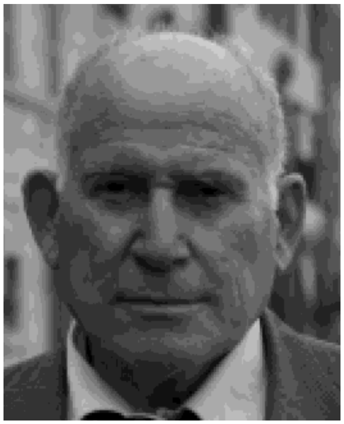
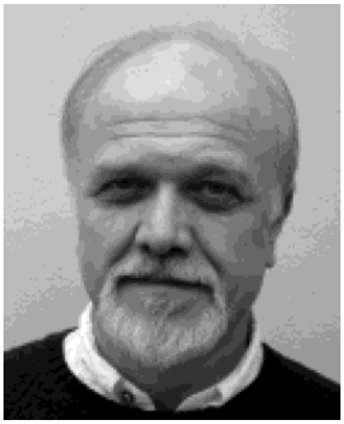
Daniela Belli Dell'Amico was born in 1947. She graduated in Chemistry at the University of Pisa. After a postdoctoral fellowship (1972–1974) with Professor Fausto Calderazzo, she became Assistant Professor and then Associate Professor at the Dipartimento di Chimica e Chimica Industriale of the University of Pisa. Her main fields of research are the chemistry of metal *N,N*-dialkylcarbamato complexes and the study of late transition metal carbonyl compounds.



Fausto Calderazzo graduated from the University of Florence, Italy, his mentor being L. Sacconi. From 1954 to 1962, he was a research associate at the Istituto Chimica Industriale, Politechnic Institute of Milan, Italy, and from 1960 to 1961, an A. P. Sloan Foundation fellow at the Massachusetts Institute of Technology, Cambridge, MA. He has served as a research associate (1963–5) and Director of Research (1965–8) for Synthetic Inorganic Chemistry Group, Cyanamid European Research Institute, Geneva, Switzerland, and Professor of General and Inorganic Chemistry (1968–2002) for University of Pisa, Italy; presently he is Professor of the University of Pisa without teaching duties. Before moving to Pisa he enjoyed being associated with the following scientists: R. Ercoli and G. Natta (1954–60), F. A. Cotton (1960–1), E. Weiss (1963–5). He has published about 290 scientific papers on (a) metal carbonyls of early and late transition metals, (b) the mechanism of insertion reactions in metal–carbon bonds, (c) carbamato complexes of transition and Main Group elements, (d) metal–arene and metal–cyclopentadienyl derivatives, (e) metal/ligand affinities studied by Group trends, and (f) surface coordination chemistry. Professor Calderazzo is a member of the following international scientific committees: International Conferences of Organometallic Chemistry, Advisory Board of International Symposia on Homogeneous Catalysis, and a present or past member of the editorial boards of *J. Chem. Soc.-Dalton Trans.*, *Organometallics*, *Inorg. Syn.*, *Gazz. Chim. Ital., J. Organometal. Chem.* (in the Emeritus Honorary Board since 2002), and *Comments Inorg. Chem*. He has been a member of Istituto Lombardo di Scienze e Lettere and of Accademia Nazionale dei Lincei (National Academy,corresponding member) since 1989 and is an honorary member of Società Chimica Italiana and Societé Chimique de Belgique. He has received awards from national institutions in 1988, 1990, and 1994 and was a recipient of the L. Sacconi Medal in 1998. Professor Calderazzo has been a full member of Accademia Nazionale dei Lincei since November 1999.

University of Glasgow, where in 1754 it was shown that CO_2 is produced by heating $MgCO_3$ or $CaCO_3$.[1]

Luca Labella graduated in Chemistry at the University of Pisa in 1988 and received his Ph.D. from the Scuola Normale Superiore under the supervision of Professor Fausto Calderazzo in 1992, after a three-year program, partially spent in the laboratories of Professor F. A. Cotton at Texas A&M University (January 1991 through December 1991). He then moved in 1993 to Oxford in the laboratories of Professor M. L. H. Green with a postdoctoral fellowship from Accademia Nazionale dei Lincei, and from 1995 he has been Researcher at the University of Pisa. His research interests are primarily in the synthesis of metal dialkylcarbamates and in the synthesis of inorganic and organometallic complexes of late transition metals.



Fabio Marchetti was born in 1950 and graduated in Chemistry at the University of Pisa in 1974. In the following years he carried on his research activity at the University of Pisa by specialising in solid-state chemistry and structural studies. In 1998 he was promoted Associate Professor of Chemistry and moved to the University "La Sapienza" of Roma, Faculty of Engineering. He returned to the University of Pisa in 2001.

The corresponding anions with sulfur completely or partially substituting oxygen are well-known. For example, the dithiocarbamato-,[2a] thiocarboxylato-,[3a] or trithiocarbonato metal complexes are usually easily obtained through syntheses involving CS_2.[4] These compounds will be considered only marginally within this review article. However, it is of interest to note that one of the first metal dithiocarbamato complexes dates back to 1907,[2b] when the dialkyldithiocarbamates of copper(II) of formula $Cu(S_2CNR_2)_2$ were isolated. *N*,*N*-Dialkyldithiocarbamates of some transition metals were further investigated in the thirties of last century for their interesting magnetic properties,[2c,d] while the free acid H_2NCS_2H, although being of a limited stability, was isolated as early as 1867,[2e] being obtained by acidification of a concentrated solution of the ammonium derivative $NH_4[S_2CNH_2]$. However, it was not until very recently that two derivatives of dithiocarbamic acid

Guido Pampaloni was born in 1955; he received his Degree in Chemistry from the University of Pisa in 1979. After a postdoctoral fellowship at RWTH in Aachen (Germany) with Prof. G. E. Herberich (1979–1980), in 1983 he received his Ph.D. in Chemistry from the Scuola Normale Superiore of Pisa. Since 1992, G. Pampaloni has been an associate professor at the Dipartimento di Chimica e Chimica Industriale of the University of Pisa. His main interests concern the synthesis and the reactivity of inorganic and organometallic compounds of early transition elements.

have been investigated by X-ray diffraction methods, namely potassium 3-dithiocarboxy-3-aza-5-aminopentanoato, $K[O_2CCH_2NC(S)SHCH_2CH_2NH_2]\cdot 2H_2O$ {**RAVKUU**-CSD},[2f] and *N*-(2-aminoethyl)dithiocarbamic acid, $^{(+)}H_3N(CH_2)_2NHCS_2{}^{(-)}$, which has been established to exist as its zwitterionic form {http://journals.iucr.org/e/issues/2002/03/00/issconts.html}.[2g]

Within the category of metal complexes containing a "CO_2" fragment in their composition, mention should be made of the fact that the first metal carboxylato derivatives were discovered and recognized as such much earlier,[5a] and, of course, the corresponding acids are chemicals of fundamental importance and extensive use. For example, the simplest carboxylic acid HCOOH (mp, 8.26 °C) was obtained as a 99.9% pure substance in 1928.[5b] On the other hand, the preparation of pure samples of the so-called glacial acetic acid (mp 16.55 °C) goes back to early experiments carried out at the beginning of last century.[5c] The $CO_2/CaCO_3$ equilibrium, which is the basis of the chemistry of cement, has played an important role in the study of heterogeneous equilibria, the carbon dioxide pressure (mmHg) as a function of temperature being[6] 420 (1130 K), 716 (1167 K), 773 (1173 K), 1490 (1223 K), and 2710 (1273 K).

As far as derivatives containing the carbon dioxide fragment are concerned, carbamic acid itself H_2NCO_2H and its derivatives are thermally unstable, and the isolation and structural characterization of the dibenzyl derivative Bz_2NCO_2H, is quite recent, vide infra.[7a] The elusive character of carbamic acid derivatives originates from their tendency to lose carbon dioxide, thus reverting to the amine. The basis of the different behavior between carbamic and dithiocarbamic acids is presumably thermodynamic in nature, about 460 kJ mol^{-1} separating the enthalpy of formation of CO_2 from that of CS_2. The chemistry of carbamato metal complexes is quite recent in the scientific literature, its development dating back to the 1970s. The first homoleptic derivative of this class, tetrakis(*N*,*N*-dimethylcarbamato)titanium(IV), of formula $Ti(O_2CNMe_2)_4$, was reported in 1965[7b,c] and was synthesized by exhaustive carbonation of the dimethylamido precursor $Ti(NMe_2)_4$. The metal−amido/CO_2 route to *N*,*N*-dialkylcarbamato complexes was further pursued in 1974, for early transition metals,[8] which are known to form stable dialkylamido complexes. Shortly thereafter, the first dialkylcarbamato complexes of metal cations of groups 5 and 6[8] and of uranium(IV), $[U(O_2CNR_2)_4]_n$,[9] were prepared by carbonation of the corresponding dialkylamido precursors

$$M(NR_2)_n + nCO_2 \rightarrow M(O_2CNR_2)_n \qquad (1)$$

An alternative synthetic route to *N*,*N*-dialkylcarbamato metal complexes from metal chloride in the presence of the secondary amine and carbon dioxide was also found to be viable. This route was first adopted for the synthesis of *N*,*N*-dialkylcarbamato derivatives of uranium(IV)[10a] and later extended to several halides of transition d and f metals, whose amido complexes are not easily available. This is essentially a ligand substitution reaction whereby the anionic chloride ligand of the starting material is substituted by the carbamato group, formed in situ by the R_2NH/CO_2 system, vide infra.

$$MCl_n + nCO_2 + 2nR_2NH \rightarrow M(O_2CNR_2)_n + n[R_2NH_2]Cl \quad (2)$$

Other synthetic methodologies based on the substitution of a preexisting anionic ligand were also found, as detailed later on.

This review article deals mainly with carbamates originated from secondary amines because they are generally more soluble in organic solvents, more easily crystallized, and thus amenable to structural investigations.

As it will be detailed in section 4, metal carbamato derivatives are characterized by an interesting reactivity, which allows these systems to be regarded as important intermediates to both inorganic and organic systems.

Concerning the nomenclature used in this review article, we shall refer to homoleptic derivatives as those containing anionic ligands of the same type,[10b] regardless of the additional neutral ligands being present in the formula. This extends an accepted definition in the field of inorganic compounds.[10c]

The classification[10d] into transition- (d or f) and nontransition (s−p) elements is based on the electronic configuration of the central metal atom, as a function of its oxidation number: configurations d^n (with $1 \leq n \leq 9$), or f^n (with $1 \leq n \leq 13$) classify the central metal atom as transitional. Group numbering within the Periodic Table is according to the new notation.[10e]

A few significant graphical representations of molecular structures are reported in this review-article, and structural details are cited, when necessary. Molecular complexity or unicity of structural details and chemical composition have been the criterion of choice for the graphical representation of molecular structures. For deposited crystal structures, further information is available at the Cambridge Structural

Database (CSD) (e-mail: deposit@ccdc.cam.ac.uk; web site: http://www.ccdc.cam.ac.uk), by using the classification reported in this review-article for each compound. For structures of inorganic compounds, information is available at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany; e-mail: crystaldata@fiz-karlsruhe.de. For structures not yet available at these data banks, reference is made to the preliminary deposition data reported in any given paper. The structural diagrams presented in this review-article have been obtained through the DIAMOND 2.1 program by Crystal Impact, Bonn, Germany, the atomic parameters for their elaboration originating from CSD.

2. The Ammonia/CO_2 and Amine/CO_2 Systems

Section 2 deals with the interaction of carbon dioxide with ammonia or amines, and both kinetic and thermodynamic aspects are considered. In the recent years, efforts have been devoted to the isolation of some elusive species containing the NCO_2 fragment. Solid-state structures are now available for several ammonium or alkylammonium carbamates, vide infra, starting with the isolation and X-ray structural investigation of $NH_4[O_2CNH_2]$ in 1974. Alkyl-substituted carbamic acids have recently been structurally investigated. In view of the labile character of these systems, this is a remarkable result.

2.1. Introduction

Carbon dioxide is a stable compound ($\Delta G_f^0 = -394.4$ kJ mol^{-1})[11] whose reactions with Lewis bases are of paramount importance in biology, geology and for industrial applications.

In the case of a proton-containing substance of formula BH, equilibria 3 and 4 involving carbon dioxide can operate, the extent of displacement depending on (a) the nature of the nucleophilic portion of the molecule, (b) the reaction medium, and (c) the temperature.

$$CO_2 + BH \rightleftharpoons B-COOH \tag{3}$$

$$B-COOH + BH \rightleftharpoons [BH_2]^+[BCOO]^- \tag{4}$$

$$(BH = H_2O, NH_3, NH_2R, NHR_2)$$

As some of the reactions of CO_2 with nitrogen-containing bases have been carried out in the presence of water, the interaction of carbon dioxide with H_2O deserves some preliminary comments due to the possible, and experimentally verified (vide infra), competing formation of carbonato and bicarbonato ions. Equilibria 5, 6, and 7 operate in water, the sum of eqs 5 and 6 being slightly exothermic (−19.7 kJ mol^{-1}), while the first dissociation constant of carbonic acid in water (eq 7) is $(1.72 \pm 0.05) \times 10^{-4}$ mol kg^{-1} at 25 °C.[12] Moreover, carbonic acid $OC(OH)_2$ and carbamic acid $OC(NH_2)(OH)$ are strictly related species, and information on the latter may be obtained from the data available on the former compound.

$$CO_{2(g)} + n\ H_2O \rightleftharpoons CO_{2(aq)} \tag{5}$$

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_{3(aq)} \tag{6}$$

$$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO_3{}^-{}_{(aq)} \tag{7}$$

The elusive species dihydrogen carbonate H_2CO_3 has been characterized as follows: (a) by elemental analysis, as the etherate $H_2CO_3\cdots OR_2$ produced by reacting $NaHCO_3$ or Na2CO_3 with dry hydrogen chloride in diethyl- or dimethyl ether at ∼ −30 °C;[13a,b] (b) by mass spectrometry, upon thermal decomposition of $NH_4[HCO_3]$;[13c] (c) by ^{13}C NMR ($\delta = 162.9$ ppm) spectroscopy, as produced by reacting $BaCO_3$ with HCl in CH_3OH at −40 °C.[13d] Also the protonated species $H_3CO_3{}^+$ [i.e., $C(OH)_3{}^+$] has been characterized in $FSO_3H^-SbF_6$ as medium,[13d,14] and recently the X-ray structure {**HIWQEJ**-CSD} of $[C(OH)_3][AsF_6]$ has been reported, the data being collected at 173 K.[15] The carbon and oxygen atoms within the cation are essentially coplanar, with a net of $O-H\cdots F$ hydrogen bonds contributing to the stability of the system. The cation has C_3 symmetry, and all atoms are almost coplanar (the carbon atom and the hydrogen atoms deviate 0.067 Å and 0.013 Å, respectively, from the plane containing the oxygen atoms).

IR data have been reported for systems suggested to contain dihydrogen carbonate H_2CO_3, as produced by proton irradiation of solid H_2O/CO_2 (1:1) at 20 K[16] or by addition of dry hydrogen chloride to $KHCO_3$ in CH_3OH at 140−160 K.[17] Specifically, an absorption at 1705 cm^{-1} in the residual spectrum of CO_2/H_2O in the 1:1 molar ratio at 250 K has been assigned to the C═O stretching vibration of dihydrogen carbonate.[16] IR data are also available on amorphous dihydrogen carbonate and on two polymorphs, α- and β-H_2CO_3 obtained by warming a glassy solution (initially at 78 K) obtained by treating $KHCO_3$ with HX (X = Cl, Br) in methanol or water.[17,18] Sublimation without decomposition of crystalline dihydrogen carbonate has also been reported.[19]

Several theoretical studies on gaseous dihydrogen carbonate and its production from CO_2 and H_2O have appeared.[20] Dihydrogen carbonate $CO(OH)_2$ in its more stable geometry (trans,trans) was calculated to be endothermic with respect to water and carbon dioxide with all species in the gas phase (for instance, 43.4 kJ mol^{-1} at the QCISD(T)/6311++G** level, including zero-point energy corrections).[20e] The formation of the more stable hydrogen-bonded dimer $[CO(OH)_2]_2$, could decrease the enthalpy gap, leading to $\Delta H^0 \cong 0$ kJ mol^{-1} or even to a slightly negative value.[20f] It has been calculated that, despite its low stability, it might be possible to isolate dihydrogen carbonate in the gas phase as a kinetic product, in view of its high barrier to decomposition (calculated[20h] to be 184 kJ mol^{-1}). On the other hand, it has been suggested that the addition of one water molecule to dihydrogen carbonate strongly accelerates its decomposition, the addition of a second molecule further accelerating the process.

As far as the reactions in water are concerned, the catalyzed and uncatalyzed kinetics pertaining to equilibria 5−7, which are of paramount importance in several scientific and applied domains, have been studied in detail.[12,21,22]

There has been a long-standing interest for the interaction of CO_2 with ammonia or amines, especially in connection with industrially relevant processes. Old and new applications deal with: the production of $NaHCO_3$ from NaCl, CO_2, and NH_3 (Solvay process),[23] probably involving $Na[O_2CNH_2]$, the synthesis of urea from NH_3 and CO_2,[24a−f] the synthesis of *N*-alkyl substituted ureas from mono- or dialkylamines and CO_2,[24g−i] the recent utilization of the $NHRR'/CO_2$ system for the synthesis of alkylcarbamates $NHRCO_2R$, and alkylisocyanates.[25] Moreover, the use of amines for the removal of both carbon dioxide and dihydrogen sulfide from gas streams is a successful industrial operation:[26] 35 commercial units around the world using sterically hindered amines to sweeten the gaseous streams were in operation by 1995.[26d]

Uptake of CO_2 by ionic liquids incorporating $-NH_2$ groups have been studied and proposed as an attractive method for gas purification. On the basis of spectroscopic data (IR, ^{13}C NMR spectroscopies) and of carbon dioxide uptake, it was concluded that carbon dioxide is fixed as a carbamate, the process being reversed by heating at 80−100 °C.[27]

The reversible reaction of amines with CO_2 have been used to prepare chemically reversible organo gels.[28] Carbon dioxide uptake and subsequent release upon heating have been reported,[28a] as applied to the formation of the so-called low-molecular mass gelators (LMOG) obtained through CO_2 uptake by long-chain aliphatic primary or secondary amines. In the presence of carbon dioxide, these amines produce the appropriate alkylammonium carbamate $[RR'NCO_2][NH_2RR']$, according to the well-established chemical behavior of amines with carbon dioxide (vide infra). This corresponds to retaining one mol of CO_2 for every two mol of the amine at room temperature, followed by release upon heating at temperatures $\geq$ 100 °C for several minutes.

2.2. Alkylammonium Alkylcarbamates

Some pioneering studies in the first decades of last century[29,30] showed that amines react with CO_2 producing alkylammonium alkylcarbamates, $[NH_2RR'][O_2CNRR']$. This reactivity was confirmed in subsequent papers.[31] Of particular interest are the studies[31b−p] on the rate constants for amine carbonation and on the equilibrium constants for amine/water competition toward CO_2, see section 2.2.1 for further details, and Table 1 for thermodynamic and kinetic data of these systems.

2.2.1. Preparation and Characterization

Several $[NH_2RR'][O_2CNRR']$ derivatives have been prepared[31] under anhydrous conditions, by reacting NHRR′ with CO_2 in diethyl ether or in the absence of a solvent ($R = R' =$ H, Me, Et, Pr, ^{i}Pr, Bu, ^{s}Bu; $R =$ H, $R' =$ Me, Et, allyl, Bu, ^{s}Bu, ^{i}Bu, ^{t}Bu).[31b−o] Alkylammonium carbamates $[NH_3R][O_2CNHR]$, $R =$ $ArCH_2CH_2$,[31a] Bz,[31a,32] have been obtained by reacting primary amines with CO_2 in anhydrous Et_2O. Carbonation of primary amines [$BzNH_2$, 1,2-diarylethylamines, $HO(CH_2)_2NH_2$] and secondary amines [BzNHMe, $(HOCH_2CH_2)_2NH$] produces the appropriate carbamato derivative.[33] The tertiary amine $PhCH_2NMe_2$ does not absorb CO_2 under anhydrous conditions.[32] The system $[NH_2(CH_2)_nNH_2)]/CO_2$, which was suggested to[32] yield the zwitterionic carbamate, $^{(+)}NH_3(CH_2)_nNHCOO^{(-)}$, has been further studied and it has been observed that a mixture of both the zwitterion, $^{(+)}NH_3(CH_2)_nNHCOO^{(-)}$, and the diammonium dicarbamate, $[NH_3(CH_2)_nNH_3][O_2CNH(CH_2)_nNHCO_2]$, is formed in Et_2O solution.[34] Two polymorphs, orthorhombic and monoclinic, of the zwitterion $^{(+)}NH_3(CH_2)_2NHCOO^{(-)}$ have been characterized {**CAXMOD**-CSD} in the solid state,[35a] while further evidence of the presence of the dicarbamate in D_2O solution at relatively high pH values has been gathered by ^{13}C NMR spectrometry.[35b] The zwitterion $^{(+)}NH_3(CH_2)_2NHCOO^{(-)}$ has been observed recently as a μ-*O*,*O*′-bridging bidentate ligand in the tetranuclear anion of the salt-like derivative $(enH_2)[Fe_4(\mu_3\text{-}O)(heidi)_4(\mu\text{-}O_2CNHC_2H_4NH_3)]\cdot 4H_2O$ [in this formula heidi is the deprotonated conjugate base of *N*-(2-hydroxyethyl)-iminoacetic acid]. The product was obtained by addition of H_3heidi to an aqueous solution of iron(III), followed by addition of ethylenediamine at pH 7, with no carbon dioxide intentionally added.[36]

Also the hexyl, octyl, decyl, dodecyl, and cyclohexyl derivatives $[NH_3R][O_2CNHR]$ have been prepared by carbonation of the neat amine NH_2R, or in benzene as solvent, and the products were characterized by elemental analysis.[37]

Primary amines in the presence of a strong base such as penta-alkylguanidines, $R_2N(C{=}NR)NR_2$ in MeCN undergo double carbonation, as evidenced by ^{15}N NMR spectrometry when $^{13}CO_2$ was reacted, under those conditions, with $^{15}NH_2Et$ and $^{15}NH_2Cy$.[25a,b]

^1H- and ^{13}C NMR spectra in solutions containing the $NHRR'/CO_2$ systems have been measured:[38] the $O_2CNR'R^-$ anions show typical $^{13}CO_2$ signals in the 160−170 ppm range from TMS. ^1H NMR spectra prove the presence of an equilibrium between alkylammonium alkylcarbamate, amine and CO_2; when water is present, additional equilibria involving HCO_3^- are observed and a quantitative determination of the dissolved species by NMR spectrometry has been proposed.[38c]

An IR study on thin solid films obtained by reacting NH_3 (or ND_3) with CO_2 at low temperature[39] evidenced the formation of $NH_4[O_2CNH_2]$ or $ND_4[O_2CND_2]$: the bands at 1525 and 1404 cm^{-1}, not appreciably shifted on deuteration, have been assigned to the antisymmetric stretching of the CO_2 moiety and to the NC stretching, respectively. As far as the anion is concerned, two bands at 3446 and 3295 cm^{-1}, which shift to 2583 and 2424 cm^{-1} in the deuterated compound, have been attributed to the NH_2 antisymmetric and symmetric stretching modes, respectively. A band at 1624 cm^{-1} (1199 cm^{-1} in the deuterated ion) was assigned to the NH_2 bending vibration. No evidence of carbamic acid formation was apparently detected in this study.

IR spectra of the solid species $[NH_3R][O_2CNHR]$ obtained from some primary amines (R = Bz, allyl, ^{t}Bu, cyclohexyl) and CO_2, together with the $^{13}CO_2$-enriched analogues, have been discussed.[40] The band at 1567 cm^{-1}, attributed to a vibration involving the NCO_2 group, is shifted to 1559 cm^{-1} (a $\Delta\nu$ of 8 cm^{-1} only) in the isotopically labeled sample. The decomposition of the compounds in THF under N_2 was followed by IR spectroscopy: in addition to the band at 1545 cm^{-1} assigned to the carbamato anion, bands due to CO_2 and to free amine were observed, together with absorptions at 1725 and 1685 cm^{-1} (shifted to 1678 and 1643 cm^{-1}, respectively, upon $^{13}CO_2$ isotopic labeling). These bands have been attributed to monomeric and dimeric alkylcarbamic acids, $NHRCO_2H$ and $[NHRCO_2H]_2$, respectively. At that time neither carbamic acid nor *N*-alkyl substituted carbamic acids had been characterized. This topic will be further discussed in section 2.3.

Only a few crystallographic data are available on ammonium- and alkylammonium carbamates, in addition to the two polymorphs of the zwitterionic carbamate $[^{(+)}NH_3(CH_2)_2NHCOO^{(-)}]$ cited above.[35a] The ammonium derivative itself, $[NH_4][O_2CNH_2]$, studied independently by two different laboratories {**ACARBM**-CSD}[41b] consists of tetrahedral cations and couples of planar anions held together by hydrogen bonds.[41] Later on, the structure of 4-methylbenzylammonium 4-methylbenzylcarbamate, $[NH_3(CH_2C_6H_4\text{-}p\text{-}Me)][O_2CNH(CH_2C_6H_4\text{-}p\text{-}Me)]$ was described, {**ZUHMEU**-CSD}, the authors underlining that at the time of their publication, this was only the fourth structurally characterized ammonium carbamate in the literature.[42] Recently the X-ray diffraction study of the dibenzylammonium derivative $[NH_2Bz_2][O_2CNBz_2]$ {**MASQOM**-CSD} has appeared.[7a] The dibenzylammonium cation has the expected geometry, with the aromatic rings bent toward the nitrogen atom. In the anion, the aromatic rings are almost perpendicular to the planar O_2CN group (maximum deviation, 0.03 Å). Each cation forms two hydrogen bonds with two different anions and each anion is hydrogen-bonded to two different cations.

2.2.2. Kinetic Studies

The kinetics of the reaction of CO_2 with ammonia or amines to give the appropriate carbamate have been extensively studied, mostly in water as medium, see eq 8−10. These are conditions which favor the hydrolytic process to the bicarbonate anion, the prevalence of eq 8 or 10 being a function of pH.

$$CO_{2(aq)} + 2NHRR'_{(aq)} \rightleftharpoons [NH_2RR'][O_2CNRR']_{(aq)} \tag{8}$$

$$[NH_2RR'][RR'NCO_2] + H_2O \rightleftharpoons NHRR' + [NH_2RR'][HCO_3] \tag{9}$$

$$CO_{2(aq)} + OH^-_{(aq)} \xrightarrow{k_{10}} HCO_3^-{}_{(aq)} \tag{10}$$

The equilibrium constants of reaction 9 were found to be <1 at 18 °C, consistent with the greater basicity of amines in comparison with water. Addition of a $Ba(OH)_2$ solution causes $BaCO_3$ to precipitate, while barium carbamate remains in solution. This method has been used[31b−p] to measure the kinetic constants for a series of amines, see Table 1. All references in this Table pertain to work carried out at the beginning of last century.

Table 1. Rate (*k*) and Equilibrium (K_{CBM}) Constants at 18 °C for the Reaction {$2NHRR' + CO_2 \rightleftharpoons [NH_2RR'][O_2CNRR']$} in Water {$v = k[Amine][CO_2]$}, and Equilibrium Constants (K_{HYD}) at 18 °C for the Reaction {$NRR'CO_2^- + H_2O \rightleftharpoons HCO_3^- + NHRR'$} in Water

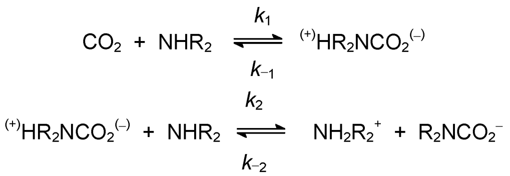
amine	pK_b[a]	k (M^{-1} min^{-1})	K_{HYD}	K_{CBM}	ref
NH_3	4.76	3.8×10^3	4.4×10^{-1}	2.3×10^3	31d
NH_2Me	3.38	8.3×10^4	6.0×10^{-3}	4.0×10^6	31d
$NHMe_2$	3.22	6.7×10^5	2.2×10^{-2}	1.6×10^6	31d
NH_2Et	3.19	1.5×10^5	1.8×10^{-2}	2.0×10^6	31e
$NHEt_2$	3.51	2.9×10^5	2.4×10^{-1}	7.4×10^4	31e
NH_2Pr	3.41	1.6×10^5	1.3×10^{-2}	1.5×10^6	31h
$NH_2{}^iPr$	3.37	6.8×10^4	6.3×10^{-2}	3.6×10^5	31h
piperidine	2.95	7.8×10^5	8.1×10^{-2}	7.9×10^5	31i
NH_2Bz	4.74	1.1×10^5	1.2×10^{-2}	8.5×10^4	31i
NH_2Ph	9.3	$\sim 10^3$	3.6	8.1×10^{-3}	31i
NH_2allyl	4.38	1.1×10^5	1.5×10^{-2}	1.6×10^5	31j
$NHPr_2$	3.09	3.0×10^5	1.5×10^{-1}	3.0×10^5	31k
NH^iPr_2	3.17	–	–	*b*	31k
MEA	4.42	8.3×10^4	1.9×10^{-2}	6.0×10^4	31l
DEA	4.98	1.0×10^5	1.5×10^{-1}	2.1×10^3	31l
NH_2Bu	3.24	2.0×10^5	1.6×10^{-2}	1.1×10^6	31n
$NH_2{}^sBu$	3.44	7.1×10^4	4.9×10^{-2}	3.8×10^5	31n
$NH_2{}^iBu$	3.58	1.6×10^5	1.0×10^{-2}	1.3×10^6	31n
$NH_2{}^tBu$	3.55	1.9×10^4	1.4×10^{-1}	1.1×10^5	31n
$NHBu_2$	2.54	3.1×10^5	1.9×10^{-1}	4.6×10^5	31n
NH^sBu_2	–	–	–	*b*	31n
NH^iBu_2	3.41	1.3×10^5	1.2×10^{-1}	1.9×10^5	31n

[a] The values of pK_b are from refs 31 ($K_w = 10^{-14.27}$). For a more recent collection of pK_b, see ref 31p. [b] No carbamate is formed in aqueous solution.

The kinetics of carbamate formation were studied[43] in water with an improvement consisting of using $^{14}CO_2$ and by assuming the value 2.4×10^3 M^{-1} s^{-1} at 10 °C for k_{10}. The rate was found to be pH-dependent, a hydroxide-catalyzed path being therefore suggested.

Further studies on the reactions of carbon dioxide with primary amines[44,45] showed complicated reaction orders with respect to amine concentration. Scheme 2 shows a mechanism[46,47] involving the formation of the zwitterion $^{(+)}HNR_2CO_2{}^{(-)}$, the observed reaction order depending on the k_{-1}/k_2[amine] ratio. The results[46] in anhydrous ethanol are consistent with both a two-step mechanism and a single-step termolecular reaction. Experiments[47] carried out in water with 10 different amines led to the conclusion that a termolecular single-step mechanism is a good model for the reaction, as supported by the strongly negative value of the entropy of activation.

Scheme 2



Tertiary amines NR_3 and CO_2,[48] which are unable to form carbamates, produce the hydrogencarbonate anion in the presence of water with a complex rate law.

Kinetic studies have shown that *N*-substituted carbamates undergo[43] acid-catalyzed decomposition, and the pH dependence of the reaction for a series of *N*-arylcarbamates has been studied.[49] The conclusion was that the unimolecular decarboxylation of the intermediate zwitterionic carbamic acid is the main mode of decomposition of carbamates.[50] Although it is now known that *N*,*N*-dialkylcarbamic acids exist in the solid state as R_2NCO_2H,[7a] rather than as the zwitterionic form, it cannot be excluded that the latter is involved in the decomposition process.

The kinetics of formation/decomposition of solid ammonium carbamate from/to gaseous ammonia and carbon dioxide have been studied.[51] According to a manometric method,[51a] the experimental data were interpreted by a mechanism where crystal growth (and crystal decay for the reverse process) is rate-determining, the rate being proportional to ΔP^2 ($\Delta P = P - P_{eq}$). The possibility that carbamic acid[51b] could be an intermediate of the process was taken into consideration. Computational ab initio studies on gaseous carbamic acid indicate that the inertness of this molecule is incompatible with its role as a transient species. A solid-state mechanism was suggested involving reversible decomposition of surface-bound carbamic acid into ammonia and carbon dioxide, with the latter two species undergoing reversible physi-/chemisorption on the surface.

Several theoretical studies focused on the mechanism of the reaction between ammonia (or amines) and carbon dioxide.[52] The activation enthalpies of this process in aqueous solution for some amines containing alcohol functions range[47] from 18 to 27 kJ mol^{-1}. The reaction between NH_3 and CO_2 in the gas-phase producing solid $NH_4[O_2CNH_2]$ gave initial first-order kinetics for both reagents, with activation enthalpies of about 75 kJ mol^{-1}.[51a] Most of the theoretical studies[52] assume the 1:1 reaction model to be operative, carbamic acid being postulated as a transient species. The calculated activation enthalpies ($130 \div 190$ kJ mol^{-1}) are higher than the experimental values. By modeling the reaction in the presence of a second amine molecule, a lower activation enthalpy (40 kJ mol^{-1}), in better agreement with the experimental values, was obtained for the $NHMe_2/CO_2$ system.[52d] The reaction product is described as the adduct of dimethylcarbamic acid with dimethylamine, stabilized by hydrogen bonds.

2.2.3. Thermodynamic Considerations

With BH equal to ammonia or to a secondary or a primary amine, the sum of eqs 3 and 4 is exothermic in the majority of the cases.

The NH_3/CO_2 system, see eq 11, has been studied by measuring the dissociation pressure of solid ammonium carbamate at different temperatures,[53,54] and the values $\Delta H^0 \cong +160$ kJ mol^{-1} and $\Delta S^0 \cong +460$ J mol^{-1} K^{-1} have been reported.[53]

$$NH_4[O_2CNH_2]_{(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)} \qquad (11)$$

In a patent,[55] the preparation of $[NH_2Me_2][O_2CNMe_2]$ from $NHMe_2$ and CO_2 was reported to be exothermic, the ΔH^0 of the reaction being estimated[56] to be -42 kJ mol^{-1}. It is interesting to note that $NHMe_2$ reacts with CO_2 forming a liquid of analytical composition close to $[NH_2Me_2][O_2CNMe_2]$.[38b,56] The liquid can be distilled without decomposition and can be routinely used as a dimethylamine (bp 7 °C) source.

Under strictly anhydrous conditions and at atmospheric pressure, the CO_2 uptake by some neat amines NHR_2 (R = Bu, ^{i}Pr, Cy), affording colorless solids, was measured:[7a] it corresponds to a final CO_2/amine molar ratio close to 0.5, as expected for the predominant formation of $[NH_2R_2][O_2CNR_2]$. This ratio was 0.56 for $NHBu_2$ at 9.6 °C, 0.44 for NH^iPr_2 at 19.3 °C, and 0.53 for $NHCy_2$ at 24.9 °C. In heptane solution, molar ratios of 0.43 for $NHEt_2$ (initial amine concentration 0.14 M, 20.8 °C); 0.08 for $NHBz_2$ (initial amine concentration 0.12 M, 22.4 °C); 0.07 for NH^iPr_2 (initial amine concentration 0.26 M, 25.8 °C)[57] and 0.02 for $NHCy_2$ (initial amine concentration 0.19 M, 23.3 °C) were measured.[58] The uptake of CO_2 by $NHBz_2$ affording the corresponding carbamic acid will be discussed in section 2.3.

On the other hand, the majority of the studies on the amine/CO_2 equilibria have been performed in aqueous solution. In water the system containing ammonia or amines and CO_2 is governed by the nature of the solvent, pH, the presence of metal cations, and by temperature, the predominance of carbamate with respect to bicarbonate or carbonate depending on the experimental conditions. By making reference to the data of Table 1, particularly to the values of K_{CBM} and K_{HYD}, it appears that there is no simple correlation between K_{HYD} and basicity of the amine. Carbamate hydrolysis is slightly unfavorable, suggesting that reagents and products have about the same energy. Steric effects probably play an important role and are responsible for the relatively high K_{HYD} values of strongly basic, sterically hindered amines. It must be added that severely hindered amines are not reactive toward CO_2 in water, while steric hindrance does not appear to prevent carbamate formation under anhydrous, non competitive conditions.[7a,57,58] The data of Table 1 refer to equilibria studied from both sides.[31b−p] In an article[59] on paper ionophoresis of amines, the authors conclude that carbamates are not formed directly from amines and carbonate ion, but through the assistance of CO_2.

From recently published ^{13}C NMR data, K_{CBM} values for amines bearing alcoholic functionalities on their alkyl groups[60a] can be calculated [9×10^4 (MEA), 4×10^3 (DEA), 6×10^4 (DGA), and 5×10^3 (DIPA) at 25 °C]. From an independent study on MEA and DEA carried out by using acid−base titration methods,[60b] K_{HYD} values (25 °C) of 5.0×10^{-2} and 1.4×10^{-1}, respectively, can be deduced. The thermodynamic parameters for the hydrolysis of the carbamates derived from MEA and DEA can be calculated from the literature data:[60b] ΔH_{HYD}(MEA) = +12.8 and ΔH_{HYD} (DEA) = +34.0 kJ mol^{-1}; ΔS_{HYD} (MEA) = +17.9 and ΔS_{HYD} (DEA) = +97.9 J mol^{-1}

K^{-1}. As far as equilibrium data are concerned, comparison with the early literature[311] shows a reasonable agreement. On the other hand, the data reported in a recent Raman study on the $NH_3/CO_2/H_2O$ system correspond to a K_{HYD} value of about 4 at 22 °C[61] (to be compared with 0.4 at 18 °C).[31d] The discrepancy is not too surprising in view of the completely different analytical methods used in these studies. From the available data, it is clear that in aqueous solution, alkylammonium (or ammonium) *N*-alkylcarbamates (or carbamate) show a certain degree of stability with respect to decomposition to amine (or ammonia) and CO_2 and that alkylcarbamates (or carbamate) are equilibrium components of the aqueous systems containing amines (or ammonia) and carbonates.

The presence of a finite concentration of dialkylammonium carbamate in the presence of water under carbon dioxide has been exploited for the extraction of some transition metal cations, such as lanthanides, copper(II), and zinc(II) with a hydrocarbon (heptane or toluene).[62a] For example, an essentially quantitative transfer of copper(II) and zinc(II) into heptane or toluene promptly occurs under carbon dioxide starting from an aqueous solution of the corresponding sulfates, in the presence of NHR_2 (R = Bu, Bz). In this process the homoleptic carbamato complex $Cu(O_2CNBz_2)_2(NHBz_2)_2$ and the μ-oxo derivative $Zn_4(\mu_4-O)(O_2CNBu_2)_6$ were extracted into the hydrocarbon layer and completely characterized, including X-ray diffraction methods.[62b] For structural details about these compounds of copper(II) and zinc(II), see sections 3.2.2 and 3.4.1, respectively.

These new findings on the existence of carbamato complexes in an aqueous medium are presumably important for biologically relevant systems. In fact, carbon dioxide is believed to be one of the regulators of the affinity of dioxygen for hemoglobin. The α- and ϵ-amino groups of deoxyhemoglobin and oxyhemoglobin are involved in carbonation phenomena; the corresponding CO_2 hydration equilibria are about 100 times faster than the uncatalyzed one.[63] It was then concluded that the ϵ-site is the preferred one for the carbonation process. The measurements were carried out at 37 °C, at ionic strength 0.15, in the pH range 6.2 ÷ 8.8, at a CO_2 partial pressure comprised between 15 and 140 Torr.

2.3. Alkylcarbamic Acids

As this review article is dedicated to metal complexes containing the carbamato ligand, and taking into consideration that the simplest Lewis acid is the proton, it is mandatory to first discuss the preparation and properties of carbamic acid itself, NH_2CO_2H, and its *N*-alkyl-substituted derivatives.

Carbamic acid, NH_2CO_2H, although not yet isolated, has been detected by neutralization−reionization mass spectrometry (NRMS)[64] and by IR at low temperature,[65] and some of its properties have been calculated theoretically.[61,66] In a thermochemical study,[53b] the standard enthalpy of formation of gaseous carbamic acid was calculated to be −381 kJ mol^{-1} ($\Delta G_f^0 = -317$ kJ mol^{-1}), and that of solid $NH_4[O_2CNH_2]$ has been determined ($\Delta H_f^0 = -646$ kJ mol^{-1}; $\Delta G_f^0 = -459$ kJ mol^{-1}). According to these figures, it can be calculated that gaseous carbamic acid should be unstable with respect to both $NH_4[O_2CNH_2]_{(s)} + CO_{2(g)}$ ($\Delta H_r^0 = -277$ kJ mol^{-1}; $\Delta G_r^0 = -219$ kJ mol^{-1}), and to $NH_{3(g)} + CO_{2(g)}$ ($\Delta H_r^0 = -58$ kJ mol^{-1}; $\Delta G_r^0 = -93$ kJ mol^{-1}). Theoretical calculations[66a] suggest that gaseous monomeric carbamic acid decomposes exothermically to ammonia and carbon dioxide ($\Delta H° = -26$ kJ mol^{-1}). However, the formation of the hydrogen-bonded dimer $(NH_2CO_2H)_{2(g)}$ could be slightly favored, taking into consideration that, for example, stabilization by hydrogen bond in the formic acid dimer has been evaluated to be 60 kJ mol^{-1}.[67] Computational studies on the decomposition of ammonium carbamate[51b,61,66a] favor carbamic acid NH_2CO_2H as the intermediate and its zwitterionic form as the transition state.

N-Substituted carbamic acids are believed to be key intermediates in biological carbonations, e.g., in metabolic reactions via CO_2 transfer through *N*-carboxybiotin,[68] and in the photosynthetic activation of CO_2 promoted by Rubisco (ribulose 1,5-biphosphate carboxylase).[69] It is remarkable that 2-imidazolidone, a cyclic urea-like derivative, which can be regarded as a model of biotin, is a poor nucleophile and does not absorb carbon dioxide.[58a] On the other hand, its lithium derivative, as obtained by deprotonation with phenyl-lithium, undergoes carbonation, thus forming the corresponding lithium carbamate.[68b] Carbon dioxide exchange in this compound has been studied, the kinetics being independent of the CO_2 concentration.

In a paper dealing with the kinetics and mechanism of urea hydrolysis catalyzed by palladium(II) complexes,[70] the intermediate formation of carbamic acid coordinated to palladium(II) via the nitrogen atom was suggested on the basis of a ^{13}C NMR peak at 174.3 ppm attributed to the *N*-bonded carbamic acid. This structural hypothesis should be compared with the X-ray characterization of a square-planar *N,N*-dialkylcarbamato complex of palladium(II) of formula $Pd(NHEt_2)_2(O_2CNEt_2)_2$, where the carbamato ligand is *O*-bonded to the central metal atom.[10b,71]

In a study of the $NHMe_2/CO_2$ system, the involvement of dimethylcarbamic acid in the equilibrium mixture was claimed on the basis of the ester formation with diazomethane.[38b] The same paper reports that methanolysis of $NMe_2CO_2SiMe_3$ at −78 °C affords a crystalline product, probably NMe_2CO_2H, which decomposes just above −50 °C with CO_2 loss and formation of $[NH_2Me_2][O_2CNMe_2]$.

Only recently,[7a] a simple alkyl-substituted carbamic acid has been isolated, namely, dibenzylcarbamic acid, $Bz_2NC(O)OH$, whose molecular and crystal structure {**MASQUS**-CSD} has been described. In the same paper a carbonated cobalt-aminophosphane species {**MASRAZ**-CSD} was shown to contain a carbamic acid functionality, $\#NCO_2H$ {$\# = CoCl(NO)_2[PhP(OCH_2CH_2)_2]$}. Both acids are not in their zwitterionic structure (that assigned[65] to carbamic acid on the basis of IR data), but organized in hydrogen-bonded pairs of molecules, $[R_2NCO_2H]_2$, similar to carboxylic acids. Spectroscopic (IR) and gasvolumetric experiments have shown that Bz_2NC-

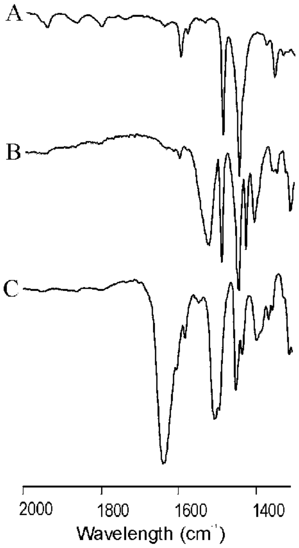


Figure 1. IR spectra. (A) dibenzylamine (neat liquid). (B) $[NH_2Bz_2][O_2CNBz_2]$ after exposure of neat dibenzylamine to dry carbon dioxide under anhydrous conditions at 10 °C. (C) further exposure of sample B to carbon dioxide at atmospheric pressure forming NBz_2CO_2H.

(O)OH is formed by carbonation of neat dibenzylamine, through the intermediacy of $[Bz_2NH_2][O_2CNBz_2]$. The suggestion[66c] that Bz_2NCO_2H has been intercepted due to its kinetic inertness related to the presence of the large benzyl substituents, is not tenable. As a matter of fact, the carboxylation of benzylamine goes to completion both in heptane (gasvolumetric measurements, 10 °C) and in neat dibenzylamine at 9.5 °C (IR spectra).[7a] Figure 1 shows the IR spectra of dibenzylamine, of the transient $[NH_2Bz_2][O_2CNBz_2]$, and of the final product NBz_2CO_2H after prolonged exposure to carbon dioxide at atmospheric pressure under strictly anhydrous conditions. The ν_{CO} band of the carbamic function of NBz_2CO_2H at 1640 cm^{-1} agrees with the presence of intermolecular hydrogen bonds, as evidenced by the X-ray diffraction study. The frequency value is lower than that obtained by theoretical calculations[66c] and higher than that assigned to $^{(+)}H_3NCO_2^{(-)}$ on the basis of spectroscopic data at low temperature for the NH_3/CO_2 system.[65] It is interesting to note that NBz_2CO_2H decarboxylates to $[NBz_2H_2][O_2CNBz_2]$ and free amine in the presence of toluene. Thus, the formation of NBz_2CO_2H is primarily a solid-state phenomenon (the solubility of the product in heptane is low) and is related to the small amount of stabilization connected with the formation of hydrogen bonds. These findings are relevant, inter alia, to the problem of carbon dioxide fixation by amino groups in biopolymers in the solid state.[72]

NMR and theoretical studies of protonated carbamic acids have been published, and $H_2NC(OH)_2^+$ was obtained by protolytic ionization of H_2NCO_2-^{t}Bu in FSO_3H at −78 °C in SO_2ClF as solvent and characterized by ^1H, ^{13}C, and ^{15}N NMR spectra.[73]

Recent results concerning the use of supercritical carbon dioxide (*sc*-CO_2) as solvent in organic synthesis show that, when amine (=NH or $-NH_2$) functionalities are present in the substrate, a ^1H NMR signal at low field (δ 8.5 ÷ 12) appears, attributed to the carbamic acid function $=NCO_2H$. According to these studies, the use of *sc*-CO_2 as medium can be exploited to protect the amine function, in some cases allowing a selective control of the reaction.[74]

According to a recent communication,[75] some primary amines containing condensed aromatic rings (1-aminomethylnaphthalene, 1-aminomethylpyrene) react with CO_2 in polar aprotic solvents, affording the corresponding carbamic acid. The products have been identified spectroscopically, and the acids were reported to be mainly characterized by a broad NMR peak at about 10.7 ppm assigned to the −COOH proton. However, caution should be used about NMR assignments. In fact, $[NR_{4-n}H_n]^+$ cations, $0 < n < 4$, in organic solvents show NMR signals at low field, which are solvent dependent. For example, dibenzylammonium benzoate, $[NH_2Bz_2][O_2CPh]$, absorbs at 10.2 ppm in $CDCl_3$ and at 11.4 ppm in C_6D_6.[76] Independent gasvolumetric measurements carried out in dry DMSO at 20 °C have shown that an approximately 6×10^{-2} M solution of 1-aminomethylnaphthalene absorbs one mol of CO_2, the IR spectrum in the same solvent showing a band at 1699 cm^{-1} attributed to the CO stretching vibration of the carbamic acid.[76] These new data therefore support the information based on NMR and fluorescence measurements.[75] On the basis of these new data, the previous assignment[40] of the IR bands at 1725 and 1685 cm^{-1} to, respectively, the monomeric and dimeric acids $NHBzCO_2H$ and $[NHBzCO_2H]_2$ finds further support.

It is quite evident that the interaction, in organic solvents, of carbon dioxide with amines under different conditions is a subject to be further pursued.

3. *N,N*-Dialkylcarbamato Metal Complexes

3.1. Introduction

Derivatives of transition and main group elements will be considered separately. In doing so, we shall adhere to the more classical, but perhaps less precise, inclusion of metals of Groups from 4 to 12 as being transitional, independent of the oxidation state, thus deviating for convenience from the definition given in the Introduction. However, for electronic, spectroscopic and structural properties, reference will be made to the specific d^n (or f^n) electronic configuration of the central metal atom.

3.2. Homoleptic Compounds

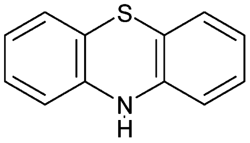
Homoleptic compounds, see section 1, will be considered first. This class of carbamato complexes of nontransition elements have been mostly prepared by carbonation of the corresponding amides, the latter being readily available. On the other hand, carbamato derivatives of transition elements often require more sophisticated preparative routes. This justifies the classification introduced at this point, in terms of synthetic methodologies.

3.2.1. Main Group Elements

Among alkali- and earth-alkali metal cations, lithium and magnesium carbamato complexes have been studied to some extent. The diethylcarbamato derivatives of formula $M(O_2CNEt_2)$, M = Li, Na, K, have been prepared[25d,77] by treating a suspension of the alkali metal in toluene at about 50 °C with the appropriate amine, in the presence of CO_2. The products were found to be insoluble in ethers or in hydrocarbons and soluble in the presence of an excess of amine or in polar solvents such as MeOH or dimethylformamide. Similar results were obtained[77,78] when the reaction between the alkali metal and diethylamine or primary amines was carried out in THF as medium at room temperature, followed by reflux.

An early patent[79] reports that sodium dialkylcarbamato derivatives were obtained by a two-step process first converting a suspension of sodium metal in a hydrocarbon medium into the appropriate sodium amide by reaction with the amine, followed by carbonation at atmospheric pressure. This patent reports similar procedures for the preparation of carbamato derivatives of lithium, calcium, magnesium, barium, strontium, aluminum, tin, and lead. The understanding of some of these systems has considerably increased since then, vide infra.

In a study aimed at clarifying the mechanism of the protection by carbon dioxide of the α-position in NH-contaning heterocycles, it has been found that the lithium derivative of phenothiazine, see below, is carbonated forming the corresponding lithium-carbamato derivative.[80]



Phenothiazine

An insight into the structure of the resulting compound was obtained from lithiation of diphenylamine, followed by carbonation in THF and recrystallization of the resulting product from toluene/TMEDA. The X-ray structure of the dinuclear carbamato derivative, of formula $Li_2(O_2CNPh_2)_2(TMEDA)_2$ showed that each tetracoordinated lithium is bonded to two oxygen atoms of the bridging carbamato groups and to the two nitrogen atoms of TMEDA {**YUBVOG**-CSD}. A carbamato derivative of lithium has also been obtained[81] by reacting 2,3-dimethylindole with LiBu and CO_2 in THF; lithiation of the indole ring, followed by carbonation, gives the tetranuclear product of formula $Li_4(O_2CNC_{10}H_{10})_4(THF)_4$ which contains tetracoordinated lithium atoms {**TOWRIG**-CSD}.

The first carbamato derivative of magnesium was obtained[82] by reacting $MgCp_2$ with $Ti(O_2CN^iPr_2)_3$, the latter probably being a carbamato-bridged dimer of hexacoordinated titanium(III), see section 3.2.2. In the course of the ligand exchange process, the insoluble magnesium derivative $Mg(O_2CN^iPr_2)_2$ was formed in good yields, and easily separated from the $TiCp_2(O_2CN^iPr_2)_2$ coproduct by filtration.

$$MgCp_2 + Ti(O_2CN^iPr)_3 \rightarrow Mg(O_2CN^iPr)_2 + Ti(O_2CN^iPr)Cp_2 \quad (12)$$

Scheme 3 refers to homoleptic dialkylcarbamates of magnesium(II) being obtained by carbonation of the appropriate bis-amido derivative, either prepared in situ from MgR_2/NHR_2,[83a] or preformed.[83b] The additional neutral ligand eventually found in the composition of the final product originates from the solvent used for the reaction. Alternatively, the diethylcarbamato complex of magnesium can be prepared[83a,c] via the $MgBr_2/CO_2/NHEt_2$ route.

Scheme 3

$$Mg(NR_2)_2 + 2CO_2 \xrightarrow{m/n\ L} 1/n[Mg_n(O_2CNR_2)_{2n}L_m]$$

R	L	*n*	*m*
Me	THF	3	2
Me	HMPA	3	2
Et	---	6	0
Ph	---	6	0

The compounds $Mg_6(O_2CNEt_2)_{12}$ {**QESJON**-CSD; **QESJON01**-CSD}, $Mg_6(O_2CNPh_2)_{12}$ {**QESJUT**-CSD}, and $Mg_3(O_2CNMe_2)_6(HMPA)_2$ {**QESJIH**-CSD} were studied by X-ray diffraction methods. Of particular interest is the hexanuclear compound of magnesium $Mg_6(O_2CNEt_2)_{12}$, which has been structurally studied by two different research groups, see Figure 2.[83a,b]

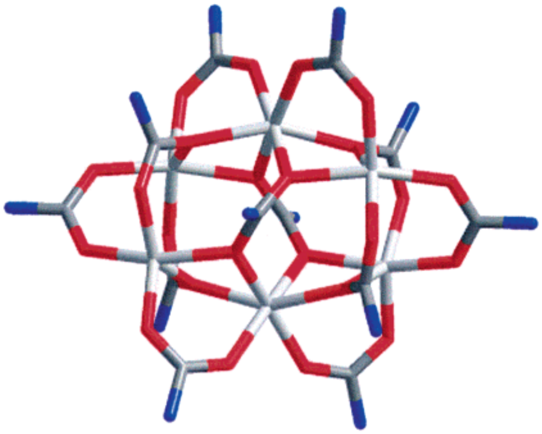


Figure 2. Schematic molecular structure of $Mg_6(O_2CNEt_2)_{12}$. Centers of sticks: light-gray, metal atoms; gray, carbon atoms; red, oxygen atoms. Blue stick, nitrogen atoms. Alkyl groups not shown. Drawings obtained using the published structural data.[83a,b]

It was pointed out[83a] that the unit cell contains four hexanuclear molecules, in pairs of Δ and Λ configurations. The crystal is a racemic mixture of the stereoisomers. The orthorhombic modification of $Co_6(O_2CNEt_2)_{12}$ [space group *Ccca*, $a = 20.712$, $b = 25.040$, $c = 16.498$ Å] was found to be isostructural with the corresponding magnesium compound $Mg_6(O_2CNEt_2)_{12}$, such that it has been possible to cocrystallized the two products, thus obtaining mixed magnesium−cobalt hexamers $Co_nMg_{6-n}(O_2CNEt_2)_{12}$.[83c] As it will be pointed out in the following section, 3.2.2, another structural modification of the cobalt derivative $Co_6(O_2CNEt_2)_{12}$ has been found.[83d]

The reaction of the MgMeX Grignard reagent with oxalic amidines, followed by exposure to carbon dioxide at atmospheric pressure gave the trinuclear carbamato complex of formula $Mg_3(THF)_6[RNC(NR-CO_2)C(NRCO_2)NR]$.[84] The X-ray structural investigation (R = Ph) {**KOKWIQ**-CSD} has shown the trinuclear compound to contain a linear arrangement of the magnesium atoms at a nonbonding distance of 4.211 Å.

In papers[85] dedicated to carbamato complexes of groups 13 and 14 (vide infra), the aluminum(III) derivatives, as prepared from Al_2Br_6, CO_2, and the appropriate amine, have been described. Aluminum bromide, which is well soluble in the reaction medium (toluene), is more advantageously used than the corresponding chloride.

$$Al_2Br_6 + 12{}^iPr_2NH + 6\,CO_2 \rightarrow Al_2(O_2CN{}^iPr_2)_6 + 6\,[{}^iPr_2NH_2]Br \quad (13)$$

In $Al_2(O_2CN{}^iPr_2)_6$ each of the two hexacoordinated aluminum atoms {**WAKREF-**CSD} is surrounded by four oxygen atoms of two terminal bidentate- and by two oxygens of two bridging groups.[85b] The *iso*-propyl derivative maintains its nuclearity in benzene and is fluxional, as suggested by the NMR data. The ^1H NMR spectrum showed one type only of *iso*-propyl groups at room temperature, suggesting fast exchange between terminal and bridging positions. By lowering the temperature down to −55 °C, two carbamato ^{13}C resonances appear at 165.4 and 156.8 ppm, and two types of methine groups at 46.8 and 43.8 ppm, while the methyl groups give a single resonance at 20.6 ppm, even at low temperature, suggesting that they are averaged out.

N,*N*-dialkylcarbamato derivatives of silicon(IV) have been prepared from $SiCl_4$ and the appropriate secondary amine[85] in toluene as the medium.

$$SiCl_4 + 8R_2NH + 4CO_2 \rightarrow Si(O_2CNR_2)_4 + 4[R_2NH_2]Cl \quad (14)$$

$$(R = Me, Et, {}^iPr)$$

X-ray diffractometry has shown the *iso*-propyl- {**TAKPEA10**-CSD} and the ethyl {**WAKRAB**-CSD} derivatives to be both mononuclear with all monodentate carbamato groups. This is the only case known of a homoleptic complex of this series containing monodentate groups only. The IR absorption at about 1710 cm^{-1}, one of the highest values so far observed for the entire family of compounds, was readily assigned to the C=O stretching vibration of the monodentate ligands, which are equivalent by symmetry.

The tin(IV) and lead(IV) carbamato derivatives have been mentioned in a patent,[79] as previously indicated. However, a better description of these derivatives has appeared in the literature more recently. The tin(IV) derivatives have been prepared[86] by the usual route, according to the following stoichiometry:

$$SnCl_4 + 8R_2NH + 4CO_2 \rightarrow Sn(O_2CNR_2)_4 + 4[R_2NH_2]Cl \quad (15)$$

$$(R = Et, {}^iPr)$$

Crystallographic data show the *iso*-propyl derivative $Sn(O_2CN{}^iPr_2)_4$ to be mononuclear {**196069-**CCDC} with all terminal bidentate carbamato groups; the coordination geometry is best described as derived from two tetrahedra of oxygen donors, one alongated [Sn−O bond distances, 2.193−2.218 Å] and one flattened [Sn−O bond distances, 2.123−2.124 Å] around the eight-coordinated central metal atom.

The ethyl derivative $Sn(O_2CNEt_2)_4$ [monoclinic, *C*2/*c*, $Z = 4$; $a = 13.965$, $b = 12.082$, $c = 16.675$ Å; $\beta = 108.20°$] has recently been synthesized[87] by a similar procedure and shown by X-ray crystallography to be mononuclear {**http://pubs.acs.org**} with octacoordinated tin. Accordingly, a further case of isostructural behavior has been found within this class of compounds: in fact, $Sn(O_2CNEt_2)_4$ is isostructural with the corresponding[88] zirconium derivative {**HILJUH**-CSD} published earlier (vide infra) [$Zr(O_2CNEt_2)_4$, monoclinic, *C*2/*c*, $Z = 4$; $a = 14.057$, $b = 12.168$, $c = 16.746$ Å; $\beta = 108.07°$]. The Sn−O average bond distance in $Sn(O_2CNEt_2)_4$ is 2.181 Å, while the corresponding Zr−O average distance in $Zr(O_2CNEt_2)_4$ is 2.226 Å, the difference $r(Zr^{4+}) - r(Sn^{4+})$ being 0.04 Å. This is in good agreement with the ionic radii differing by 0.03 Å on going from zirconium(IV) (0.84 Å) to tin(IV) (0.81 Å) for CN = 8, according to a well-established collection of crystallographic data.[89]

The homoleptic derivatives of antimony(III) $Sb(O_2CNR_2)_3$, R = Me, Et, ^iPr, have been prepared[87] by carbonation of the dimethylamido derivative, or by the $SbCl_3/NHR_2$ reaction to give the amido intermediate, followed by its carbonation in situ. The X-ray structural investigation of the three compounds has been reported {http://pubs.acs.org}

$$Sb(NMe_2)_3 + 3CO_2 \rightarrow Sb(O_2CNMe_2)_3 \quad (16)$$

$$SbCl_3 + 6NHR_2 + 3CO_2 \rightarrow Sb(O_2CNR_2)_3 + 3[NH_2R_2]Cl \quad (17)$$

$$(R = Et, {}^iPr)$$

The methyl compound shows some intermolecular contacts within pairs of molecules, while the other two compounds are mononuclear, the ethyl derivative possessing a pyramidal geometry which is compatible with the presence of a stereochemically active lone pair, typical of several coordination compounds of antimony(III).

For the preparative aspects concerning these compounds, it is appropriate to mention that the above reactions should not perhaps be regarded as real insertion reactions of carbon dioxide between the $Sn-NR_2$ bond (vide infra) but, rather, as a NR_2^-/O_2CNR^- exchange processes.

3.2.2. Transition Elements

In this part, the preparative aspects will especially be stressed. Matter will therefore be separated ac-

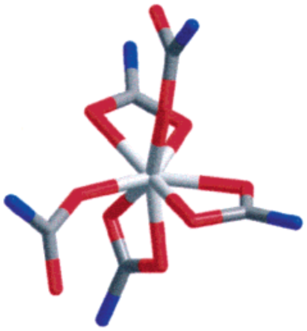


Figure 3. Schematic molecular structure of $Nb(O_2CNMe_2)_5$. Centers of sticks: light-gray, metal atoms; gray, carbon atoms; red, oxygen atoms. Blue sticks, nitrogen atoms. Alkyl groups not shown. Drawing obtained using the published structural data.[8b]

cording to the synthetic methodologies, although also the sequence from left to right of the elements within the Periodic Table will generally be followed. Lanthanides, i.e., 4f transition elements, will be discussed toward the end of this part.

As anticipated in the Introduction, *N*,*N*-dialkylcarbamato derivatives of early transition metals were the first to be prepared, as obtained through the $M(NR_2)_n/CO_2$ route. The first homoleptic derivative to be prepared was $Ti(O_2CNR_2)_4$[7b] due to the availability of the corresponding homoleptic *N*,*N*-dialkylamido complexes as starting materials. Other compounds of the same class prepared by this route are $Nb(O_2CNMe_2)_5$ {**PMCBNB**-CSD},[8b] $Ta(O_2CNMe_2)_5$,[8c,d] and $W_2(O_2CNMe_2)_6$ {**DECMDW10**-CSD} [the dinuclear derivative of tungsten(III), as obtained by carbonation of $W_2(NMe_2)_6$, has a short W−W distance of 2.279 Å, suggestive of a W−W triple bond].[8e] To the best of our knowledge, the homoleptic derivative of niobium(V), see Figure 3, is the structurally characterized compound of this class with the highest oxidation state of the central metal atom. The central atom is octa-coordinated with both bidentate- and monodentate carbamato groups.

However, a more general preparative method was necessary (vide infra) in order to overcome the initial restriction that *N*,*N*-dialkylamido metal complexes with aryl- or simple alkyl groups are sometimes difficult to prepare or are not reported in the literature. The use of other more viable preparative methods initiated with the finding[10a] that $[U(O_2CNR_2)_4]_n$ can readily be produced by a $R_2NCO_2^-/Cl^-$ metathetical reaction. As discussed in section 2, the amine/CO_2 system in a hydrocarbon medium forms the carbamato ion in variable concentrations depending on the nature of the R group. Thus, the $NR_2CO_2^-$ anion should be present in a sufficient concentration to become the main reactive species on a preparative scale. The formation of the homoleptic dialkylcarbamato complex of uranium(IV) can thus be described as in eq 18:

$$UCl_4 + 4[R_2NH_2][O_2CNR_2] \rightarrow 1/n[U(O_2CNR_2)_4]_n + 4[R_2NH_2]Cl \quad (18)$$

$$(R = Me, Et)$$

This methodology can be applied to several other metal halides. Due to the elevated solubility of *N*,*N*-dialkylcarbamato derivatives and to the negligible solubility of the appropriate dialkylammonium chloride in the reaction solvent (toluene or an aliphatic hydrocarbon), product separation is generally easily achieved.

The $TaCl_5/Et_2NH/CO_2$ route gives the homoleptic compound of tantalum(V), $Ta(O_2CNEt_2)_5$, which has been shown by X-ray crystallography to be mononuclear[90] {**ZOVVOV**-CSD} with the central metal atom surrounded by three bidentate and two monodentate diethylcarbamato groups in a slightly distorted square-antiprismatic geometry. On the other hand, the $Ta(NMe_2)_5/CO_2$ route[8f] affords the product of partial substitution $Ta(NMe_2)_2(O_2CNMe_2)_3$, vide infra.

N,*N*-Di-*iso*-propylcarbamato derivatives of group 4 (Ti, Hf) have been synthesized starting from the anhydrous metal chloride.[91] The mononuclear compounds in the IV oxidation state, of formula $M(O_2CN^iPr_2)_4$ [M = Ti {**XECCEN**-CSD},[92] Hf {**JIKPIC**-CSD}],[91] containing the octacoordinated central metal atom have been reported and shown by X-ray crystallography to be isostructural. Most interesting is the fact that the *iso*-propyl derivative of tin(IV),[86] see section 3.2.1, is isostructural with those of titanium(IV) and hafnium(IV).

The isostructural relationship holds also for the ethyl derivatives $M(O_2CNEt_2)_4$, [M = Zr(IV) {**HILJUH**-CSD},[88] M = Nb(IV), {**ZOVVUB**-CSD},[90] and M = Sn(IV)[87]]. The compounds show dodecahedral coordination, with an M−O average distance of 2.20 Å for the zirconium derivative,[88] to be compared with the distance of 2.16 Å for the niobium(IV) compound. The difference $r(Zr^{4+}) - r(Nb^{4+}) = 0.04$ Å corresponds exactly, within experimental error, to the difference of the ionic radii of these cations for CN = 8 ($\Delta = 0.04$ Å).[89] The availability of the niobium(IV) compound of $4d^1$ electronic configuration offered the possibility of diluting the latter into the diamagnetic matrix of the corresponding complex of zirconium(IV). The dilution was carried out by in vacuo evaporation of a toluene solution containing both $Zr(O_2CNEt_2)_4$ and $Nb(O_2CNEt_2)_4$ in the molar ratio of 11:1. The ESR spectrum of the resulting solid solution was simulated[88] with the following parameters: $g_{xx} = 2.0174$, $g_{yy} = 1.9374$, $g_{zz} = 1.8980$, $A_{xx} = 73.2$ G, $A_{yy} = 149.0$ G, $A_{zz} = 260.7$ G, $\Delta H(p-p)_{xx} = \Delta H(p-p)_{yy} = 6.4$ G, $\Delta H(p-p)_{zz} = 7.1$ G. The angle of 7° of noncoincidence between g_{yy}/A_{yy} and g_{zz}/A_{zz} indicates a monoclinic EPR symmetry, corresponding to C_2 point symmetry, thus confirming the results of the solid-state X-ray diffraction study on $Nb(O_2CNEt_2)_4$.

Neutral and anionic derivatives of titanium(III) and vanadium(III), of $3d^1$ and $3d^2$ configurations, respectively, were prepared by reacting $TiCl_3$ [better as its tetrahydrofuran adduct, $TiCl_3(THF)_3$], or VCl_3, respectively, with NH^iPr_2 and carbon dioxide.[57] As the reactions are slow, both systems were reacted with carbon dioxide under pressure at 80 °C (titanium) or at room temperature (vanadium). Both neutral and anionic complexes were isolated, and the X-ray structure of $[NH_2{}^iPr_2][Ti_2(O_2CN^iPr_2)_7]$ {**FOVBIB**-CSD} was solved after recrystallization at 5 °C in the presence of carbon dioxide. An equilibrium between neutral and anionic species was suggested to be operating in hydrocarbon solution.

$$\mathrm{Ti_2(O_2CN^{\mathit{i}}Pr_2)_6 + O_2CN^{\mathit{i}}Pr_2^- \rightarrow [Ti_2(O_2CN^{\mathit{i}}Pr_2)_7]^-} \quad (19)$$

The dinuclear anion of titanium(III) contains three bridging carbamato groups; each titanium center is hexacoordinate with monodentate and bidentate terminal groups. In agreement with the structural data in the solid state, the IR spectra in PCTFE show a band at 1620 $\mathrm{cm^{-1}}$ assigned to the terminal monodentate carbamato group. In the dinuclear anion the nonbonding Ti···Ti distance is 4.30 Å, thus showing that no important metal−metal interaction occurs, in agreement with the magnetic moment of 1.84 μ_B, substantially the calculated value for a noninteracting $3d^1$ system, with a small contribution from spin−orbit coupling. The di-*iso*-propyl derivative of titanium(III) belongs to the class of the anionic carbamato complexes, still rather poorly represented in the literature.

N,*N*-di-*iso*-propylcarbamato derivatives of niobium(II) and tantalum(II) of d^3 electronic configuration were prepared[90] in excellent yields by carbonation of $\mathrm{M_2(\eta^6\text{-}C_6Me_6)_2Cl_4}$ in the presence of $\mathrm{NH^{\mathit{i}}Pr_2}$.

$$\mathrm{M_2(\eta^6\text{-}C_6Me_6)_2Cl_4 + 8NH^{\mathit{i}}Pr_2 + 4CO_2 \rightarrow M_2(\eta^6\text{-}C_6Me_6)_2(O_2CN^{\mathit{i}}Pr_2)_4 + 4[^{\mathit{i}}Pr_2NH_2]Cl} \quad (20)$$

$$(\mathrm{M = Nb, Ta})$$

Although the solid-state structural data of these compounds are not yet available, the experimentally verified diamagnetism suggests the compounds to be dinuclear with a single metal−metal bond and four bridging carbamato groups, formally corresponding to a closed-shell configuration of 18 electrons for both niobium(II) and tantalum(II).

An interesting comparison can be made between the carbamato derivatives of copper(II), a d^9 system,[93] and chromium(II),[94] a d^4 system, $\mathrm{Cu_2(O_2CNEt_2)_4(NHEt_2)_2}$ {**DEBRUX**-CSD} and $\mathrm{Cr_2(O_2CNEt_2)_4(NHEt_2)_2}$ {**ECBACR**-CSD}, respectively. The copper(II) derivative was prepared by carbonation of copper(II) chloride in the presence of the appropriate amine, while the chromium complex was prepared both by carbonation of the amido derivative $\mathrm{Cr(NEt_2)_4}$ [94a] and via the metal chloride/amine route from anhydrous chromium(II) chloride in the presence of $\mathrm{NHEt_2}$.[94b] Both compounds have a dinuclear structure with four bridging carbamato groups. The copper(II) and chromium(II) derivatives were found to be isostructural by X-ray diffraction methods. In the copper dimer, the metal−metal distance is 2.658 Å, to be compared with a metal−metal distance of 2.384 Å in the chromium(II) derivative, thus suggesting a multiple metal−metal bond in the latter. The corrected magnetic susceptibility of the copper(II) derivative in the range of temperature $4.2\ \mathrm{K} \le T \le 256\ \mathrm{K}$[93] was interpreted on the basis of a singlet ground state and a triplet lying $|J|$ higher in energy, due to unpaired electrons in the d_{x2-y2} orbital ($2J = -80.2 \pm 04\ \mathrm{cm^{-1}}$; $g = 2.137 \pm 0.004$). A paramagnetic impurity, possibly $\mathrm{Cu(O_2CNEt_2)_2(NHEt_2)_2}$, was assumed to be present in order to explain the discontinuity of the magnetic susceptibility versus temperature showing a maximum centered at 65 K, the susceptibility increasing again below 20 K. It is interesting to note that later a compound of analytical composition $\mathrm{Cu(O_2CNMe_2)_2(NHMe_2)_2}$ was in fact isolated by another research group. Details on this and other mononuclear *N*,*N*-dialkylcarbamato complexes of copper(II) will be presented further on.

Redox reactions accompanied by ligand transfer can be used for preparative purposes. For example, the reaction between $\mathrm{Pd(O_2CNEt_2)_2(NHEt_2)_2}$ and $\mathrm{Cr_2(O_2CNEt_2)_4(NHEt_2)_2}$ gives palladium metal and the derivative of chromium(III),[95] identical with the chromium(III) complex prepared by the traditional ligand exchange reaction from anhydrous $\mathrm{CrCl_3}$ with $\mathrm{NHEt_2/CO_2}$.

$$\mathrm{Pd(O_2CNEt_2)_2(NHEt_2)_2 + Cr_2(O_2CNEt_2)_4(NHEt_2)_2 \rightarrow Pd + 2Cr(O_2CNEt_2)_3 + 4NHEt_2} \quad (21)$$

The ethyl derivative of manganese(II) of formula $\mathrm{Mn_6(O_2CNEt_2)_{12}}$ was prepared[96,97] by two different methods, i.e. from bis(cyclopentadienyl)manganese(II), $\mathrm{MnCp_2}$,[98] and through the more direct route from the anhydrous chloride. The compound, as recrystallized from hot heptane showed the following cell parameters: monoclinic, space group $C2/c$, $Z = 4$, $a = 18.546$, $b = 19.287$, $c = 24.877$ Å, $\beta = 95.38°$. The molecular structure {**KADJOO**-CSD} consists of four five-coordinated manganese atoms in an approximately trigonal bipyramidal coordination, the remaining two manganese atoms displaying a distorted octahedral geometry. The manganese(II) derivative is isostructural with the corresponding cobalt(II) compound.[83d]

$$\mathrm{6\ MnCp_2 + 12\ CO_2 + 12\ NHEt_2 \rightarrow Mn_6(O_2CNEt_2)_{12} + 12CpH} \quad (22)$$

$$\mathrm{6\ MnCl_2 + 12\ CO_2 + 24\ NHEt_2 \rightarrow Mn_6(O_2CNEt_2)_{12} + 12\ [Et_2NH_2]Cl} \quad (23)$$

The magnetic susceptibility of the hexanuclear manganese(II) derivative $\mathrm{Mn_6(O_2CNEt_2)_{12}}$ was measured between 70 and 250 K. The corrected molar magnetic susceptibility $\chi_{\mathrm{corr}}{}^{\mathrm{M}}$ [expressed per mol of manganese] decreases from 4.36×10^{-2} cgsu (70 K) to 1.53×10^{-2} cgsu (250 K). This corresponds[99] to a magnetic moment μ_{eff} slightly increasing from 4.97 μ_B at 70 K to 5.56 μ_B at 250 K. A small degree of magnetic coupling at low temperatures is suggested by these data. The hexanuclear complex is to be regarded as a high-spin d^5 system of manganese(II) with $S = 15$ at room temperature, a small interaction within the metal centers being indicated by the magnetic susceptibility data. This compound may be therefore of potential interest in some fields of application.[100]

The hexanuclear cobalt derivatives[83d] $\mathrm{Co_6(O_2CNR_2)_{12}}$, R = Et, ^{i}Pr, were prepared by reacting anhydrous cobalt(II) chloride with the appropriate amine under carbon dioxide at atmospheric pressure in toluene as the medium.

$$6CoCl_2 + 24R_2NH + 12CO_2 \rightarrow Co_6(O_2CNR_2)_{12} + 12[NH_2R_2]Cl \quad (24)$$

The following crystallographic data were obtained[83d] on $Co_6(O_2CNEt_2)_{12}$ {**CETXUU**-CSD} [*iso*-octane as solvent of recrystallization upon refluxing and cooling, space group $C2/c$, monoclinic, $a = 18.428$, $b = 19.189$, $c = 24.654$ Å, $\beta = 95.90°$, $U = 8672$ Å^3, $T = 298$ K]. These data are to be compared with those obtained[83c] later for the same compound recrystallized under different conditions [from MeCN, space group $Ccca$, orthorhombic, $a = 20.712$, $b = 25.040$, $c = 16.498$ Å, $U = 8557$ Å^3, $T = 298$ K]. This sets an example of systems for which the different recrystallization conditions may produce a different crystal packing.

In the case of ruthenium(II), complete removal of the chloride ligands from $[Ru(\eta^6\text{-cymene})Cl_2]_2$ requires the dialkylcarbamato derivative of silver to be used.

$$^1/_2[Ru(\eta^6\text{-cymene})Cl_2]_2 + Ag_2(O_2CNR_2)_2 \rightarrow Ru(\eta^6\text{-cymene})(O_2CNR_2)_2 + 2AgCl \quad (25)$$

$$(R = Me, Et)$$

The crystal structure {**176780**-CCDC} of the ethyl derivative $Ru(\eta^6\text{-cymene})(O_2CNEt_2)_2$ shows[101] the compound to be mononuclear with both monodentate and bidentate carbamato groups. Taking into account the electronic contribution by the ligands to the ruthenium(II) center of $4d^6$ configuration, it is concluded that the metal in this compound acquires the EAN of the next inert gas.

The chlorides of platinum(II) and palladium(II) do not afford the carbamato derivatives with NHR_2/CO_2. Thus, alternative synthetic methodologies had to be used. Although uncertainties still exist about metal−chloride bond enthalpies[102] for platinum(II) and palladium(II), the presumably high metal−halide bond enthalpy is responsible for the lack of reactivity of the dihalides MX_2L_2, M = Pd, Pt; X = Cl, I; L = PR_3, toward the Et_2NH/CO_2 system. In the case of palladium(II), the problem could be circumvented by reacting the acetonitrile complex $[Pd(MeCN)_4]^{2+}$ with Et_2NH/CO_2, which led to the successful preparation of the appropriate carbamato complex.[10b,71]

$$[Pd(MeCN)_4]^{2+} + 6Et_2NH + 2CO_2 \rightarrow trans\text{-}Pd(O_2CNEt_2)_2(NHEt_2)_2 + 4MeCN + 2NH_2Et_2^+ \quad (26)$$

The molecular structure of the mononuclear derivative of palladium(II) is shown in Figure 4.

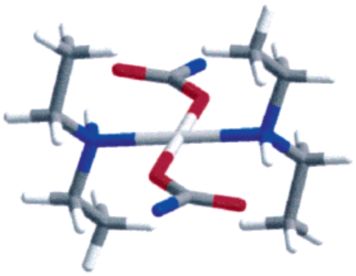


Figure 4. Schematic molecular structure of $Pd(O_2CNEt_2)_2(NHEt_2)_2$. Centers of sticks: light-gray, metal atoms; gray, carbon atoms; red, oxygen atoms. Blue sticks, nitrogen atoms. Alkyl groups not shown. Intramolecular NH···O hydrogen bonds form an angle of 154°. Drawing obtained using the published structural data.[71a]

Silver oxide Ag_2O, characterized[103] by the low ΔH_f^0 of −31.1 kJ mol^{-1}, can be appropriately used as starting material to prepare the silver carbamato complexes.[104] The water formed in the reaction, which could induce the system to revert to the products, was removed with a dehydrating agent (R = Et), or else by solvation with MeCN (R = Me).

$$Ag_2O + 2R_2NH + 2CO_2 \rightarrow 2Ag(O_2CNR_2) + H_2O \quad (27)$$

$$(R = Me, Et)$$

The ethyl derivative is dinuclear by cryoscopy in benzene. For the synthesis of the methyl derivative, the addition of a dehydrating agent is not required, when the product is prepared in MeCN. The compound is polynuclear {**SAQPUV**-CSD}, the dinuclear building blocks $Ag_2(O_2CNMe_2)_2$ constitute an infinite chain formed by the eight-membered Ag−O−C−O−Ag−O−C−O rings [with intra-annular Ag−O bond distances of 2.156 and 2.219 Å], held together by relatively long inter-annular Ag−O bonds of 2.600 Å.

The silver carbamato derivatives may be used for synthetic purposes as ligand-transfer reagents, with metal halides characterized by a robust metal−chloride bond. For example, the platinum(II) derivative *trans*-$Pt(O_2CNEt_2)_2(NHEt_2)_2$ has been prepared by using $Ag(O_2CNEt_2)$ as halide scavenger, and $PtI_2(NHEt_2)_2$ as the platinum-containing precursor.[105]

$$PtI_2(NHEt_2)_2 + 2Ag(O_2CNEt_2) \rightarrow 2AgI + trans\text{-}Pt(O_2CNEt_2)_2(NHEt_2)_2 \quad (28)$$

As a matter of fact, the $PtI_2/CO_2/R_2NH$ system simply yields the $PtI_2(R_2NH)_2$ adduct. Even the acetonitrile complex $[Pt(MeCN)_4]^{2+}$ is not an appropriate starting material for the preparation of the carbamato complex of platinum(II), due to the side-reaction by the secondary amine on the coordinated acetonitrile, which is faster than ligand substitution.[106]

In addition to the already mentioned $Cu_2(O_2CNEt_2)_4(NHEt_2)_2$, isostructural with the corresponding chromium(II) compound of analogous formula $Cr_2(O_2CNEt_2)_4(NHEt_2)_2$, the mononuclear derivative of copper(II) $Cu(O_2CNMe_2)_2(NHMe_2)_2$ has been obtained from copper metal and $[NH_2Me_2][O_2CNMe_2]$

in the presence of dioxygen,[107] in a reaction which may be formulated as in the following equation:

$$2Cu + O_2 + 4[NH_2Me_2][O_2CNMe_2] \rightarrow 2Cu(O_2CNMe_2)_2(NHMe_2)_2 + 2H_2O \quad (29)$$

In this compound the central copper atom is pseudo-octahedrally coordinated {**JAFQOW**-CSD} to two terminal bidentate carbamato groups and to two trans amine groups. It is worth mentioning that the existence of a small percentage of a mononuclear copper(II) carbamato derivative such as $Cu(O_2CNEt_2)_2(NHEt_2)_2$ in the dinuclear $Cu_2(O_2CNEt_2)_4(NHEt_2)_2$, was anticipated[93] (vide supra) on the basis of the anomalous magnetic behavior of the dinuclear system at temperatures around 20 K. This hypothesis lends further support from the new findings on $Cu(O_2CNMe_2)_2(NHMe_2)_2$.

In a systematic study[62a] on the extraction of metal cations from aqueous solution into hydrocarbons by the NHR_2/CO_2 system, copper(II) was found to be solvent-extracted from aqueous solutions of $CuSO_4$ in the presence of a secondary amine NHR_2 (R should be a primary alkyl group such as butyl or benzyl) under carbon dioxide. The mononuclear dialkylcarbamato derivatives of copper(II) of formula $Cu(O_2CNR_2)_2(NHR_2)_2$ were identified as the hydrocarbon-soluble species.[62b] The benzyl derivative $Cu(O_2CNBz_2)_2(NHBz_2)_2$ thus obtained was studied by X-ray crystallography {**190080**-CCDC} and found to be mononuclear with tetracoordinated copper in a trans square-planar geometry. The carbamato groups are monodentate, with intramolecular hydrogen bonds between the amine hydrogen and the uncoordinated oxygen of the carbamato ligand. Of interest is the fact that the hydrophobic benzyl groups pack efficiently around the central metal atom, thus presumably preventing the product from undergoing ready hydrolysis, under the conditions of its formation.

Homoleptic derivatives of zinc(II) have been reported.[107] The ionic carbamato derivative $[NH_2Me_2][O_2CNMe_2]$ dissolves in MeCN and reacts under an argon atmosphere with zinc powder evolving dihydrogen and producing the homoleptic ionic zinc(II) derivative, $[NH_2Me_2][Zn_2(O_2CNMe_2)_5]\cdot MeCN$, eq 30, in excellent yields.

$$2Zn + 5[NH_2Me_2][O_2CNMe_2] + MeCN \rightarrow [NH_2Me_2][Zn_2(O_2CNMe_2)_5]\cdot MeCN + 2H_2 + 4NHMe_2 \quad (30)$$

The X-ray data {**JAFQUC**-CSD} confirm the presence of the $[Zn_2(O_2CNMe_2)_5]^-$ anion with three bidentate bridging carbamato groups and one terminal monodentate anionic ligand on each zinc atom, see Figure 5. This is one of the few examples of structurally characterized anionic *N*,*N*-dialkylcarbamato derivatives reported in the literature.

The homoleptic diethylcarbamato derivative of zinc(II) of formula $Zn(O_2CNEt_2)_2(TMEDA)$ was obtained from the reaction of the methyl derivative $Zn_4Me_2(O_2CNEt_2)_6$ with TMEDA, together with other products. The mononuclear compound contains hexacoordinated zinc {**ZIPPOD**-CSD} with two bidentate carbamato groups, the coordination sphere being completed by the bidentate amine.[108]

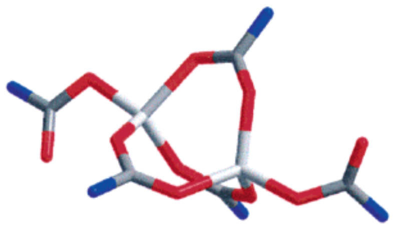


Figure 5. Schematic molecular structure of the dinuclear anion $[Zn_2(O_2CNMe_2)_5]^-$. Centers of sticks: light-gray, metal atoms; gray, carbon atoms; red, oxygen atoms. Blue sticks, nitrogen atoms. Alkyl groups not shown. Drawing obtained using the published structural data.[107]

The first *N*,*N*-dialkylcarbamato derivatives of lanthanides (Ln) were synthesized[109a,b] by reacting the anhydrous chlorides of ytterbium(III) and erbium(III) with the NHR_2/CO_2 system in a hydrocarbon medium

$$4LnCl_3 + 24NH^iPr_2 + 12CO_2 \rightarrow Ln_4(O_2CN^iPr_2)_{12} + 12[NH_2{}^iPr_2]Cl \quad (31)$$
$$(Ln = Yb, Er)$$

Also in this case product separation was facilitated by the satisfactory solubility of the lanthanide product with respect to the dialkylammonium chloride coproduct. The crystallographic study of the ytterbium derivative {**IPCBYB10**-CSD} has shown [monoclinic, space group $C2/c$, $Z = 4$, $a = 29.069$, $b = 19.591$, $c = 23.193$ Å, $\beta = 107.70°$, $U = 12583$ Å^3, $T = 298$ K] the product $[Yb_4(O_2CN^iPr_2)_{12}]\cdot 2C_7H_{16}$ to be tetranuclear with a 2-fold axis of symmetry. The ytterbium atoms are heptacoordinated being joined by bridging and chelating carbamato groups, while terminal monodentate ligands are absent.

At the time the ytterbium(III) and erbium(III) products were prepared, the synthesis could not be extended to other lanthanides. In fact, anhydrous lanthanide chlorides, other than those of ytterbium(III) and erbium(III), as obtained by the classical Ln_2O_3/NH_4Cl route at high temperature,[109c] were found to be totally unreactive toward the NHR_2/CO_2 system. Moreover, the yields of the erbium(III) derivative were low, even at elevated temperature and pressure of carbon dioxide. No attempt was made to use the chlorides, as prepared from the metal and hydrogen chloride.[109d] A substantial breakthrough toward extending the synthesis of these compounds to other lanthanide elements came from the use of the THF or DME adducts of the metal chlorides. These complexes[109e] of formula $LnCl_3(DME)_2$ or $LnCl_3(THF)_n$ were found to be readily prepared under mild conditions by treating the lanthanide oxide or carbonate (in the range from La to Gd) with thionyl chloride in the presence of the appropriate ether.

$$Ln_2O_3 + 3SOCl_2 \rightarrow 2LnCl_3 + 3SO_2 \quad (32)$$

$$LnCl_3 + 2DME \rightarrow LnCl_3(DME)_2 \quad (33)$$

Over a large portion of the lanthanide series, the DME adducts of MCl_3 have been found to be mono-

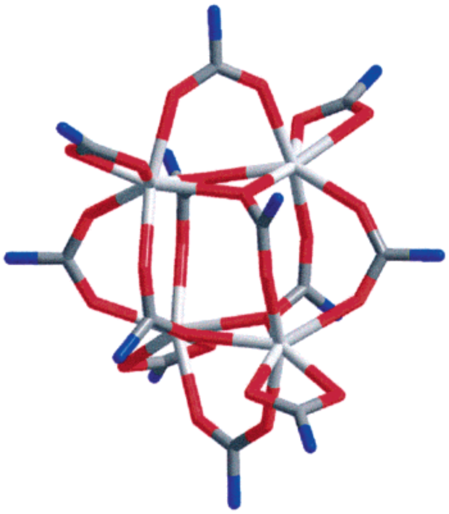


Figure 6. Schematic molecular structure of the tetranuclear lanthanide complexes $Ln_4(O_2CN^iPr_2)_{12}$. Centers of sticks: light-gray, metal atoms; gray, carbon atoms; red, oxygen atoms. Blue sticks, nitrogen atoms. Alkyl groups not shown. Drawing obtained using the published structural data.[71a]

nuclear, the central metal atom being heptacoordinated. For example, $EuCl_3(DME)_2$ is monoclinic, space group $P2_1/c$, $a = 11.53$, $b = 8.930$, $c = 15.656$ Å, $\beta = 105.07°$, $U = 1556$ Å^3, $T = 258$ K. From a preparative viewpoint, it is important that the DME or THF adducts of MCl_3 are readily reactive toward the NH^iPr_2/CO_2 system, giving the tetranuclear carbamato derivatives. The $Ln_4(O_2CN^iPr_2)_{12}$ products were found to be isostructural from neodymium(III) ($Z = 60$) to ytterbium(III) ($Z = 70$), thus spanning a range of 11 atomic numbers along the series.[110]

The typical molecular structure of this class of compounds is shown in Figure 6.

The accurate determination by X-ray diffraction methods of the four different types of Ln–O interatomic distances in the carbamato derivatives provided an internal check of the lanthanide contraction along the series.[110,111] The even more extended series of the isostructural aquo lanthanide complexes, namely, $[M(H_2O)_9][EtOSO_3]_3$ and $[M(H_2O)_9][CF_3SO_3]_3$, further established that the ionic radii contraction, as a function of the f^n configuration, is best represented by a quadratic expression.[111]

3.3. Non-Homoleptic Compounds

Incomplete removal of the anionic ligands by $R_2NCO_2^-$ in reactions using a metal-containing precursor or partial carbonation of the amido precursor by carbon dioxide leads to nonhomoleptic compounds, i.e., containing anionic ligands of a different nature. As stated earlier, reacting an amido precursor with carbon dioxide actually consists of setting up the conditions for an amido/carbamato exchange. Normally, a chloride/carbamato exchange, beside being more facile from a synthetic viewpoint is more effective due to the low solubility of the ammonium (or substituted ammonium) halide in the reaction mixture, thus leading the reaction to normally proceed to completion.

3.3.1. Main Group Elements

The nonhomoleptic carbamato derivative of magnesium of formula $[Mg(O_2CNEt_2)Br(THF)_2]_2$, characterized by X-ray diffraction methods {**HOYVUM**-CSD}, was prepared by reacting the methyl-bromide Grignard reagent with CO_2 and Et_2NH in THF.[112]

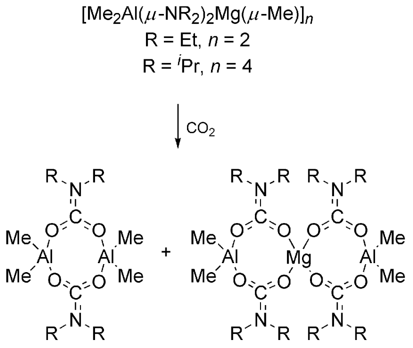
Scheme 4

$$MgMeBr \xrightarrow[CO_2]{NHEt_2\ /\ THF} [Mg(O_2CNEt_2)Br(THF)_2]_2$$

The carbamato groups are in a bridging position, while the bromides are terminal. The crystal of the product contains molecules **1** and **2**, of the same composition, differing from one another by the coordination mode. In **1**, each magnesium is pentacoordinated with a Mg···Mg contact of 3.354 Å, while in **2** the Mg···Mg contact is 3.779 Å. The interconversion of the two species in solution corresponds to a small energy change ($\Delta G° \approx 0$ kJ mol^{-1}). In an almost simultaneous paper,[84] the bromo di-*iso*-propylcarbamato derivative $Mg_2(O_2CN^iPr_2)_2Br_2(THF)_4$ was synthesized in high yields by a substantially identical procedure. The crystals {**KOLBES**-CSD} have a molecular structure corresponding to that of the ethyl derivative **1**, with a Mg···Mg contact of 3.277 Å.

The reaction of $Mg(N^iPr_2)_2$ [83b] with carbon dioxide, followed by recrystallization from a HMPA/toluene mixture gave crystals of the pentanuclear derivative $Mg_5(O_2CN^iPr_2)_8(CO_3)(HMPA)_2$ {**QESKII**-CSD}. In this compound the carbonato ligand occupies a central position inside the pentanuclear system, with all three oxygen atoms acting as bridging donor atoms. The C–O distances within the carbonato ligand are 1.282, 1.276, and 1.282 Å. Moreover, a mixed magnesium/aluminum amide of formula $Al_4Mg_4(\mu\text{-}N^iPr_2)_8(\mu\text{-}Me)_4Me_8$ was reacted with CO_2 in a hydrocarbon solvent[113] and gave a *N*,*N*-dialkylcarbamato derivative of methyl-aluminum and a *N*,*N*-dialkylcarbamato compound containing both magnesium and methyl-aluminum moieties. The resulting dinuclear {**ZIQLEQ**-CSD}, $Al_2(O_2CN^iPr_2)_2Me_4$, and trinuclear {**ZIQLIU**-CSD}, $Al_2Mg(O_2CN^iPr_2)_4Me_4$, compounds were structurally characterized.

Scheme 5



In the dinuclear compound, aluminum is tetracoordinated with Al–O distances to the bridging carbamato groups of 1.802 and 1.811 Å; in the trinuclear Mg/Al compound, containing tetracoordinated aluminum too, the Al–O distances range from 1.776 to 1.795 Å. As stated earlier, the homoleptic derivative $Al_2(O_2CN^iPr_2)_6$ contains hexacoordinated aluminum,[85b] and the Al−O distance within the bridging carbamato groups is 1.821 Å, thus somewhat longer, as justified by the higher coordination number.

The *N*-alkyl- or *N*,*N*-dialkylcarbamato derivatives of boron, $B(O_2CNR_2)_2X$ ($X = Ph$, $o\text{-}C_6H_4O_2$, $R_2 = Et_2$; H, Et; H, ^tBu),[114] aluminum, $Al(O_2CNEt_2)Et_2$,[115] or thallium(III), $Tl(O_2CNMe_2)Me_2$,[116] have been obtained from $B(NR_2)_2X$, $Al_2(NEt_2)_2Et_4$, or $Tl(NMe_2)Me_2$, respectively, upon reaction with CO_2. In the case of aluminum,[115a] both *N*-methylimidazole, and pyridine were found to accelerate the reaction. The additional base is believed to cause the rupture of the diethylamido bridge in the $Al_2(NEt_2)_2Et_4$ dimer,[115b,117] thus increasing the nucleophilicity of the amido ligand, once converted to a terminal group. The aluminum derivative shows IR stretching vibrations at 1580 and 1490 cm^{-1}, suggestive of a bidentate carbamato ligand, see Appendix.

$$Al_2(NEt_2)_2Et_4 + 2CO_2 \rightarrow 2Al(O_2CNEt_2)Et_2 \tag{34}$$

In the case of the thallium(III) derivative, $TlMe_2(O_2CNMe_2)$,[116] the low wavenumber values of the strong absorptions at 1557, 1507 and 1391 cm^{-1} suggest a bidentate coordination of the carbamato ligand, see IR data in the Appendix. Although no MW was measured, the thallium compound is probably mononuclear with an approximately tetrahedral coordination of the central metal atom.

As far as the elements of Group 14 are concerned, the reactions of $ER^1{}_nR^2{}_m(NR^3R^4)_p$, E = Si, Ge, Sn, with CO_2 afford moderate to high yields of the appropriate carbamato complexes, see Table 2.

It is interesting to note that $Si(O_2CNMe_2)H_3$, as produced by carbonation of the corresponding dimethylamido derivative, shows a strong IR absorption at 1710 cm^{-1}, which is not affected on deuteration to $Si(O_2CNMe_2)D_3$.[119] This suggests that the band is associated with the carbamato group and the high wavenumber value indicates a monodentate ligation, see Appendix.

$$Si(NMe_2)H_3 + CO_2 \rightarrow Si(O_2CNMe_2)H_3 \tag{35}$$

Carbamato complexes of silicon of formula $Si(O_2CNHR)Me_3$, R = Me, Bu, allyl, Ph have been prepared by reacting $NH(SiMe_3)_2$ with RNH_2/CO_2 at atmospheric pressure.[130,131] In the course of the carbonation of $Si(NMe_2)_2Me_2$, it has been noted[118] that the reaction does not proceed at a satisfactory rate, unless some free amine is present. This is almost certainly associated with the formation of the corresponding ammonium carbamate $NH_2Me_2[O_2CNMe_2]$, see section 2.2, which is presumably the actual reactive species in the $NMe_2^-/Me_2NCO_2^-$ exchange process.

The reaction of NH_3/CO_2 with $SiClMe_3$ in THF at low temperature affords the trimethyl carbamate $Si(O_2CNH_2)Me_3$, which, however, could not be isolated since it decomposes during chromatography to give the *N*-trimethylsilyl-substituted carbamate of formula $Si(O_2CNHSiMe_3)Me_3$.[132]

Table 2. Carbonation of Amido Derivatives of Group 14 $E(R^1)_n(R^2)_m(NR^3R^4)_p + pCO_2 \rightarrow E(R^1)_n(R^2)_m(O_2CNR^3R^4)_p$

E	R^1	R^2	*n*	*m*	*p*	R^3	R^4	ref
Si	Me		3	0	1	Et	Et	118
Si	Me		3	0	1	H	Me	118
Si	H		3	0	1	Me	Me	119
Si	D		3	0	1	Me	Me	119
Si	Me		3	0	1	Me	Me	120
Si	Me		3	0	1	Et	Et	120,121 122,123
Si	Me		3	0	1	Me	Cy, Bz	124
Si	Me		3	0	1	Et	Cy	124
Si	Me		3	0	1	^iPr	Cy, Bz	124
Si	Me		3	0	1	Cy	Cy	124
Si	Me		3	0	1	^tBu	Bz	124
Si	Me		3	0	1	2,6-Me_2-pip	2,6-Me_2-pip	124
Si	^tBu	H	2	1	1	Me	Me	124
Si	Me	thex	2	1	1	Me	Me	124
Si	Ph		3	0	1	Me	Me	124
Si	Me		3	0	1	Me	H, Me, Me_3Si	125
Si	Me		3	0	1	Et	H, Et	125
Si	Me		3	0	1	Pr	H, Pr	125
Si	Me		3	0	1	^iPr	H, ^iPr	125
Si	Me		3	0	1	Bu	H, Bu, Me_3Si	125
Si	Me		3	0	1	^iBu	H, ^iBu	125
Si	Me		3	0	1	$(CH_2)_5$		125
Si	Me		3	0	1	$(CH_2)_2O(CH_2)_2$		125
Si	Me		3	0	1	^sBu	H	125
Si	Me		3	0	1	^tBu	H	125
Si	Me		3	0	1	$CH_2{=}CHCH_2$	H	125
Si	Me		3	0	1	Cy	H	125
Si	Me		3	0	1	Bz	H	125
Si	Me		3	0	1	4-Br-phenyl	H	126
Si	Me		3	0	1	^tBu	Ph	126
Sn	Me		3	0	1	Me	Me	127,128
Sn	Me		3	0	1	Et	Et	128
Sn	Me		3	0	1	pyrrolidyl	pyrrolidyl	128
Sn	Me		3	0	1	pyrrolyl	pyrrolyl	128
Sn	Me		3	0	1	H	Ph	128
Sn	Me		3	0	1	Me	Ph	128
Sn	Me		3	0	1	Me	$SnMe_3$	128
Sn	Me	Me	1	1	2	Me	Me	128
Sn	Me	Me	1	1	2	Et	Et	128
Sn	Ph		3	0	1	Me	Me	128
Sn	Ph	Ph	1	1	2	Me	Me	128
Sn	Ph		3	0	1	Me	Me	128
Ge	Et		3	0	1	Me	Me	129
Ge	Et		3	0	1	Et	Et	129

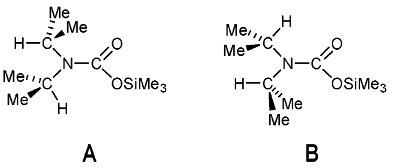
Scheme 6

$$2\,NH_3 + CO_2 + SiClMe_3 \xrightarrow{THF/\ 0\ °C} Si(O_2CNH_2)Me_3 + NH_4Cl$$

Structural studies on carbamato complexes of silicon have beeen reported: $Si(O_2CNRR')Me_3$, $R = R' = {}^iPr$ {**FUNZOD**-CSD};[133] R = H, R′ = Ph {**MSIPCM**-CSD};[130] R = H, R′ = 4-Br-phenyl {**TEHFUH**-CSD};[126a] R = H, R′ = 4-Me-phenyl {**TUKSOH**-CSD};[126b] $R = CMe_3$, R′ = Ph {**TEHGAO**-CSD}.[126a] In all these cases a distorted tetrahedral geometry around silicon, with monodentate carbamato groups, was observed. In solution, two conformers of $Si(O_2CN^iPr_2)Me_3$, **A** and **B**, presumably arising from restricted rotation also around the C_{sp^3}−N bond at temperatures around 220 K, see Scheme 7, have been detected by NMR.[133]

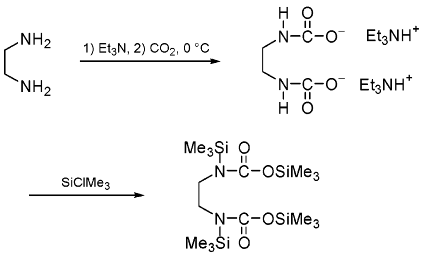
Trimethylsilyl carbamato complexes have also been obtained from $SiMe_3Cl$ with a bidentate amine (e.g.,

Scheme 7



ethylenediamine, propylenediamine) and CO_2 with,[134] or without a catalyst.[135] Scheme 8 refers to the reaction with ethylenediamine.

Scheme 8



The product appearing in Scheme 8, $SiMe_3[O_2CN(SiMe_3)(CH_2)_2(SiMe_3)NCO_2]SiMe_3$, has been studied by X-ray diffraction {**TEXHIN**-CDC}. Two additional products, derived from propylenediamine, have been synthesized, one similar to the preceding one with the propylene bridge $(CH_2)_3$, and a third one, which contains a propylene bridge and two carbamato groups{**TEXHUZ**-CDC}, of formula $SiMe_3[O_2CNH(CH_2)_3NHCO_2]SiMe_3$.[135]

The complexes $NMe(SnMe_3)_2$ [128] and $NH(GeEt_3)_2$ [129] show a different reactivity toward carbon dioxide. The tin(IV) derivative gives the mono-insertion product of formula $Sn[O_2CNMe(SnMe_3)]Me_3$. The germanium compound gives the double insertion product $(Et_3Ge)(O_2CNHCO_2)(GeEt_3)$, which, however, is not stable and decomposes to the isocyanato derivative of germanium(IV), $GeEt_3(NCO)$, and to triethylgermanium oxide.[130]

$$NMe(SnMe_3)_2 + CO_2 \rightarrow Sn[O_2CNMe(SnMe_3)]Me_3 \quad (36)$$

$$NH(Ge\ Et_3)_2 + 2CO_2 \rightarrow (Et_3Ge)O_2CNHCO_2(GeEt_3) \quad (37)$$

$$(Et_3Ge)O_2CNHCO_2(GeEt_3) \rightarrow GeEt_3(NCO) + 1/2(Et_3Ge)_2O + 1/2H_2O + CO_2 \quad (38)$$

Attempts to convert tetrakis(dimethylamido)tin(IV) into the corresponding homoleptic derivative $Sn(O_2CNMe_2)_4$ were unsuccessful, and the bis(dimethylcarbamato) product $Sn(O_2CNMe_2)_2(NMe_2)_2$ was obtained instead.[128]

As stated above, see section 3.2.2, $Ta(NMe_2)_5$ behaves similarly giving the product of partial carbonation, at least at the initial stages of the reaction,[8f] see eq 39. As mentioned in section 3.2.1, the homoleptic carbamato derivatives of tin(IV) have now become available by the $SnCl_4/R_2NH/CO_2$ route;[86,87,136] this is a simplified methodology with respect to carbonation of the amido derivatives, the latter requiring the use of $LiNMe_2$ to be synthesized.[136]

$$Sn(NR_2)_4 + 2CO_2 \rightarrow Sn(O_2CNR_2)_2(NR_2)_2 \quad (39)$$
$$R = Me, Et$$

Noteworthy are the reactions of the hydrazido complexes of formula $M[N(R)NMe_2]Me_3$, M = Si, Ge, with CO_2.[137] The compounds with R = H readily react forming the carbamato derivative, while the fully substituted, sterically hindered, compounds (R = Me, $GeMe_3$) require forcing conditions.

Scheme 9

$$M[N(R)NMe_2]Me_3 \xrightarrow{CO_2} M[O_2CN(R)NMe_2]Me_3$$

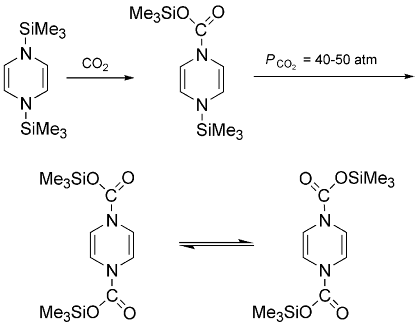
R = H; M = Si, Ge; 25 °C

R = Me; M = Si, Ge; 90 °C

R = Ge Me$_3$; M = Ge; 90 °C

By reaction of the electron-rich 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine with CO_2, mono- and double insertions of carbon dioxide into the Si−N bond have been observed,[138] see Scheme 10. Two isomers of the product of formal double insertion, which interconvert slowly due to restricted rotation around the N−C(=O) bond, have been detected by ^1H NMR spectra.

Scheme 10



The synthesis of $E[O_2CN(ER_3)(R')]R_3$, E = Ge, Sn, is based on the reaction of bis(trialkyl)metal oxides $(R_3E)_2O$ with alkyl or aryl isocyanates[139,140]

$$(R_3E)_2O + R'NCO \rightarrow E[O_2CN(ER_3)R']R_3 \quad (40)$$

$$(E = Sn; R = Bu, Et; R' = Me, Ph, naphthyl; E = Ge; R = Me, R' = Ph)$$

The reaction of $Sn[O_2CN(SnBu_3)Ph]Bu_3$ with aniline gives a mixture of tributyltin-*N*-phenylcarbamate, $Sn(O_2CNHPh)Bu_3$ and *N*-tributylstannylaniline, $NHPh(SnBu_3)$, the latter being converted to the former with CO_2.[139]

Scheme 11

$$Sn[O_2CN(SnBu_3)Ph]Bu_3 + NH_2Ph \longrightarrow Sn(O_2CNHPh)Bu_3 + \text{products}$$

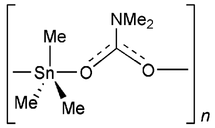
$$NHPh(SnBu_3) \xrightarrow{CO_2} Sn(O_2CNHPh)Bu_3$$

Tributyltin-*N*-ethylcarbamate, $Sn(O_2CNHEt)Bu_3$ was prepared by a similar procedure from tributyltin-*N*-phenyl-*N*-tributylstannylcarbamate, $Sn[O_2CN(SnBu_3)Ph]Bu_3$, ethylamine, and carbon dioxide in what may be substantially classified as a carbamato group exchange process[139]

$$\mathrm{Sn[O_2CN(SnBu_3)Et]Bu_3 + [NH_3Et][O_2CNHEt] \rightarrow Sn(O_2CNHEt)Bu_3 + [NH_2Et_2][O_2CN(SnBu_3)Et]} \quad (41)$$

The IR data on these tin derivatives are consistent with a bidentate nature of the carbamato ligand, as evidenced by the absorptions observed between 1600 and 1500 $\mathrm{cm^{-1}}$. A polynuclear structure with bridging carbamato groups has been proposed[127] for $\mathrm{Sn(O_2CNMe_2)Me_3}$. An IR absorption of medium intensity at 1695 $\mathrm{cm^{-1}}$ with a shoulder at 1642 $\mathrm{cm^{-1}}$ has been attributed to the presence of small amounts of the mononuclear species $\mathrm{Sn(O_2CNMe_2)Me_3}$ containing a monodentate *N*,*N*-dimethylcarbamato ligand.

Scheme 12



A dimethyl carbamato derivative of germanium of formula $\mathrm{Ge(O_2CNMe_2)Me_3}$, a colorless liquid at room temperature, was obtained by the reaction of $\mathrm{GeMe_3Cl}$ with $\mathrm{[NH_2Me_2][O_2CNMe_2]}$.[141] The ν_{CO} of the carbamato was detected at 1662 $\mathrm{cm^{-1}}$ in $\mathrm{CCl_4}$ solution, again suggesting the monodentate nature of the ligand, and a tetrahedral arrangement of the ligand donor atoms around the central metal atom

$$\mathrm{GeMe_3Cl + [NH_2Me_2][O_2CNMe_2] \rightarrow Ge(O_2CNMe_2)Me_3 + [NH_2Me_2]Cl} \quad (42)$$

Within elements of Group 15, phosphorus derivatives have been the most investigated ones. Some examples are reported below[123,142,143]

$$\mathrm{P(NMe_2)_3 + CO_2 \rightarrow P(O_2CNMe_2)(NMe_2)_2} \quad (43)$$

$$\mathrm{P(NMe_2)_3 + 2CO_2 \rightarrow P(O_2CNMe_2)_2(NMe_2)} \quad (44)$$

$$\mathrm{P(NMe_2)_2F + CO_2 \rightarrow P(O_2CNMe_2)F(NMe_2)} \quad (45)$$

$$\mathrm{P(NMe_2)Me(CF_3)_3 + CO_2 \rightarrow P(O_2CNMe_2)Me(CF_3)_3} \quad (46)$$

$$\mathrm{PR(NR'_2)_2 + CO_2 \rightarrow PR(O_2CNR'_2)(NR'_2)} \quad (47)$$

$$\mathrm{P(NR'_2)(OR)_2 + CO_2 \rightarrow P(O_2CNR'_2)(OR)_2} \quad (48)$$

$$(\mathrm{R} = \text{alkyl, aryl; } \mathrm{R'} = \text{alkyl})$$

$$\mathrm{As(NMe_2)_3 + CO_2 \rightarrow As(O_2CNMe_2)(NMe_2)_2} \quad (49)$$

The crystal structure determination of $\mathrm{P(O_2CNMe_2)Me(CF_3)_3}$ {**FMTCBP10**-CSD}[143] has shown the phosphorus central metal atom to be hexacoordinated with trans $\mathrm{CF_3}$ groups and the bidentate carbamato group in the equatorial plane. Trifluoromethyl-dimethylcarbamato derivatives of phosphorus can be obtained by a ligand exchange reaction, as for eq 50.[144]

$$\mathrm{PF_{5-\mathit{n}}(CF_3)_{\mathit{n}} + Si(O_2CNMe_2)Me_3 \rightarrow P(O_2CNMe_2)F_{4-\mathit{n}}(CF_3)_{\mathit{n}} + SiMe_3F} \quad (50)$$

$$(n = 1-3)$$

The compound $\mathrm{P(O_2CNMe_2)F(CF_3)_3}$ was shown by X-ray diffraction methods {**CIXTEI10**-CSD}[144] to have a structural arrangement similar to that of the corresponding methyl derivative, the phosphorus atom being in a pseudo-octahedral environment. Both molecules contain a plane of symmetry bisecting the segment connecting the two $\mathrm{CF_3}$ groups.

3.3.2. Transition Elements

In view of the importance of organometallic derivatives of transition elements, this section is divided into (a) classical coordination compounds, with donor atoms, other than carbon, contributing to the oxidation state of the central metal atom, see section 3.3.2.1 and (b) organometallic compounds, containing metal−carbon bonds to formally anionic ligands (mainly, alkyl, aryl, cyclopentadienyl), see section 3.3.2.2. This section also contains hydrides. Strictly speaking, μ-oxo carbamato derivatives belong to category a). However, these compounds will be discussed in the separate section 3.4.1 dedicated to the reactions of homoleptic carbamato complexes with water. It has in fact been amply demonstrated that in most cases the μ-oxo ligand derives from water through a well-established hydrolytic process and, in addition, these compounds have now become of increasing importance in the study of the reactivity of these systems.

3.3.2.1. Classical Coordination Compounds. Dialkylamides of general formula $\mathrm{M(NR_2)_{\mathit{n}}}$, containing the central metal atom in its maximum oxidation state ($3d^0$ electronic configuration), react in solution with $\mathrm{CO_2}$ yielding the corresponding carbamato complexes.[8b−c] As mentioned earlier, the mononuclear dialkylamides of Group 4 (titanium and zirconium) react exhaustively, giving the corresponding homoleptic derivatives. This is due to the possibility offered by these elements to expand their coordination number up to eight, particularly with oxygen-donor ligands, and specifically with bidentate carbamato groups. The compromise between expansion of the coordination and stability of the system is mediated by the possibility of the *N*,*N*-dialkylcarbamato group to act as a monodentate or a bidentate ligand, depending on the nature of the ancillary ligands

$$\mathrm{M(NR_2)_{\mathit{n}} + \mathit{n}CO_2 \rightarrow M(O_2CNR_2)_{\mathit{n}}} \quad (51)$$

$$\mathrm{M = Ti, Zr;}\ n = 4$$

$$\mathrm{M = Nb, Ta;}\ n = 5$$

With $\mathrm{W(NMe_2)_6}$,[8a,8e] partial carbonation to $\mathrm{W(O_2CNMe_2)_3(NMe_2)_3}$ was observed even in the presence of excess $\mathrm{CO_2}$. The crystal and molecular structure of the amido-carbamato complex {**TACBMW**-CSD} shows the central metal atom to be hexacoordinated with monodentate carbamato groups in a slightly distorted *fac* geometry.

With the amido complexes of titanium(IV) and tantalum(V), only the use of carbon dioxide in substoichiometric amounts allows the isolation of partly carbonated compounds, such as $Ti(O_2CNMe_2)_2(NMe_2)_2$, $Ti(O_2CNMe_2)_3(NMe_2)$,[8c] and $Ta(O_2CNMe_2)_3(NMe_2)_2$.[8f] The X-ray studies on $Ti(O_2CNMe_2)_2(NMe_2)_2$ {**MACBTI**-CSD}[8d] and $Ta(O_2CNMe_2)_3(NMe_2)_2$,[8f] {**MAMCTA**-CSD} confirm the coordination flexibility of the carbamato ligand. The former compound, which is mononuclear, contains hexacoordinated titanium(IV) with bidentate carbamato ligands, while the tantalum(V) compound is heptacoordinated with one mono- and two bidentate O_2CNMe_2 ligands. Although the crystal structure of $Ti(O_2CNMe_2)_3(NMe_2)$ is unknown, on the basis of the IR spectra (strong absorption at 1576 cm^{-1}),[8d] all the carbamato ligands should be bidentate in this mixed amido-carbamato complex of titanium(IV).

By treating $Cr(NEt_2)_4$ with carbon dioxide,[94a] two compounds showing an oxidation state lower than IV are formed depending on the amount of carbon dioxide used in the reaction. As already mentioned in section 3.2.2, the homoleptic carbamato-bridged derivative of chromium(II), $Cr_2(O_2CNEt_2)_4(NHEt_2)_2$, was obtained with an excess of CO_2. On the other hand, by using a CO_2/Cr molar ratio of 2, high yields of an amido-bridged nonhomoleptic carbamato complex of chromium(III), $Cr_2(O_2CNEt_2)_4(\mu\text{-}NEt_2)_2$, were obtained. The molecular structure {**EACBCT**-CSD} of this compound contains two coordination octahedra bridged by the dialkylamido groups, the Cr−O bond distances to the terminal bidentate carbamato groups ranging from 1.988 to 2.066 Å. It is of interest to note that the corresponding molybdenum compound of formula $Mo_2(O_2CNEt_2)_4(NEt_2)_2$ [145] was suggested to be a dimethylcarbamato-bridged compound with terminal amido groups. No X-ray structure determination has appeared in the literature to confirm the suggestion of a change of structure on going from chromium to molybdenum. The IR spectrum shows an intense band at 1578 cm^{-1}, which by itself is not able to distinguish in a clear-cut manner between a bridging- and a terminal bidentate bonding arrangement, see Appendix.

A unifying reaction mechanism proposed by the authors,[94a] leading to both $Cr_2(O_2CNEt_2)_4(NHEt_2)_2$ and $Cr_2(O_2CNEt_2)_4(\mu\text{-}NEt_2)_2$, is based on the formal CO_2 insertion into the Cr−N bond of $Cr(NEt_2)_4$ giving $Cr(O_2CNEt_2)(NEt_2)_3$, followed by β-hydrogen elimination to give an intermediate compound of chromium(IV), $Cr((NEt_2)_2(O_2CNEt_2)H(EtN{=}CHMe)$, further undergoing loss of $NHEt_2$ and $HEtNCH{=}CH_2$. The resulting $\{Cr(NEt_2)(O_2CNEt_2)\}$ would be responsible for the formation of the observed products, $Cr_2(O_2CNEt_2)_4(NHEt_2)_2$ and $Cr_2(O_2CNEt_2)_4(\mu\text{-}NEt_2)_2$, by, respectively, carbonation/(amine coordination)/dimerization or by (reaction with $Cr(NEt_2)_4$)/(partial carbonation/dimerization). At low CO_2 concentrations in solution, the intermediate would be intercepted by unreacted $Cr(NEt_2)_4$ to give $Cr_2(O_2CNEt_2)_4(\mu\text{-}NEt_2)_2$. On the other hand, under conditions of a relatively high CO_2 concentration, the intermediate would be converted to $\{Cr(O_2CNEt_2)_2\}$, followed by addition of free amine and dimerization to give the final product $Cr_2(O_2CNEt_2)_4(NHEt_2)_2$. Of course, direct insertion of carbon dioxide between the $Cr-NR_2$ bond is unlikely to occur, as established for some dialkylcarbamato complexes of titanium(IV), niobium(V), tantalum(V), tungsten(III), and tungsten(VI).[8d]

The metal−chloride/NHR_2/CO_2 route to *N,N*-dialkylcarbamato metal complexes, see section 3.2.2, sometimes leads to incomplete halide removal, thus forming mixed chloro-carbamato derivatives. This is exemplified by the reactions of anhydrous $TaCl_5$ [146a] or $CrCl_3$ [146b] with the corresponding NHR_2/CO_2 system[93,96]

$$TaCl_5 + 3CO_2 + 6NHEt_2 \rightarrow Ta(O_2CNEt_2)_3Cl_2 + 3[NH_2Et_2]Cl \quad (52)$$

$$2CrCl_3 + 10NH^iPr_2 + 5CO_2 \rightarrow Cr_2(O_2CN^iPr_2)_5Cl + 5[NH_2Et_2]Cl \quad (53)$$

In the case of the tantalum(V) derivative, the room-temperature reaction of $TaCl_5$ with $NHEt_2$ at atmospheric pressure of carbon dioxide gives the product of partial substitution $Ta(O_2CNEt_2)_3Cl_2$. By using a high $NHEt_2/TaCl_5$ molar ratio and by forcing the reaction conditions (50 °C, 6 atm of CO_2), it was possible to remove the two chlorides and to form the homoleptic pentakis(*N,N*-diethylcarbamato)tantalum(V).[93]

The dinuclear chromium(III) derivative $Cr_2(O_2CN^iPr_2)_5Cl$ {**ZOBDEZ**-CSD} is a three carbamato-bridged dimer. No further chloride removal was observed with the chromium(III) derivative even by using an excess of amine, with CO_2 under pressure and at high temperature. However, with diethylamine, complete chloride removal was obtained, thus suggesting that the equilibria involved in the NHR_2/CO_2 system, see section 2.2.3, may be of importance in the formation of the final products, especially when the substitution rates are small.[96]

By treating $Mo_2(NMe_2)_2(OAr)_4$, a compound of $4d^3$ molybdenum(III), with CO_2 at atmospheric pressure and at 25 °C,[147] the binuclear $Mo_2(\mu\text{-}O_2CNMe_2)_2(OAr)_4$, ArO = 2,6-dimethylphenoxide, {**CIRDIQ**-CSD} was obtained. This product, which contains bridging O_2CNMe_2 and terminal aryloxy groups, is characterized by an internuclear distance of 2.220 Å, attributed to a molybdenum−molybdenum triple bond.

The rhenium(V) compound of $5d^2$ electronic configuration $ReO_2I(PPh_3)_2$ was reacted with phenyl isocyanate, and the formation [148] of a carbamato−nitrene−amino derivative of formula $Re(O_2CNHPh)(NPh)I_2(NH_2Ph)(PPh_3)$ was observed, showing a monodentate coordination of the *N*-phenylcarbamato group {**VIJCOG**-CSD}.

Chloro−carbamato complexes of platinum(IV) of formula $Pt(O_2CNHR)_2Cl_2(NH^iPr_2)_2$ have been isolated [149] from the reaction of a bis-hydroxo derivative of $5d^6$ platinum(IV) with the appropriate alkyl isocyanate, a reaction which can be envisaged to proceed through the attack of the isocyanate to the platinum-coordinated hydroxyl. The products were suggested to contain trans terminal monodentate carbamato groups.

$$\textit{cis,trans,cis}\text{-PtCl}_2(\text{OH})_2(\text{NH}^i\text{Pr}_2)_2 + 2\text{RNCO} \rightarrow \textit{trans,cis,cis}\text{-Pt}(\text{O}_2\text{CNHR})_2\text{Cl}_2(\text{NH}^i\text{Pr}_2)_2 \quad (54)$$

$$(\text{R} = \text{Me, Et, Pr})$$

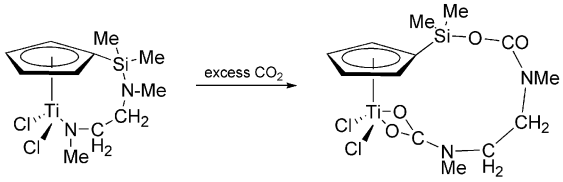
The reaction of (*N*-methyltetraphenylporphynato)ethylzinc(II), Zn(NMTPP)Et, with secondary amines in the presence of CO_2 has been used to prepare *N*,*N*-dialkylcarbamato derivatives,[150] the reaction being accelerated by visible light. The authors propose that the zinc−carbon bond of Zn(NMTPP)Et is activated via excitation of the porphyrin ring. Spectroscopic product identification showed a ^{13}C NMR signal at 157 ppm typical of the carbamato function.

$$\text{Zn(NMTPP)Et} + \text{CO}_2 + \text{NHR}_2 \xrightarrow{h\nu} \text{Zn}(\text{O}_2\text{CNR}_2)(\text{NMTPP}) + \text{EtH} \quad (55)$$

$$(\text{R} = \text{Et, Pr, }^i\text{Pr, }^i\text{Bu})$$

3.3.3.2. Organometallic Compounds. Organometallic derivatives containing carbamato ligands are still relatively uncommon. The following cyclopentadienyl compounds have been obtained through the metal−chloride or the metal−amido routes, see Scheme 13 and the following eqs 56−63[82,96,151,152,153,154,155,156]

Scheme 13



$$[\text{TiCp}_2\text{Cl}]_2 + 2\text{CO}_2 + 4\text{NHR}_2 \rightarrow 2\text{Ti}(\text{O}_2\text{CNR}_2)\text{Cp}_2 + 2[\text{NH}_2\text{R}_2]\text{Cl} \quad (56)$$

$$(\text{R} = \text{Et, }^i\text{Pr})$$

$$\text{TiCp*}(\text{NR}_2)_3 + 3\text{CO}_2 \rightarrow \text{Ti}(\text{O}_2\text{CNR}_2)_3\text{Cp*} \quad (57)$$

$$2\text{M}(\text{O}_2\text{CNEt}_2)_4 + \text{MgCp}_2 \rightarrow 2\text{M}(\text{O}_2\text{CNEt}_2)_3\text{Cp} + \text{Mg}(\text{O}_2\text{CNEt}_2)_2 \quad (58)$$

$$(\text{M} = \text{Zr, Hf})$$

$$2\text{MCp}_4 + 3\text{Fe}(\text{O}_2\text{CNEt}_2)_2 \rightarrow 2\text{M}(\text{O}_2\text{CNEt}_2)_3\text{Cp} + 3\text{FeCp}_2 \quad (59)$$

$$(\text{M} = \text{Zr, Hf})$$

$$2\text{VCp}_2\text{Cl} + 4\text{CO}_2 + 6\text{NHEt}_2 \rightarrow \text{V}_2(\text{O}_2\text{CNEt}_2)_4\text{Cp}_2 + 2[\text{NH}_2\text{Et}_2]\text{Cl} + 2\text{CpH} \quad (60)$$

$$\text{TaCp*}(\text{N}^t\text{Bu})(\text{O}_2\text{CX})\text{Y} + \text{CO}_2 \rightarrow \text{Ta}(\text{O}_2\text{CX})\text{Cp*}(\text{N}^t\text{Bu})\text{Y} \quad (61)$$

$$(\text{X} = \text{NMe}_2,\ \text{Y} = \text{Me};\ \text{X} = \text{NH}^t\text{Bu},\ \text{Y} = \text{Me})$$

$$\text{RuCp}(\text{NH}_2)(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2) + \text{CO}_2 \rightarrow \text{Ru}(\text{O}_2\text{CNH}_2)\text{Cp}(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2) \quad (62)$$

$$\text{UCp}_2(\text{NEt}_2)_2 + 2\text{CO}_2 \rightarrow \text{U}(\text{O}_2\text{CNEt}_2)_2\text{Cp}_2 \quad (63)$$

The products $Zr(O_2CNEt_2)_3Cp$ {**PUKZOK**-CSD}[153] and $V_2(O_2CNEt_2)_4Cp_2$ {**JONSEK**-CSD}[82] have been studied by X-ray diffraction methods. In the zirconium derivative, the central metal atom is surrounded by six oxygens of the three bidentate carbamato groups and by the cyclopentadienyl (Cp) ring. The coordination geometry of the zirconium may be described as a distorted pentagonal bipyramid with the apical positions occupied by one of the oxygens of a diethylcarbamato ligand and by the Cp ring. In the vanadium centrosymmetric dimer each vanadium(III) atom of $3d^2$ electronic configuration is surrounded by the oxygens of the four bridging bidentate *N*,*N*-diethylcarbamato groups and by the Cp ligand. Each metal atom may be regarded to exhibit a square-pyramidal coordination with the oxygens occupying the basal plane and with the Cp ring at the apex. The V···V nonbonding distance is 3.552 Å. The magnetic moment of 1.76 μ_B at 19 °C, reduced with respect to the spin-only value of 2.83 μ_B, suggests some degree of ligand-mediated metal−metal interaction for this $3d^2$ system.

The formation of $Mo(O_2CNH_2)_2Cp_2$ and $W(O_2CNH_2)_2Cp_2\cdot H_2O$ by reacting MCp_2Cl_2, M = Mo, W, with NaOCN in boiling water has been reported.[157] The compounds were identified by conventional spectroscopic methods and suggested to contain the metal-bonded carbamato ligand O_2CNH_2; this would therefore represent one of the few examples of a transition metal system containing the unsubstituted carbamato ligand.

The niobium and tantalum dicarbollide dimethylamido complexes $M(NMe_2)_3(C_2B_9H_{11})$, with a d^0 electronic configuration of the central metal atom, react with CO_2 affording the tris(*N*,*N*-dimethylcarbamato) complexes $M(O_2CNMe_2)_3(C_2B_9H_{11})$ of niobium(V) and tantalum(V).[158] The molecular structure of the tantalum derivative $Ta(O_2CNMe_2)_3(C_2B_9H_{11})\cdot$toluene, {**LAQTEC**-CSD}, has been reported to consist of discrete molecules with the tantalum atom in an approximate pentagonal bipyramidal geometry, five carbamato oxygens defining the pentagonal plane, the axial positions being occupied by the sixth oxygen and by the dicarbollide centroid.

$$\text{M}(\text{C}_2\text{B}_9\text{H}_{11})(\text{NMe}_2)_3 + 3\text{CO}_2 \rightarrow \text{M}(\text{O}_2\text{CNMe}_2)_3(\text{C}_2\text{B}_9\text{H}_{11}) \quad (64)$$

$$(\text{M} = \text{Nb, Ta})$$

Carbamato complexes having alkyl groups as additional ligands are exemplified by: $Hf[O_2CN(SiMe_3)_2]_2R_2$, R = Me, Et, CH_2SiMe_3,[159] and $Ta(O_2CNMe_2)_4R$, R = ^{t}Bu, ^{i}Pr, Et, CH_2SiMe_3.[160] The solid-state structure {**BOBXUL**-CSD} of $Ta(O_2CNMe_2)_4(CH_2SiMe_3)$ is available. The compound has an approximate pentagonal bipyramidal structure, two monodentate carbamato groups occupying the axial positions and defining an O−Ta−O angle of 171.5°. The other two carbamato groups in the basal pentagonal plane are bidentate.

The dinuclear dialkyl derivatives of molybdenum(III) and tungsten(III) $M_2(NMe_2)_4R_2$, R = Me, Bz, react with CO_2 to give the dialkylcarbamates $M_2(O_2CNMe_2)_4R_2$. The molecular structure of $W_2(O_2CNMe_2)_4$-

Me_2 {**ECAMMW10**-CSD} shows a W−W distance of 2.272 Å, suggesting the presence of a triple tungsten−tungsten bond.[8e] By contrast, the molybdenum ethyl derivative $Mo_2(O_2CNMe_2)_4Et_2$ undergoes reduction to $Mo_2(O_2CNMe_2)_4$ upon reaction with CO_2 with formation of ethane and ethylene (^1H NMR spectrometry).[161]

Noteworthy is the reaction of the binuclear dimethylamido-benzyl derivatives of molybdenum(III) or tungsten(III), $M_2(NMe_2)_4Bz_2$, with CO_2. By operating under similar experimental conditions, the benzyl derivative of molybdenum(III) underwent reduction to the homoleptic compound of molybdenum(II) $Mo_2(O_2CNMe_2)_4$,[161] while the corresponding tungsten(III) complex exclusively gave carbon dioxide formal insertion between the W-amido bond producing $W_2(O_2CNMe_2)_4Bz_2$. This is consistent with the well-established reluctance of 5d systems to undergo reduction,[162] with respect to their 4d analogues.

$$Mo_2(CH_2Ph)_2(NMe_2)_4 + 4CO_2 \rightarrow Mo_2(O_2CNMe_2)_4 + PhCH_2CH_2Ph \quad (65)$$

$$W_2(NMe_2)_4Bz_2 + 4CO_2 \rightarrow W_2(O_2CNMe_2)_4Bz_2 \quad (66)$$

N,*N*-Dialkylcarbamato metal complexes are known which contain hydrido functionalities, such as $W[\eta^2\text{-}O_2CN\overline{(CH_2)_3C}H_2)]H(CO)(\eta^1\text{-dppe})(\eta^2\text{-dppe})$,[163] $Ru(O_2CNEt_2)H(PPh_3)_3$,[164] $Ru(\eta^2\text{−}O_2CNEt_2)H(CO)(PCy_3)_2$,[165] and *trans*-$Pt(O_2CNHPh)H(PEt_3)_2$,[166] with bidentate (W and Ru) or monodentate (Pt) carbamato ligands. The tungsten(II) {**JURDIJ**-CSD} and ruthenium(II) $Ru(O_2CNEt_2)H(CO)(PCy_3)_2$ {**QEBTEW**-CSD} derivatives have been investigated by X-ray diffraction methods. In the tungsten(II) derivative the central metal atom is seven-coordinate, the axial positions being occupied by one oxygen atom of the bidentate carbamato group and by the carbonyl ligand. In the ruthenium(II) compound, the axial positions are occupied by the tertiary phosphine ligands, while the equatorial plane of the octahedron contains the bidentate carbamato group, the hydride and the carbonyl. The carbamato derivative of platinum(II) *trans*-$Pt(O_2CNHPh)H(PEt_3)_2$ is characterized by a ^{13}C NMR signal at 160.1 ppm assigned to the carbamato ligand.

The ruthenium(II) *N*,*N*-dialkylcarbamato derivatives containing η^6-cymene as additional ligand, of formula $Ru(O_2CNR_2)Cl(\eta^6\text{-cymene})$, R = Et, ^{i}Pr, have been prepared by the chloride/*N*,*N*-dialkylcarbamato exchange reaction.[101] They have been suggested to contain a bidentate carbamato ligand, in agreement with both the absence of IR bands above 1600 cm^{-1} and the 18-e counting of the central metal atom, assuming a formal contribution of four electrons by the carbamato ligand.

$$[RuCl_2(\eta^6\text{-cymene})]_2 + 2CO_2 + 4NHR_2 \rightarrow 2Ru(\eta^2\text{-}O_2CNR_2)Cl(\eta^6\text{-cymene}) + 2[NH_2R_2]Cl \quad (67)$$

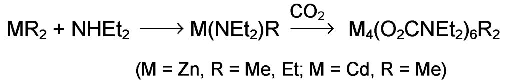
$$(R = Et, {}^iPr)$$

The methyl derivatives of palladium(II) of general formula $Pd(O_2CNR_2)MeL_2$, L = tertiary phosphine, R = H, alkyl, phenyl, have been prepared by reacting $PdMe_2L_2$ with CO_2 and the appropriate amine. The reaction of $PdMe_2L_2$, L = PEt_3, $PMePh_2$, with CO_2/$NHPh_2$ was reported to afford $Pd(NPh_2)MeL_2$ probably via decarboxylation of the intermediate palladium carbamate $Pd(O_2CNPh_2)MeL_2$.[167]

As far as elements of group 12 are concerned, it was originally reported that the reaction of $Zn(NR_2)Et$ with CO_2 affords ethyl-carbamato derivatives of zinc formulated as $Zn(O_2CNR_2)Et$, R = Ph, Et.[168] With NHMePh and CO_2 at 120 °C, $ZnEt_2$ yields $Zn(O_2CNMePh)Et$.[169] The molecular complexity of these products and of similar ones became clear subsequently with the systematic use of X-ray diffractometry.

Tetranuclear compounds of composition $M_4(O_2CNEt_2)_6R_2$, M = Zn, Cd, were obtained by reacting MR_2 with $NHEt_2/CO_2$.[170]

Scheme 14



$$MR_2 + NHEt_2 \longrightarrow M(NEt_2)R \xrightarrow{CO_2} M_4(O_2CNEt_2)_6R_2$$

(M = Zn, R = Me, Et; M = Cd, R = Me)

The compound $Zn_4(O_2CNEt_2)_6Me_2$ {**JOFVEF10**-CSD} has been studied by X-ray diffraction methods. The core of the molecule is formed by a parallelogram of the four zinc atoms with the six carbamato groups bridging them on the edges (μ) and on the diagonals (μ_3); the fourth coordination position around two of the zinc atoms is occupied by a methyl group. The molecule is shown in Figure 7.

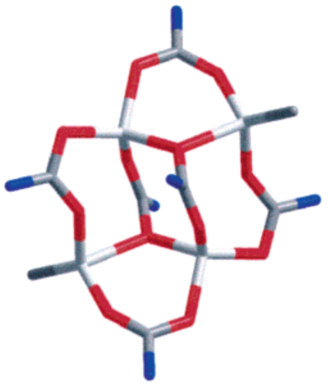


Figure 7. Schematic molecular structure of the tetranuclear zinc complex $Zn_4(O_2CNEt_2)_6Me_2$. Centers of sticks: light-gray, metal atoms; gray, carbon atoms; red, oxygen atoms. Blue sticks, nitrogen atoms. Alkyl groups not shown. Drawing obtained using the published structural data.[170]

The reaction of $Zn_4(O_2CNEt_2)_6Me_2$ with excess $ZnMe_2$ affords the tetranuclear compound $Zn_4(O_2CNEt_2)_4Me_4$ characterized by X-ray diffraction methods {**YUCBIH**-CSD}:[170a] it contains an approximately tetrahedral arrangement of zinc atoms linked by bridging carbamato groups, the coordination geometry around each zinc atom being completed by a methyl group. The dimethyl derivative $Zn_4(O_2CNEt_2)_6Me_2$ reacts with pyridine to give the dinuclear compound $Zn_2(O_2CNEt_2)_3Me(py)$ {**ZIPPUJ**-CSD}, containing four-coordinate zinc atoms. Both zinc atoms are coordinated to three oxygen atoms of the bridging carbamato groups, the fourth coordination positions being occupied by pyridine or by the methyl group.[171]

Mercury carbamates have been prepared [172] by reacting phenyl mercury hydroxide with alkyl or aryl isocyanates RNCO, R = Et, ^{t}Bu. The formation of Hg(O_2CNRH)Ph corresponds to the attack of the alkylisocyanate to the mercury-bonded OH ligand. The nature and structure of these products deserve further investigation.

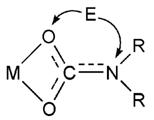
$$\mathrm{Hg(OH)Ph + RNCO \rightarrow Hg(O_2CNHR)Ph} \quad (68)$$

$$(\mathrm{R = Et, {}^tBu})$$

3.4. Reactivity of Metal Carbamato Complexes

Although carbon dioxide is well established to be reactive toward nucleophilic reagents, reactions of CO_2 with electrophiles are unprecented in the literature. As already mentioned in section 2, the reactivity of carbon dioxide differs from that of the CO_2 fragment within the carbamato ligand. As a matter of fact, metal carbamates do not generally react with nucleophiles, as exemplified by the *N*,*N*-dialkylcarbamato derivatives of manganese(II) which are inert toward organic (as in LiMe and MgBrPh) or organometallic [as in $NaMn(CO)_5$ and $NaFeCp(CO)_2$] nucleophiles.[96] Consistently, metal carbamates are readily reactive with electrophilic reagents, such as water, proton-containing substances, alkyl and aryl halides. This is in agreement with valence-bond arguments suggesting that the oxygen atoms of the CO_2 moiety in dialkylcarbamato metal derivatives acquire a partial negative charge, the coordinated ligand thus being the potential site of attack by electrophiles, see Scheme 15. Attack by electrophiles at the nitrogen atom induces elimination of CO_2, while attack at the oxygen atom may allow the CO_2 moiety to be retained in the products.

Scheme 15

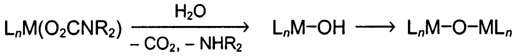


3.4.1. With Water: Formation of μ_n-Oxo Derivatives

The attack by water on metal−carbamato complexes can result in the formation of: hydroxo-, oxo-, or carbonato groups. If the attack is carried out with an excess of water, complete hydrolysis of the carbamato groups can occur, vide infra. When the amount of water is carefully controlled, μ-oxo-carbamato complexes are usually observed. A substantial contribution to the driving force of the reaction is the formation of carbon dioxide, which explains why the nature of the products is normally well defined and related to the metal/H_2O molar ratio which has been used.

Hydrolysis of $M(O_2CNR_2)_n$, see Scheme 16, produces μ-oxo complexes, accompanied by the evolution of the appropriate secondary amine. The M−OH bond presumably formed in the first step is of sufficient Brønsted acidity to bring about the further attack, generally intermolecular, leading to μ-oxo derivatives.

Scheme 16



$$\mathrm{L_nM(O_2CNR_2)} \xrightarrow[-\,\mathrm{CO_2},\,-\,\mathrm{NHR_2}]{\mathrm{H_2O}} \mathrm{L_nM{-}OH} \longrightarrow \mathrm{L_nM{-}O{-}ML_n}$$

In this section derivatives of transition elements are discussed first, followed by the derivatives of main groups elements. This is due to the fact that the hydrolytic processes have been mostly studied with carbamato derivatives of transition elements, which have therefore been the most productive systems in this area.

The first μ-oxo derivative of this class of compounds, $U_4(\mu_3\text{-}O)_2(O_2CNEt_2)_{12}$, was initially detected[173a] as a side product in the preparation of $[U(O_2CNEt_2)_4]_n$, the μ-oxo derivative being produced through a hydrolytic process with adventitious water present in the system.

$$4/n[\mathrm{U(O_2CNEt_2)_4}]_n + 2\mathrm{H_2O} \rightarrow \mathrm{U_4(\mu_3\text{-}O)_2(O_2CNEt_2)_{12}} + 4\mathrm{NHEt_2} + 4\mathrm{CO_2} \quad (69)$$

Well-formed crystals of the product were used for a X-ray diffractometric experiment {**ECBOXU**-CSD}. In this structure two triangles of uranium(IV) atoms[173a] are joined by the two μ_3-oxo ligands, in a substantially planar arrangement of the four uranium atoms.

More complex structures arise from the controlled hydrolysis of copper(II)[95] and iron(II) *N*,*N*-dialkylcarbamates.[173b] The iron(II) derivative of formula $Fe_8(\mu_4{-}O)_2(O_2CN^iPr_2)_{12}$ was synthesized by controlled hydrolysis of $[Fe(O_2CN^iPr_2)_2]_n$, under rigorous exclusion of dioxygen (the nuclearity of the starting iron(II) product is unknown). The resulting octanuclear complex {**POFYAK**-CSD} shares with the recently published [173c] neutral tetranuclear compound containing six 2,2′-dipyridylaminato (2,2′-Npy_2) ligands, of formula $Fe_4(\mu_4\text{-}O)(Npy_2)_6\cdot PhMe$ {**XIRFIN**-CSD}, the singularity to be a molecular μ-oxo derivative of iron(II). Concerning μ-oxo derivatives of iron(II), it is quite relevant to notice the formation of a mixed-valent polyiron acetato−methoxo complex of formula $Fe_4Fe_8(O)_2(OMe)_{18}(OAc)_6(MeOH)_{4.67}$ obtained by controlled oxidation of a methanol solution of iron(II) acetate and LiOMe.[173d]

The octanuclear compound[93] of copper(II) of the same chemical composition as that of iron(II), namely, $Cu_8(\mu_4{-}O)_2(O_2CN^iPr_2)_{12}$, was similarly obtained by hydrolysis of the homoleptic copper(II) precursor with the stoichiometric amount of water.

$$8/n[\mathrm{M(O_2CN^iPr_2)_2}]_n + 2\mathrm{H_2O} \rightarrow \mathrm{M_8(\mu_4\text{-}O)_2(O_2CN^iPr_2)_{12}} + 4\mathrm{NH^iPr_2} + 4\mathrm{CO_2} \quad (70)$$

$$(\mathrm{M = Fe, Cu})$$

The iron(II) and copper(II) di-*iso*-propylcarbamato derivatives were characterized by conventional methods including X-ray crystallography. These products, of formula $M_8(\mu_4\text{-}O)_2(O_2CN^iPr_2)_{12}$, contain two μ_4-O units {**POFYAK**-CSD, M = Fe(II)[173b]}; {**KAFPOW**-CSD, M = Cu(II)[93]}. As it may be seen from the structural data, these compounds have similar structures. Both molecules have an approximately ellipsoidal shape with the major axis being occupied by two of the eight metal atoms, at distances of 7.153 Å (iron) and 7.976 Å (copper). In the iron complex the two "external" atoms have a distorted tetrahedral geometry, while the six inner atoms have an approximate trigonal bipyramidal one. In the copper(II) μ_4-oxo derivative, all copper atoms are pentacoordinated.

From a hydrolytic process also originates the mixed-metal octanuclear compound, containing both zinc(II) and nickel(II), of formula $Ni_6Zn_2(\mu_4\text{-}O)_2(O_2CN^iPr_2)_{12}$. The atom connectivity {**WALHAS**-CSD} is substantially the same as that exhibited by the iron(II) system, except that the two tetrahedral sites are now occupied by zinc.[174]

More recently, new μ_4-oxo octanuclear derivatives of cobalt(II) and nickel(II) have been prepared, of general formula $M_8(\mu_4\text{-}O)_2(O_2CN^iPr_2)_{12}$.[175] They have been shown to be isostructural {cobalt: **175412**-CCDC}.

Beside the hydrolytic processes of the iron(II) carbamato complexes discussed above, derivatives of iron(III) have also been studied in connection with their behavior with water.[176] For example, by reaction of the homoleptic compound $Fe(O_2CNEt_2)_3$ with the stoichiometric amount of water in toluene solution, a product of analytical composition $[Fe_2O(O_2CNEt_2)_4]_n$ was isolated as a red-brown substance, which is soluble even in aliphatic hydrocarbons. This is suggestive of low nuclearity, which was not established, however.

$$\mathrm{2Fe(O_2CNEt_2)_3 + H_2O \rightarrow 1/}n\mathrm{[Fe_2O(O_2CNEt_2)_4]}_n \mathrm{+ 2CO_2 + 2NHEt_2} \quad (71)$$

Hydrolysis to a carbonato complex has been observed in the reaction of $Ru(O_2CN^iPr_2)_2(PPh_3)_2(CO)_2$ with the stoichiometric amount of water in toluene[177]

$$\mathrm{Ru(O_2CN^{\mathit{i}}Pr_2)_2(PPh_3)_2(CO)_2 + 2H_2O \rightarrow Ru(O_3C)(PPh_3)_2(CO)_2{\cdot}H_2O + CO_2 + 2NH^{\mathit{i}}Pr_2} \quad (72)$$

The reaction must be carried out with the stoichiometric amount of water and under an inert atmosphere of dinitrogen. In fact, under carbon monoxide, reduction to phosphine-substituted complexes of ruthenium(0) was observed. The crystal structure determination of $Ru(O_3C)(PPh_3)_2(CO)_2{\cdot}H_2O$[177] {**LOGZAI**-CSD} shows the complex to be mononuclear with the bidentate carbonato ligand.

As a further example of exhaustive hydrolysis, carbonato derivatives of general formula $Pt(CO_3)(PR_3)_2$, R = Et, Ph, and $Pt(CO_3)(dppe)$ are formed from *cis*-$Pt(O_2CNR_2)_2(PR_3)_2$ or *cis*-$Pt(O_2CNR_2)_2(dppe)$.[178a] The carbonato complexes were prepared in good to excellent yields by treating a THF solution of the tertiary-phosphine-substituted precursor with the stoichiometric amount of water.

$$\mathrm{Pt(O_2CNR_2)_2(PR_3)_2 + H_2O \rightarrow Pt(CO_3)(PR_3)_2 + 2NHR_2 + CO_2} \quad (73)$$

It is reasonable to assume that the formation of the carbonato complex, rather than that of the μ-oxo derivative, is associated with the hydroxo intermediate $Pt(O_2CNR_2)(OH)(PR_3)_2$ interacting intramolecularly with the cis carbamato ligand, thus leading to the observed product. A binuclear μ-oxo derivative would on the contrary result from an intermolecular interaction of the hydroxo intermediate.

Formation of Ag_2CO_3 was found to occur by treating Ag_2O with NH^iPr_2 under carbon dioxide[104a] in heptane as medium. As Ag_2O and CO_2 are totally unreactive under comparable conditions, the intermediacy is suggested of $Ag(O_2CN^iPr_2)$, the latter undergoing hydrolysis in the second step of the reaction, see Scheme 17. The net result is the NH^iPr_2-catalyzed formation of Ag_2CO_3 [$\Delta G^0{}_r = -31$ kJ mol^{-1}], with reagents ($Ag_2O + CO_2$) and product in their standard states at 298 K.[103]

Scheme 17

$$\mathrm{Ag_2O + 2NH^{\mathit{i}}Pr_2 + 2CO_2 \longrightarrow 2Ag(O_2CN^{\mathit{i}}Pr_2) + H_2O}$$

$$\mathrm{2Ag(O_2CN^{\mathit{i}}Pr_2) + H_2O \longrightarrow CO_2 + 2NH^{\mathit{i}}Pr_2 + Ag_2CO_3}$$

$$\mathrm{Ag_2O + CO_2 \longrightarrow Ag_2CO_3}$$

A substantially quantitative transfer of zinc(II) from aqueous solution into a hydrocarbon solvent, either heptane or toluene, has been successfully carried out in the presence of carbon dioxide and a secondary amine, namely, $NHBu_2$ or $NHBz_2$.[62b] The extraction of copper and zinc as the corresponding carbamato complexes has already been discussed in section 2.2.3. The extracted product with $NHBu_2/CO_2$ has been established to be the μ_4-oxo derivative $Zn_4(\mu_4\text{-}O)(O_2CNBu_2)_6$ {**190081**-CCDC}. The product has the well-known oxo-centered structure, the tetracoordination of the zinc atoms being completed by three oxygens of the bridging carbamato groups. A μ_4-oxo derivative of zinc(II) has been prepared by reacting dimethylamine with ZnO in the presence of carbon dioxide at atmospheric pressure.[178b] As water is produced during the reaction, the hydrophilic MeCN has been used as solvent. The crystal structure {**191652**-CCDC} determination has shown that the product obtained under these conditions, of formula $Zn_4(\mu_4\text{-}O)(O_2CNMe_2)_6$, has the oxo-centered structure, typical of this class of compounds. No other secondary amine ($NHEt_2$, NH^iPr_2, $NHBu_2$), except dimethylamine, is able to drive the reaction toward the carbamato complex, ZnO being recovered unchanged. This is presumably related to the fact that neat dimethylamine was found to absorb carbon dioxide in the $CO_2/NHMe_2$ molar ratio of 0.6, suggesting the formation of a quite consistent concentration of the carbamic acid Me_2NCO_2H in MeCN solution. It is to be noted that $Zn_4(\mu_4{-}O)(O_2CNEt_2)_6$, prepared from zinc metal, carbon dioxide, and diethylamine at high temperature (150 °C) and pressure (50 atm), has a similar structure {**JODCEK**-CCD}.[178c] A product of the same composition and structure was obtained by reacting $ZnMe_2$ with $NHEt_2$ in tetrahydrofuran, followed by carbonation.[178d] The atom arrangement of $Zn_4(\mu_4\text{-}O)(O_2CNEt_2)_6$ is schematically shown in Figure 8.

Figure 8. Schematic molecular structure of the tetranuclear zinc complex $Zn_4(\mu_4-O)(O_2CNEt_2)_6$. Centers of sticks: light-gray, metal atoms; gray, carbon atoms; red, oxygen atoms. Blue sticks, nitrogen atoms. Alkyl groups not shown. Drawing obtained using the published structural data.[178c]

Hydrolytic processes of *N*,*N*-dialkylcarbamato complexes of nontransitional elements have been studied to a lesser extent. Some representative examples are given below.

Controlled hydrolytic processes have been used to obtain an alumoxane of formula $Al_4(\mu_3\text{-}O)_2(O_2CN\text{-}{}^iPr_2)_8$ [179] {**ROJREN**-CSD}, which presents some novel features as far as the presence of the *N*,*N*-dialkylcarbamato ligand and the nuclearity are concerned. The molecular structure has two five-coordinate and two hexacoordinate aluminum atoms, in distorted trigonal-bipyramidal and octahedral geometries, respectively.

Hydrolysis of carbamato derivatives of germanium affords the oxo-alkyl of germanium(IV), CO_2, and the appropriate nitrogen-containing product[129]

$$2Ge(O_2CNMe_2)Et_3 + H_2O \rightarrow (Et_3Ge)_2O + 2CO_2 + 2NHMe_2 \quad (74)$$

$$HN(OCOGeEt_3)_2 + H_2O \rightarrow (Et_3Ge)_2O + 2CO_2 + NH_3 \quad (75)$$

A special case of combined hydrolytic and oxidation processes which operate in combination is represented by the formation of the octanuclear complex of tantalum(V) $Ta_8(\mu\text{-}O)_{12}(O_2CNEt_2)_{16}$.[180a] The preparation of the octanuclear compound of tantalum(V) in excellent yields was carried out by reducing $Ta(O_2CNEt_2)_3Cl_2$ with the stoichiometric amount of sodium required for the reduction to tantalum(III) in THF as medium.

$$8Ta(O_2CNEt_2)_3Cl_2 + 16Na + 4C_4H_8O \rightarrow Ta_8(\mu\text{-}O)_{12}(O_2CNEt_2)_{16} + HCONEt_2 + 16NaCl + 4\{C_4H_6\} \quad (76)$$

The combined action of CO_2 and H_2O (presumably originated from dehydration of THF) was regarded to be responsible for the formation of the octanuclear species of tantalum(V), whose molecular structure {**SUGDUT**-CSD}, see Figure 9, is highly symmetrical, with both terminal and bridging carbamato groups and with twelve doubly bridging oxides (μ_2-O).[180a] The eight tantalum atoms are placed at the apexes of an idealized cube, joined by 12 μ-oxo groups placed at the center of each edge. Each tantalum has one terminal monodentate carbamato group, while eight bidentate groups are on the edges. Figure 9 shows the atom connectivity of the octanuclear compound.

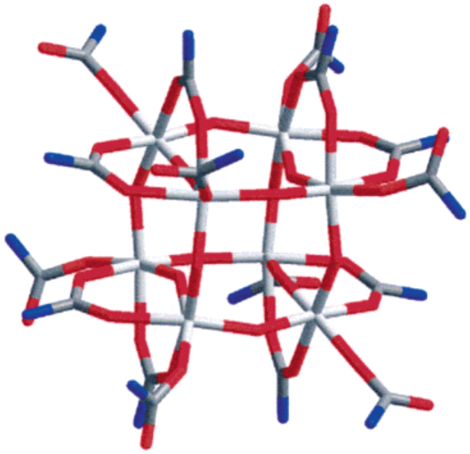


Figure 9. Molecular structure of the octanuclear tantalum(V) compound $Ta_8(\mu\text{-}O)_{12}(O_2CNEt_2)_{16}$. Centers of sticks: light-gray, metal atoms; gray, carbon atoms; red, oxygen atoms. Blue sticks, nitrogen atoms. Alkyl groups not shown. Drawing based on the published structural data.[180a]

Finally, mention should be made of the exhaustive hydrolytic processes which have been carried out on carbamato complexes of nontransition elements, particularly those of silicon, see also section 4.1.[180b−d] A recent review article has particularly dealt with this subject.[180e]

3.4.2. With Protic Reagents

The addition of H^+ to a dialkylcarbamato group can occur at the oxygen atom or at the nitrogen atom, leading, respectively, to carbamic acids R_2NCO_2H, or to $R_2NH + CO_2$. Defining the position of the attack is complicated by the tendency of carbamic acids to decarboxylate, see section 2.

$$M(O_2CNR_2)_n + nH^+ \rightarrow M^{n+} + nR_2NCO_2H \quad (77)$$

As noted in the Introduction, all transition metal carbamates reported in the literature are promptly attacked by diluted sulfuric acid. The sole exception is $Pt(O_2CNEt_2)_2(NHEt_2)_2$,[105] which is unaffected by that reagent, but is promptly attacked by acetic acid in toluene. Decarboxylation in the presence of acids has been extensively used for the quantitative determination of the combined carbon dioxide. On a preparative scale, the reaction of acetic acid with $U(O_2CNEt_2)_4$ in toluene solution has been reported[10a] to give anhydrous uranium(IV) acetate $U(O_2CCH_3)_4$.

$$U(O_2CNEt_2)_4 + 4CH_3COOH \rightarrow U(O_2CCH_3)_4 + 4CO_2 + 4NHR_2 \quad (78)$$

Carboxylic acids, acetylacetone, hydrogen halides, hydrogen sulfide, and water (for a specific discussion of μ-oxo derivatives arising from hydrolytic processes, see section 3.4.1) have been used as proton-active substances. The reactions usually proceed to completion under mild conditions and they may also be of preparative value in certain cases. Sometimes, partial substitution of the carbamato ligands is obtained. A typical example, whereby the coordination sphere of the metal is slightly changed, is represented by the attack of the carbamato derivative of ruthenium(II) $Ru(O_2CN^iPr_2)_2(CO)_2(PPh_3)_2$ (containing monodentate carbamato ligands) by triflic acid. The resulting ionic product $[Ru(O_2CN^iPr_2)(CO)_2(PPh_3)_2][CF_3SO_3]$ {**176709-**CCDC},[181] which contains a bidentate carbamato ligand, was obtained by reacting the precursor with CF_3SO_3H in the correct stoichiometric amount.

$$Ru(O_2CN^iPr_2)_2(CO)_2(PPh_3)_2 + 2TfH \rightarrow [Ru(O_2CN^iPr_2)(CO)_2(PPh_3)_2][Tf] + [NH_2{}^iPr_2][Tf] + CO_2 \quad (79)$$

This compound is one of the few examples of cationic *N*,*N*-dialkylcarbamato derivatives. In this connection, mention should be made of the cationic carbamato derivatives of ruthenium(II), prepared as early as 1976 [164] by treating the cationic complex $[RuH(PMe_2Ph)_5]^+$ with $NHMe_2/CO_2$. The products thus obtained have the formulas $[Ru(O_2CNMe_2)(PMe_2Ph)_4]^+$ and $[Ru(O_2CNMe_2)(CO)(PMe_2Ph)_4]^+$ as the hexafluorophosphate derivatives. In the $[Ru(O_2CNMe_2)(PMe_2Ph)_4]^+$ cation, the carbamato ligand is bidentate, the formal electron counting of the central metal atom being 18.

With acetylacetone, acacH, the *N*,*N*-dialkylcarbamato derivative of chromium(II) $Cr_2(O_2CNEt_2)_4(NHEt_2)_2$ [93b] gives $Cr(acac)_2$, further oxidation to Cr(III) by the third equivalent of acacH giving $Cr(acac)_3$. Displacement reactions of the carbamato ligands by acetylacetone have also been reported with titanium(III),[57] vanadium(III),[57] and nickel(II),[174] giving the corresponding β-diketonato complexes.

$$xM(O_2CNR_2)_n + nx\ acacH \rightarrow M_x(acac)_{nx} + nx\ CO_2 + nx\ NHR_2 \quad (80)$$

$$M = Ti;\ n = 3;\ R = {}^iPr;\ x = 1$$

$$M = Fe;\ n = 3;\ R = Et;\ {}^iPr;\ x = 1$$

$$M = Ni;\ n = 2;\ R = Et;\ x = 3$$

$$Cr_2(O_2CNR_2)_4(NHEt_2)_2 + 4acacH \rightarrow 2\ Cr(acac)_2 + 4CO_2 + 6NHEt_2 \quad (81)$$

$$Cr(acac)_2 + acacH \rightarrow Cr(acac)_3 + 1/2H_2 \quad (82)$$

N,*N*-Dialkylcarbamato complexes can be useful intermediates to halo-complexes; this is particularly useful for the heavier halides (Br, I) and for metal cations in a relatively high oxidation state. The reactions, usually leading to halo-metalates,[57,91] are carried out in anhydrous media, to minimize hydrolytic processes. In the case of ytterbium(III), the reaction with hydrogen halides in a hydrocarbon medium affords polyhalo metalates.[109b]

$$M(O_2CNEt_2)_3 + 6HX \rightarrow (NH_2Et_2)_3[MX_6] + 3CO_2 \quad (83)$$

$$M = Ti, V;\ X = Cl;\ M = Yb;\ X = I$$

$$M(O_2CNEt_2)_4 + 6HX \rightarrow (NH_2Et_2)_2[MX_6] + 4CO_2 + 2NHEt_2 \quad (84)$$

$$M = Zr, Hf;\ X = Cl, Br, I$$

$$Ni(O_2CNR_2)_2 + 4HI \rightarrow (NH_2R_2)_2[NiI_4] + 2CO_2 \quad (85)$$

$$(R = Et, {}^iPr)$$

The reaction with H_2S gives metal sulfido complexes as prepared in hydrocarbons, i.e., in a unusual medium for this type of compounds.[182,183,184] The reaction has been used for preparing the iron sulfides, $([NH_2Et_2]_6[Fe_8S_{15}]$ and $[NH_2{}^iPr_2]_{10}[Fe_{16}S_{29}]$[185] (the *iso*-propyl derivative shows a strongly reduced magnetic moment of 1.58 μ_B per iron atom). The similarly prepared derivatives of palladium(II) and nickel(II) have been formulated as $Pd(SH)_2(NHEt_2)_2$,[71] and $(NH_2Et_2)_2[Ni_8S_9]$,[174] respectively. The latter is a black solid as obtained in a substantially quantitative yield by treating a heptane solution of the precursor $Ni(O_2CNEt_2)_2$ with dry H_2S (the substance has a reduced magnetic moment of 0.84 μ_B per nickel atom).

Silicon carbamates, as their trimethylsilyl derivatives, have been investigated as silylating agents for alcohols, phenols and carboxylic acids [186] leading to methyl-, ethyl-, and phenyltrimethylsilyl ethers and to trimethylsilylformate and trimethylsilyl acetate, with the advantage of forming gaseous CO_2 and NH_3 as byproducts.

$$Si(O_2CNHSiMe_3)Me_3 + 2ROH \rightarrow 2ROSiMe_3 + CO_2 + NH_3 \quad (86)$$

$$(R = Me, Et, Ph, HCO, MeCO)$$

The mechanism of reaction of some trimethylsilylcarbamates with 2-propanol or 2-methylbutan-2-ol has been studied.[187] It has been suggested that the reaction proceeds via nucleophilic attack of ROH to the silicon atom of the carbamato group.

Molecular models of the silica surface such as Ph_3SiOH, $(c\text{-}C_5H_9)_7Si_7O_{12}(OH)$ and $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ have been shown to react at room temperature with $Ti(O_2CN^iPr_2)_4$,[91,188a] and with $Au(O_2CNR_2)(PPh_3)$,[188b] R = Me, Et, yielding the corresponding silanolato molecular complexes. Moreover, in the case of the gold compound, advantage was taken of the presence of a single carbamato group in the precursor to carry out a gasvolumetric control; it was thus shown that the reaction with activated silica (activation conditions: 160 °C in vacuo) was substantially quantitative.[188]

$$\mathrm{Ti(O_2CN{}^iPr_2)_4 + 2Ph_3SiOH \rightarrow Ti(O_2CN{}^iPr_2)_2(OSiPh_3)_2 + 2CO_2 + 2NH{}^iPr_2} \quad (87)$$

$$\mathrm{Au(O_2CNEt_2)(PPh_3) + Ph_3SiOH \rightarrow Au(OSiPh_3)(PPh_3) + CO_2 + NHEt_2} \quad (88)$$

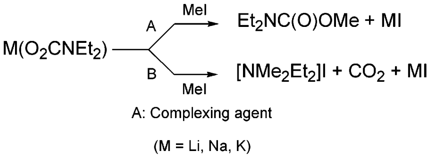
$$\mathrm{Au(O_2CNMe_2)(PPh_3)+(\mathit{c}\text{-}C_5H_9)_7Si_7O_{12}(OH) \rightarrow (\mathit{c}\text{-}C_5H_9)_7Si_7O_{12}{-}O{-}Au(PPh_3) + CO_2 + NHMe_2} \quad (89)$$

$$\mathrm{3Au(O_2CNEt_2)(PPh_3) + (\mathit{c}\text{-}C_5H_9)_7Si_7O_9(OH)_3 \rightarrow (\mathit{c}\text{-}C_5H_9)_7Si_7O_9[O{-}Au(PPh_3)]_3 + 3CO_2 + 3NHEt_2} \quad (90)$$

3.4.3. With Alkyl Halides

The reaction of alkali metal carbamates with CH_3I[77] was shown to be affected by the presence of a complexing agent for the alkali metal cation, the attack of the electrophile being in principle directed to the oxygen- (with formation of urethanes, Scheme 18, path A) or to the nitrogen atom (with evolution of carbon dioxide, Scheme 18, path B).

Scheme 18



The complexing agent (e.g., a crown ether), by spreading the positive charge, is thought to decrease the charge density and the polarizing power of the alkali-metal cation, thus enhancing the nucleophilicity of the carbamato group. It was also shown[189] that transfer of the carbamic group from phosphocarbamates $P(O_2CNR_2)_x(NR_2)_{3-x}$, occurs, the latter being obtained by carbonation of the amido precursor $P(NR_2)_3$. Alkyl urethanes were obtained when the phosphocarbamates were treated with alkyl halides in the presence of an alkali metal halide, MY, and a suitable crown ether, L.

$$\mathrm{P(O_2CNR_2)_\mathit{x}(NR_2)_{3-\mathit{x}} + \mathit{x}R'X + \mathit{x}MY + \mathit{x}L \rightarrow \mathit{x}NR_2CO_2R' + P(NR_2)_{3-\mathit{x}}Y_\mathit{x} + \mathit{x}[ML]X} \quad (91)$$

$$\text{(R = Me, Et; MY = alkali metal halide; L = 18-crown-6)}$$

Sterically hindered penta-alkylguanidines have been used to enhance the nucleophilic character of the oxygen center of the carbamato anion,[190] by formation of the penta-alkylguanidinium derivative upon reaction of the primary (or secondary) amine with carbon dioxide. Further reaction with an alkyl chloride gives the appropriate alkyl urethane.

The reaction of a metal–carbamato complex with MeI to give the metal iodide MI is the sum of the partial equations shown below. Further reaction of the urethane with MeI may, however, occur (see Scheme 19).

A reasonable estimate can be obtained of the enthalpy change associated with the iodo-methylation of the urethane by taking H_2NCO_2Me as a simplified reference molecule. The estimate led to conclude that the energetics of the process are presumably favorable.[77a]

Scheme 19

$$\mathrm{M(O_2CNEt_2) + MeI \longrightarrow Et_2NCO_2Me + MI}$$
$$\mathrm{Et_2NCO_2Me + MeI \longrightarrow [NMe_2Et_2]I + CO_2}$$
$$\overline{\mathrm{M(O_2CNEt_2) + 2\,MeI \longrightarrow [NMe_2Et_2]I + MI + CO_2}}$$

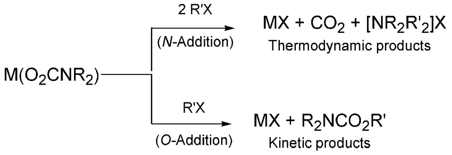
$$\mathrm{H_2NCO_2Me_{(\mathit{l})} + MeI_{(\mathit{l})} \longrightarrow [NH_2Me_2]I_{(\mathit{s})} + CO_{2(\mathit{g})}} \quad (92)$$

$$\Delta H^0 = \Delta H^0{}_f(\mathrm{CO_2}) + \Delta H^0{}_f\{[\mathrm{NH_2Me_2}]\mathrm{I}\} - \Delta H^0{}_f(\mathrm{H_2NCO_2Me}) - \Delta H^0{}_f(\mathrm{MeI}) = (-393.3 - 155.2 + 498 + 13.8) = -36.8\ \mathrm{kJ\ mol^{-1}}$$

Thus, alkylurethanes should be thermodynamically unstable toward *N*-alkylation. On the other hand, the possibility of isolating them resides in their kinetic stabilization toward further reaction. For a review of the reactions of alkylurethanes with the strong electrophile RCOX, see a comprehensive review article.[191]

The two possibilities of reaction of a metal carbamate with an alkylating agent are summarized in Scheme 20.

Scheme 20



Evolution of CO_2 and formation of the ammonium cation $[NR_2R'_2]^+$ are observed by treating a transition metal carbamate with an alkyl halide: $M_6(O_2CNEt_2)_{12}$, M = Mn,[96] Co,[83d] $Ni(O_2CNEt_2)_2$,[174] $Cu_2(O_2CNEt_2)_4(NHEt_2)_2$,[192] and $Pd(O_2CNEt_2)_2(NHEt_2)_2$ behave accordingly.[71b] The manganese derivative does not react with methyl iodide in a hydrocarbon solvent, but does so in THF, the observed product of the reaction being $[NR_2Me_2]_2[MnI_4]$.

$$\mathrm{1/6M_6(O_2CNR_2)_{12} + 4MeI \rightarrow 2CO_2 + [NMe_2R_2]_2[MI_4]} \quad (93)$$

$$(\mathrm{M = Mn, R = Et, {}^iPr; M = Co, R = Et})$$

$$\mathrm{Pd(O_2CNEt_2)_2(NHEt_2)_2 + 4MeI \rightarrow 2CO_2 + 2[NMe_2Et_2]I + PdI_2(NHEt_2)_2} \quad (94)$$

Addition of an electrophilic reagent [MeI or $(MeO)_2SO_2$] to a metal-bonded carbamato group [palladium(II),[167a] copper (I),[193,194] silver (I),[104,195] gold(I),[104a] zinc(II)[169]] or to dialkylammonium dialkylcarbamate[190,196] has been reported to proceed via *O*-alkylation to urethans.

From the data collected up to now, it appears that the regioselectivity of the reaction between a metal or an ammonium carbamate and an alkyl halide depends on the extent of negative charge on the oxygen atom of the carbamato group. It cannot be excluded that *O*-alkylation could be sterically hindered in aggregates of high nuclearity.

3.4.4. With Acyl Halides and Chloro Esters

When a metal *N*,*N*-dialkylcarbamato is treated at room temperature with an acyl chloride, a fast reaction occurs [25d,e] with formation of highly functionalized [197] carbamic-carboxylic anhydrides.

$$\mathrm{M(O_2CNR_2)}_n + n\mathrm{R'COCl} \rightarrow \mathrm{MCl}_n + n\mathrm{R_2NC(O)OC(O)R'} \quad (95)$$

For R = ^{i}Pr and R′ = Ph, the mixed anhydride can be isolated and characterized.[198,199,200] As *N*,*N*-dialkylcarbamato complexes are easily prepared from the metal chloride, a secondary amine and CO_2, a metal-assisted synthesis of the mixed anhydrides may become available. A restriction is given by the fact that some R groups give unstable compounds of this type. For example, the reaction of $Si(O_2CNR_2)Me_3$ with an acyl chloride invariably gives CO_2, $SiMe_3Cl$, and the appropriate amide.[126]

$$\mathrm{R^*Cl + Si(O_2CNR_2)Me_3} \rightarrow \mathrm{R^*NR_2 + CO_2 + SiMe_3Cl} \quad (96)$$

$$(\mathrm{R^* = alkylCO,\ arylCO,\ arylSO_2})$$

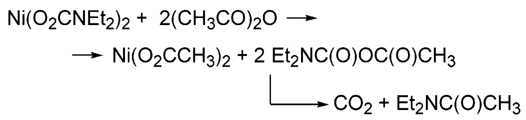
For several *N*,*N*-dialkylcarbamato complexes, the attack of the acyl electrophile occurs at the carbamato oxygen atom, independent of the nature of the metal [Na, Cu(II), Mn(II), Co(II), Ti(III), V(III), Fe(III)]. The resulting carbamic-carboxylic anhydride, incorporating carbon dioxide, sometimes undergoes decarboxylation to the appropriate amide.[77,25d,e]

Scheme 21

$$\mathrm{MCl}_n + n\mathrm{CO_2} + 2n\mathrm{NHR_2} \longrightarrow \mathrm{M(O_2CNR_2)}_n + n\mathrm{[NH_2R_2]Cl}$$
$$\mathrm{M(O_2CNR_2)}_n + n\mathrm{R'COCl} \longrightarrow \mathrm{MCl}_n + n\mathrm{R_2NC(O)OC(O)R'}$$
$$\mathrm{CO_2 + 2\,NHR_2 + R'COCl} \longrightarrow \mathrm{R_2NC(O)OC(O)R' + [NH_2R_2]Cl}$$

For the *N*,*N*-diethylcarbamato complexes of copper(II) and iron(III), evolution of CO_2 and formation of the amide $Et_2NC(O)R'$ were observed upon treatment with acyl chloride, presumably due to cleavage of the intermediate anhydride in the presence of metallic halides. This hypothesis is strengthened by the observation that a purified sample of the anhydride $Me_2NC(O)OC(O)Ph$ has been found to be stable in refluxing benzene for 24 h, although decomposition occurs in the presence of copper(I) or copper(II) salts.[201] Formation of the mixed anhydride was observed also in the reaction of $Pd(O_2CNEt_2)_2(NHEt_2)_2$ [71] or $Ni(O_2CNEt_2)_2$ [174] with acetic anhydride, the transient mixed anhydride being spectroscopically detected.

Scheme 22



$$\mathrm{Ni(O_2CNEt_2)_2 + 2(CH_3CO)_2O} \rightarrow \mathrm{Ni(O_2CCH_3)_2 + 2\,Et_2NC(O)OC(O)CH_3} \rightarrow \mathrm{CO_2 + Et_2NC(O)CH_3}$$

With $Mn_6(O_2CNEt_2)_{12}$, phosgene $COCl_2$, and chloro esters such as ClCOOEt, or ClSOOEt, react as shown below, while no CO_2 evolution occurs with $ClP(OEt)_2$[25e]

$$^1/_6\mathrm{[Mn_6(O_2CNEt_2)_{12}] + 2ClCOX} \rightarrow \mathrm{MnCl_2 + 2CO_2 + 2Et_2NCOX} \quad (97)$$

$$(\mathrm{X = Cl,\ OEt})$$

$$^1/_6\mathrm{[Mn_6(O_2CNEt_2)_{12}] + 2ClSOX} \rightarrow \mathrm{MnCl_2 + 2SO_2 + 2Et_2NSOX} \quad (98)$$

$$(\mathrm{X = Cl,\ OEt})$$

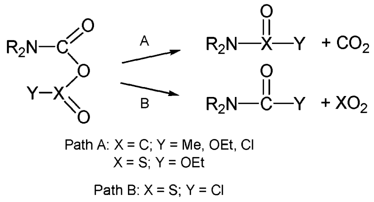
$$^1/_6\mathrm{[Mn_6(O_2CNEt_2)_{12}] + 2ClP(OEt)_2} \rightarrow \mathrm{MnCl_2 + 2Et_2NC(O)OP(OEt)_2} \quad (99)$$

In the case of the phosphorus-containing reagent, the primary product of the reaction, $Et_2NCO_2P(OEt)_2$, is stable toward CO_2 loss, in agreement with the fact that the reverse process, i.e., CO_2 insertion into the P−N bond, has been observed for the amides of phosphorus(III), $P(NR_2)_3$,[123,142] and phosphorus(V).[143,202]

Moreover, the reaction of $Si(O_2CNR_2)Me_3$ with lactones yields the corresponding siloxybutyroamides $R_3SiOCH(CH_3)CH_2C(O)NR_2$, as for the case of β-methylpropiolactone.[124]

A mechanistic study [25e] of the reaction between $Mn(O_2{}^{13}CNEt_2)_2$ and electrophiles has shown the N−^{13}C bond of the intermediate primary product to be cleaved and path A (see Scheme 23) is followed in all cases investigated, with the sole exception of $SOCl_2$.

Scheme 23

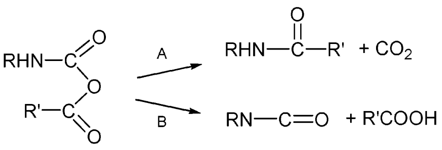


Path A: X = C; Y = Me, OEt, Cl
X = S; Y = OEt

Path B: X = S; Y = Cl

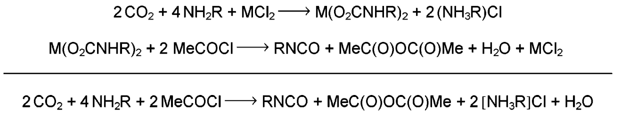
The reactions of *N*-alkylcarbamates of manganese(II) and cobalt(II), $M(O_2CNHR)_2$, R = Ph, Pr, Cy, with acyl or benzoyl chloride proceed with formation of isocyanates, carboxylic anhydrides, amides, and carbon dioxide.[77b] By assuming the reactivity of *N*-alkylcarbamato metal complexes to be similar to that of *N*,*N*-dialkylcarbamato derivatives, these observations could be explained by assuming two possible decomposition pathways starting from the mixed anhydride. In fact, both pathways A and B have been reported in the literature for the decomposition of mixed anhydrides.[203,204,205,206]

Scheme 24



It is noteworthy that the overall process from CO_2 to alkyl isocyanates corresponds to the metal-assisted incorporation of carbon dioxide into the products, see Scheme 25.

Scheme 25



$$2\,CO_2 + 4\,NH_2R + MCl_2 \longrightarrow M(O_2CNHR)_2 + 2\,(NH_3R)Cl$$

$$M(O_2CNHR)_2 + 2\,MeCOCl \longrightarrow RNCO + MeC(O)OC(O)Me + H_2O + MCl_2$$

$$2\,CO_2 + 4\,NH_2R + 2\,MeCOCl \longrightarrow RNCO + MeC(O)OC(O)Me + 2\,[NH_3R]Cl + H_2O$$

3.4.5. Anionic Ligand-Transfer Reactions

The literature reports several cases of transfer reactions of the carbamato ligand. Such reactions have been used for the synthesis of transition metal derivatives such as $Ti(O_2CNR_2)Cp_2$,[96] magnesium and phosphorus carbamates, $Mg(O_2CNR_2)_2$, R = Et,[153] ^{i}Pr,[82] and $P(O_2CNR_2)X(CF_3)_3$.[143,144] The anionic ligands are redistributed in the products and no change of oxidation state takes place

$$Mn_6(O_2CNEt_2)_{12} + 6\,(TiCp_2Cl)_2 \rightarrow 12\,Ti(O_2CNEt_2)Cp_2 + 6\,MnCl_2 \quad (100)$$

$$MgCp_2 + 2\,M(O_2CN^iPr_2)_4 \rightarrow Mg(O_2CN^iPr_2)_2 + 2\,M(O_2CN^iPr_2)_3Cp \quad (101)$$

$$(M = Zr, Hf)$$

$$MgCp_2 + Ti(O_2CN^iPr_2)_3 \rightarrow Mg(O_2CN^iPr_2)_2 + Ti(O_2CN^iPr_2)Cp_2 \quad (102)$$

$$(CH_3)(CF_3)_3PCl + Si(O_2CNMe_2)Me_3 \rightarrow P(O_2CNMe_2)(CH_3)(CF_3)_3 + Me_3SiCl \quad (103)$$

$$F(CF_3)_3PF + Si(O_2CNMe_2)Me_3 \rightarrow P(O_2CNMe_2)F(CF_3)_3 + Me_3SiF \quad (104)$$

Synthetically useful are the ligand exchange reactions consisting of treating a dialkylcarbamato derivative with the appropriate secondary amine.

$$M(O_2CNR_2)_n + nNHR'_2 \xrightarrow{CO_2} M(O_2CNR'_2)_n + nNHR_2 \quad (105)$$

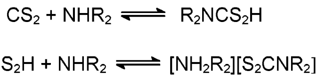
If the amine NHR_2 is more volatile than NHR'_2, the difficulties arising from possible equilibria leading to mixtures of products are readily overcome. Moreover, the equilibrium is advantageously shifted toward the required direction if the produced metal–carbamato complex has a lower solubility than the reagent. Formally the reaction is an amine exchange process; however, it has been shown [57] that the reaction does not occur in the absence of carbon dioxide. Thus, these exchange reactions are triggered by the (carbamic acid)/(carbamate anion) equilibria discussed in section 2.

The CO_2/CS_2 exchange between a metal carbamato complex and CS_2 is actually believed to be a $O_2CNR_2^-/S_2CNR_2^-$ exchange, which is promoted by accidental hydrolysis of the $M(O_2CNR_2)_n$ complex or by intentionally added amine.

$$M(O_2CNR_2)_n + n\,CS_2 \rightarrow M(S_2CNR_2)_n + n\,CO_2 \quad (106)$$

In this exchange reaction, the higher stability of the reaction product ($CO_{2(g)}$, $\Delta G_f^0 = -394.4$ kJ mol^{-1}) with respect to the reagent ($CS_{2(g)}$, $\Delta G_f^0 = +67.1$ kJ mol^{-1}), and the high concentration of CS_2 with respect to CO_2 in hydrocarbon solution explain the observed facts.[11] The presence of free amine has been established to be essential for the reaction to proceed at reasonable rates for nickel(II),[174] and palladium(II).[71] Typical is the case of the nickel(II) complexes $Ni(O_2CNR_2)_2$, whose ethyl derivative reacts slowly at room temperature in the absence of free amine. On the contrary, the *iso*-propyl derivative, which is unreactive in the absence of free amine, gives the expected CO_2/CS_2 exchange by addition of amine. Some free amine causes the setting of the following equilibria, similar to those triggered by CO_2, see section 2.

Scheme 26



$$CS_2 + NHR_2 \rightleftharpoons R_2NCS_2H$$

$$R_2NCS_2H + NHR_2 \rightleftharpoons [NH_2R_2][S_2CNR_2]$$

3.4.6. Anionic Ligand-Transfer Reactions Coupled with Electron-transfer

Ligand-transfer reactions may be accompanied by an electron-transfer process. With homoleptic carbamates, examples are known of redox reactions between Ti(III) and Cu(II),[207] Fe(III) and Ti(III),[207] and Pd(II) and Cr(II).[95,207] Carbamato ligand transfer from $Nb(O_2CNEt_2)_5$ has been observed [90] upon reduction of niobium(V) by $CoCp_2$*.

$$Nb(O_2CNEt_2)_5 + CoCp_2^* \rightarrow Nb(O_2CNEt_2)_4 + [CoCp_2^*][O_2CNEt_2] \quad (107)$$

The titanium(IV) derivative $Ti(O_2CNEt_2)_4$ undergoes ligand transfer accompanied by reduction with complexes of vanadium(0),[82] vanadium(II),[82,91] titanium(II),[82] or zirconium(II).[208]

$$3Ti(O_2CNEt_2)_4 + V(mes)_2 \rightarrow 1/n[V(O_2CNEt_2)_3]_n + 3/n[Ti(O_2CNEt_2)_3]_n + 2mes \quad (108)$$

$$(mes = 1,3,5\text{-trimethylbenzene})$$

$$2Ti(O_2CNEt_2)_4 + 2VCp_2 \rightarrow V_2(O_2CNEt_2)_4Cp_2 + 1/n\,[Ti(O_2CNEt_2)_3]_n + Ti(O_2CNEt_2)Cp_2 \quad (109)$$

$$Ti(O_2CNEt_2)_4 + TiCp_2(CO)_2 \rightarrow 1/n\,[Ti(O_2CNEt_2)_3]_n + Ti(O_2CNEt_2)Cp_2 + 2CO \quad (110)$$

$$2Ti(O_2CNEt_2)_4 + ZrCp_2(CO)_2 \rightarrow Zr(O_2CNEt_2)_4 + Ti(O_2CNEt_2)Cp_2 + 1/n[Ti(O_2CNEt_2)_3]_n + 2CO \quad (111)$$

$$Ti(O_2CNEt_2)_4 + VCp^*_2 \rightarrow 1/n\ [Ti(O_2CNEt_2)_3]_n + V(O_2CNEt_2)Cp^*_2 \quad (112)$$

3.4.7. With Carbon Monoxide

With *N*,*N*-dialkylcarbamato derivatives of transition metals, coordinative addition of CO may occur. In some cases, this process is energetically favored due to the possibility for the carbamato ligand to be converted from bidentate to monodentate, thus vacating a coordination position and relieving some steric congestion. This is evidenced by the reaction of the ruthenium(II) carbamato derivative $Ru(O_2CN{}^iPr_2)_2(PPh_3)_2$, which undergoes addition of two carbonyl groups, through the intermediacy of the product of monoaddition.[177]

$$Ru(O_2CN{}^iPr_2)_2(PPh_3)_2 + CO \rightarrow Ru(O_2CN{}^iPr_2)_2(PPh_3)_2(CO) \quad (113)$$

$$Ru(O_2CN{}^iPr_2)_2(PPh_3)_2(CO) + CO \rightarrow Ru(O_2CN{}^iPr_2)_2(PPh_3)_2(CO)_2 \quad (114)$$

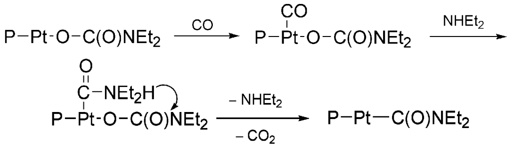
A similar situation applies in the case of the carbamato derivative of copper(I), $Cu(O_2CN{}^iPr_2)$, which absorbs CO (atmospheric pressure) up to a maximum value of 0.6 (CO/Cu molar ratio) at 269 K.[104b]

$$Cu(O_2CN{}^iPr_2) + CO \rightleftharpoons Cu(O_2CN{}^iPr_2)(CO) \quad (115)$$

The coordinative addition of CO may also precede the conversion of an oxygen-bonded carbamato group to a carbon-bonded carbamoyl ligand $-CONR_2$. For example, carbon monoxide reacts with the platinum(II) derivative *cis*-$Pt(O_2CNEt_2)_2(PPh_3)_2$ (geometry assigned on the basis of J_{Pt-P}),[178a] giving the carbamoyl compound *cis*-$Pt[(C(O)NEt_2)]_2(PPh_3)_2$, see eq 116. It is assumed that the reaction occurs through attack by the free amine (originated from fortuitous hydrolysis) at precoordinated CO, followed by protonation of the carbamato ligand to produce CO_2 and amine, see Scheme 27.

$$Pt(O_2CNEt_2)_2(PPh_3)_2 + 2CO \rightarrow Pt[(C(O)NEt_2)]_2(PPh_3)_2 + 2CO_2 \quad (116)$$

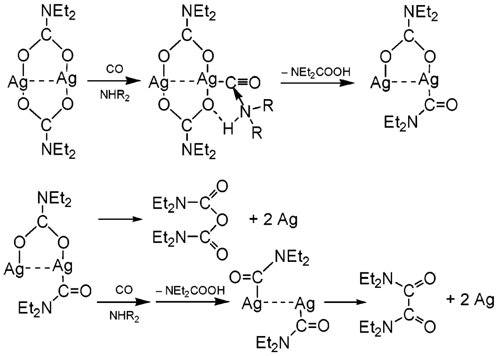
Scheme 27



P = PPh3, only the two mutually *trans* ligands are shown

A further case of interaction with CO leading to reduction of the central metal atom is represented by the silver compound $Ag(O_2CNEt_2)$, which reacts with CO[104] giving a silver mirror and carbamic anhydride (identified by IR spectroscopy and GC/MS). In the presence of excess amine, *N*,*N*-diethyloxamide is formed. A reaction mechanism has been proposed involving prior coordination of CO to silver, followed by attack of the amine to the silver-coordinated carbonyl carbon and rearrangement to the observed products (silver metal and the organic compounds), see Scheme 28.

Scheme 28



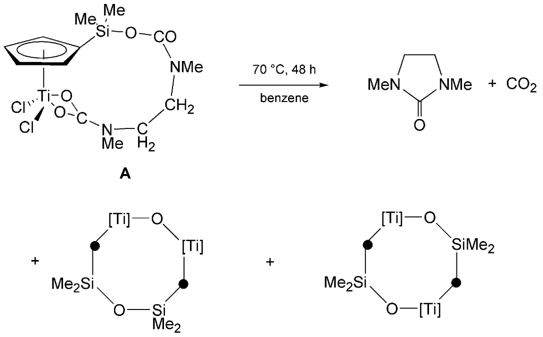
3.5. Thermal Reactions

Mironov and co-workers[209] reported the thermal (100−150 °C) decomposition of the silyl carbamates $Si[O_2CNR(SiMe_3)]Me_3$ as a new phosgene-free method to obtain isocyanates. More recently, trimethylsilyl esters of dicarbamic acids were heated at 100−150 °C in an alkane medium obtaining quantitative conversion to isocyanate and bis(trimethylsilyl)oxide.[135]

$$Si[O_2CNR(SiMe_3)]Me_3 \rightarrow RNCO + (Me_3Si)_2O \quad (117)$$

Thermal decomposition of compound **A** in benzene gave[151] 1,3-dimethyl-2-imidazolidinone and CO_2, together with dinuclear derivatives of titanium(IV).

Scheme 29



[Ti] = TiCl2

● = C5H4 ring

Analogous thermal decompositions under CO_2, through the probable intermediacy of carbamato derivatives, have been reported for amido derivatives of titanium(IV) (with RNCO as byproduct),[210] zirconium(IV),[211] germanium(IV), and tin(IV).[212]

4. Applications

Complexes reported in this review article are relatively new and may have important technical applications, both in the area of surface science and in that of organic synthesis. We shall deal in the following sections with both aspects.

4.1. Reactions with Inorganic Surfaces

Despite the structural similarities between carboxylato and carbamato metal complexes, the reactivity of the latter compounds is of considerable greater interest. Restricting our attention for the moment to the alkyl disubstituted *N*,*N*-dialkylcarbamato derivatives, which have been up to this moment the most studied ones, it will be noted that they are easily subjected to electrophilic attack by a number of electrophilic reagents. The rupture of the R_2N-CO_2 bond causing evolution of carbon dioxide allows the reactions to go frequently to completion. Section 3.4.1 defines the products which have been obtained by controlled, partial hydrolysis of several *N*,*N*-dialkylcarbamato derivatives. As the thermodynamics of the hydrolytic process are favorable due to the evolution of carbon dioxide, the nature of the resulting products largely depends on the amount of water used in the correct stoichiometric amount for the formation of the expected products of partial hydrolysis. On several occasions it has been noted that the products of hydrolysis have twelve alkyl groups. In fact, these are some of the products obtained by hydrolysis: $U_4(\mu_3\text{-O})_2(O_2CNEt_2)_{12}$,[173a] $Fe_8(\mu_4\text{-O})_2(O_2CN^iPr_2)_{12}$,[173b] $Cu_8(\mu_4\text{-O})_2(O_2CN^iPr_2)_{12}$.[93] These hydrolytic processes are rather selective, and mixtures of oxides are normally not observed.

In addition to the use of *N*,*N*-dialkylcarbamato complexes in processes of partial controlled hydrolysis, carbamato derivatives can be used as reagents toward the hydroxyl groups of an oxide surface. Previously dehydrated commercial silica of known surface area has been used extensively for this purpose. This leads to a grafting reaction completely shifted toward the product due to the formation of carbon dioxide. Equation 118 represents such a grafting reaction for a *N*,*N*-dialkylcarbamato derivative of nuclearity *m*, whereby a ≡Si−O−M bond is formed on the silica surface

$$[M(O_2CNR_2)_n]_m + {\equiv}Si(OH) \rightarrow {\equiv}SiO[M_m(O_2CNR_2)_{nm-1}] + CO_2 + NHR_2 \quad (118)$$

In principle, the grafted carbamato product should maintain its nuclearity and all the functional groups, except the one(s) which has(ve) been used for the grafting reaction. Depending on the nature and the nuclearity (and therefore the size of the metal precursor), more than one of the dialkylcarbamato groups per metal atom M can be involved in the grafting reaction. This method of functionalizing the silica surface has been used extensively, with the *N*,*N*-dialkylcarbamato derivatives of tin(IV),[86b] palladium(II),[213] platinum(II),[105a] and gold(I).[188b] It has been conclusively shown that the carbamato function is used for grafting the metal on the silica surface; thus, the remaining carbamato groups being still present on the grafted metal may be used for further reactions. That the carbamato groups contained in a heteroleptic molecular precursor are the most reactive part of the molecule has been shown through the reaction of tris(*N*,*N*-diethylcarbamato)cyclopentadienylzirconium(IV), $ZrCp(O_2CNEt_2)_3$, with dehydrated silica, showing that carbon dioxide is evolved, while no C_5H_6 is produced.[153] As far as the applications of these systems are concerned, the use of silica-supported titanium catalysts for olefin epoxidation has been recently reported using siloxy-alkoxides of titanium as precursors.[214]

Finally, it should be pointed out that carbamato complexes of silicon,[180b,c] aluminum, or titanium[215a] have been used to produce the corresponding oxide in the form of functionalized, predominantly amorphous oxides of elevated surface area. Recently[215b] $Zn_4(\mu_4-O)(O_2CNEt_2)_6$ has been employed for the chemical vapor deposition (CVD) of ZnO on a Si[111] surface; the films were grown at 400 °C with a source temperature of 185−195 °C. The films so produced were found to be of a higher density than those obtained with $Zn_4(\mu_4-O)(O_2CMe)_6$ under the same conditions.

4.2. Organic Syntheses via the CO_2/Amine System

One of the main goals of CO_2 chemistry is its incorporation into organic substrates.[25f,216] This may occur through processes involving the formation of $C-CO_2$,[217] $O-CO_2$,[218] or $N-CO_2$ [197,219] bonds. These reactions, whenever thermodynamically feasible, are frequently carried out in the presence of metal cations or of substances with proton activity. When new $N-CO_2$ bonds are formed, the intermediacy of metal carbamates, carbamic acid, or ammonium carbamates has been claimed or demonstrated.

Carbamic acid esters NR_2CO_2R' as obtained by reactions involving the CO_2/amine system have played an important role in industrial chemistry. The compounds $NHRCO_2R'$ and NR_2CO_2R' are the mono- and dialkyl esters, respectively, of the unstable carbamic acid, see section 2.3. Their derivatives are important precursors to pharmaceuticals, in agriculture as herbicides, fungicides and pesticides,[191,220] as precursors to isocyanates, which in turn, are intermediates in the production of high-performance plastics, polyurethanes, elastomers, and adhesives.[221]

The earlier synthetic methods of carbamic acid esters have in common the use of phosgene $COCl_2$ as starting material, as obtained from the combination of carbon monoxide with dichlorine in the presence of light (the name phosgene, i.e. generated by light, clearly defines the synthetic route to this important chemical).[222] This type of chemistry produced ethyl chloroformate OC(OEt)Cl, urea $OC(NH_2)_2$ and diethyl carbonate $OC(OEt)_2$. These three fundamental building blocks were used to produce ethyl carbamate $OC(OEt)NH_2$ by three different laboratories in the first decades of the 19th century.[223]

$$OC(OEt)Cl + NH_3 \rightarrow NH_2CO_2Et + HCl \quad (119)$$

$$OC(NH_2)_2 + EtOH \rightarrow NH_2CO_2Et + NH_3 \quad (120)$$

$$OC(OEt)_2 + NH_3 \rightarrow NH_2CO_2Et + EtOH \quad (121)$$

However, it may be possible to prepare these products via alternative routes not involving phosgene, vide infra.

In this section, preparative routes will be considered concerning the reaction of the CO_2/amine system with (a) organic carbonates, (b) substrates with a carbon−carbon unsaturation, namely, olefins and acetylenes, and (c) epoxides. Moreover, the preparation of carbamic acid esters via oxidative carbonylation of amines and via electrochemical synthesis will be reviewed.

4.2.1. With Organic Carbonates

The traditional synthetic routes to carbamic esters[224] have experienced important changes in the recent years due to the discovery of alternative synthetic routes to dialkyl carbonates.[225] Dialkyl carbonates are important ingredients for their further reaction with primary or secondary amines to give carbamic esters, sometimes in the presence of a suitable catalyst, such as a metal alkoxide[226] of zinc, cobalt, tin, aluminum, or titanium.[227] A study on the formation of *N*-propyl-ethyl carbamate from diethyl carbonate and 1-propylamine showed that the best results in terms of yields are obtained with anhydrous $SnCl_2$.[228]

The reaction of a primary or a secondary amine with dialkyl carbonates, $OC(OR)_2$,[25f,203,229] is of primary importance and it will be discussed in some detail. As stated above, the reaction, first discovered in 1845, is best carried out in the presence of carbon dioxide[229a] and is an efficient way to produce alkylcarbamates, once dialkyl carbonate has been made available. Mechanistic studies[229a] with $^{13}CO_2$ have shown that carbon dioxide incorporated in the alkylammonium carbamate $[NH_3R][O_2{}^{13}CNHR]$ is not found in the final alkyl carbamate product.

$$^{13}CO_2 + 2NH_2R \rightarrow [NH_3R][O_2{}^{13}CNHR] \qquad (122)$$

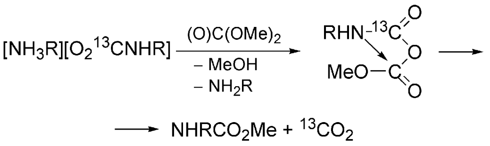
$$[NH_3R][O_2{}^{13}CNHR] + (O)C(OMe)_2 \rightarrow NHRCO_2Me + {}^{13}CO_2 + NH_2R + MeOH \qquad (123)$$

$$(R = Bz, \text{cyclohexyl, allyl})$$

The reaction between primary amines and dimethyl carbonate was found to be accelerated by carbon dioxide,[229a] the suggestion therefore being that carbon dioxide acts as a catalyst. This conclusion comes from comparative experiments carried out in the presence of CO_2 (at substantially atmospheric pressure) and in the absence of intentionally added carbon dioxide. For example, a conversion of about 70% into the benzyl carbamic ester $NHBzCO_2Me$ was found after 24 h at 90 °C.

Additional insight into the nature of the catalytic effect of carbon dioxide comes from earlier experiments[25d] showing that alkylammonium carbamates undergo reaction with a number of electrophiles. The suggested intermediate $[NH_3R][O_2{}^{13}CNHR]$ in the RNH_2/CO_2 system would undergo attack by dimethyl carbonate $(O)C(OMe)_2$ giving a mixed carboxylic-carbamic anhydride, the latter undergoing carbon dioxide elimination by cleavage of the C−N bond and formation of the observed products.

Scheme 30



These findings are to be related to the general reactivity of alkylcarbamato metal complexes with electrophilic reagents, see section 3.4.4. Electrophilic reagents are well-known to react with the dialkylcarbamato anion, as first applied to an acyl chloride in its reaction with the dialkylcarbamates of sodium, copper(II), titanium(III), and vanadium(III).[25d,e,77b,229a] Labeling work on the reaction between $Mn_6(O_2{}^{13}CNEt_2)_{12}$ and MeCOCl, $COCl_2$, ClCOOEt, or $ClSO_2Et$ has shown that $^{13}CO_2$ is evolved and no labeling is found in the organic products. In the only case of $SOCl_2$, on the contrary, labeling was retained in the product. Furthermore, in two substantially adjacent papers,[77b,229b] it has been pointed out that the addition of a crown ether has a dramatic effect on both the kinetics of the reaction and its outcome.

$$1\backslash n\ M(O_2{}^{13}CNR'_2)_n + MeC(O)Cl \rightarrow 1\backslash n\ MCl_n + \{NR'_2{}^{13}C(O)OC(O)Me\} \qquad (124)$$

$$\{NR'_2{}^{13}C(O)OC(O)Me\} \rightarrow NR'_2C(O)Me + {}^{13}CO_2 \qquad (125)$$

Similarly, the reaction of a secondary amine with ortho esters $R^1C(OR^2)_3$ [230] was reported to give the expected urethane. The reaction was shown to be accompanied by a parasitic alkylation to give the appropriate tertiary amine.

$$CO_2 + NHR_2 + R^1C(OR^2)_3 \rightarrow R_2NCO_2R^2 + R^2OH + R^1CO_2R^2 \qquad (126)$$

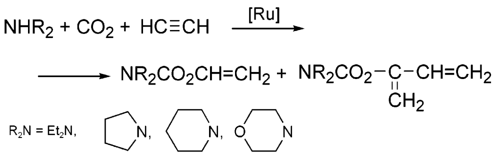
$$(NHR_2 = NHEt_2, \text{piperidine, morpholine, } NH_2Pr, NHPhMe)$$

$$NHR_2 + R^1C(OR^2)_3 \rightarrow NR_2R^2 + R^2OH + R^1COOR^2 \qquad (127)$$

4.2.2. With Substrates Containing Carbon–Carbon Unsaturations

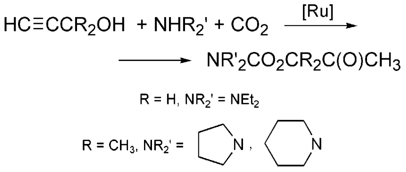
The synthesis of vinylcarbamates was reported to be based on the reaction of CO_2 with a secondary amine and a terminal alkyne in the presence of a catalytic amount of $Ru_3(CO)_{12}$ in toluene, MeCN, or THF as solvent.[231,232] Also $RuCl_3{\cdot}xH_2O$ and mononuclear ruthenium(II) complexes were found to catalyze the reaction of a terminal alkyne to vinylkcarbamates; the reaction was suppressed in halogenated media. The yields ranged from low to medium, and the *Z* isomer was always the major component. The reaction with acetylene was carried out at 80−100 °C with CO_2 under pressure and with a secondary amine, such as Et_2NH, piperidine, morpholine, or pyrrolidine.[219a,233]

Scheme 31



By using α-ethynyl alcohols in the presence of a ruthenium catalyst, high yields of *β*-oxoalkylcarbamates have been obtained.[234] For example, propargyl alcohol $HC{\equiv}CCH_2OH$ and diethylamine in acetonitrile with carbon dioxide under pressure (50 atm) at 70 °C give a 40% yield of $NEt_2CO_2CH_2C(O)CH_3$, in the presence of $[RuCl_2(NBD)]_n$ as catalyst.

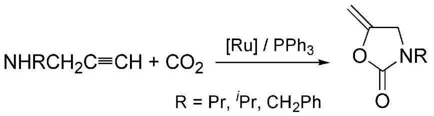
Scheme 32



Yields up to about 65% of 1,1-dialkyl-2-oxopropyl-*N*,*N*-dialkylcarbamates and 2-oxopropyl-*N*,*N*-diorganylcarbamates have been secured by using iron catalysts,[235] based on 1,1′-bis(diphenylphosphino)ferrocene.

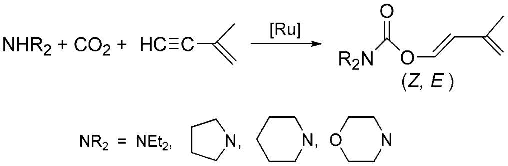
Cyclic carbamates have been obtained by the interaction of CO_2 with *N*-substituted propargylamines.[236] The catalytic precursors are based on ruthenium(0) olefin complexes in the presence of PPh_3.

Scheme 33



The preparation of *O*-1-(1,3-dienyl)carbamates, which have a potential use as Diels–Alder substrates,[237] or as intermediates,[238] has been reported by regioselective addition of CO_2 and a secondary amine to *iso*-propenylacetylene in the presence of $Ru[Ph_2P(CH_2)_nPPh_2][\eta^3\text{-}CH_2C(Me){=}CH_2]_2$ as catalyst.[239]

Scheme 34



Mechanistic studies concerning the formation of vinylcarbamates catalyzed by ruthenium or iron compounds have suggested that vinylcarbamate formation involves the addition of the carbamate anion to an active alkyne–ruthenium species (the ruthenium-catalyzed addition of carbamates occurs with terminal alkynes only). Moreover, the selective addition at the terminal alkyne carbon suggests the formation of a ruthenium-vinylidene active species.[233c,240]

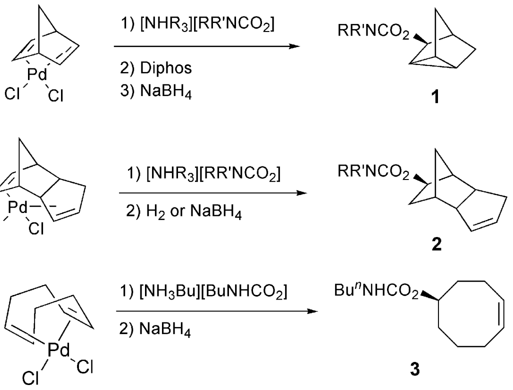
Formation of carbamic esters was observed in the reaction of CO_2 with a vinyl ether and a secondary amine.[241] In this case, no metal catalyst was required.

$$NHR_2 + CO_2 + CH_2{=}CHOEt \rightarrow NR_2CO_2CH(CH_3)OEt \quad (128)$$

$$(R = Me, Et)$$

Preformed carbamate anions $NRR^1CO_2^-$ derived from primary or secondary amines and CO_2, added to $Pd(norbornadiene)Cl_2$, followed by treatment with diphos and $NaBH_4$, gave good yields of the nortricyclo carbamate esters, **1**. When $Pd(dicyclopentadiene)Cl_2$ or $Pd(1,5\text{-cyclooctadiene})Cl_2$ was used as the olefin source, the corresponding carbamate **2** or **3** was obtained in good yields by reductive cleavage with $NaBH_4$ or dihydrogen, see Scheme 35.[242]

Scheme 35

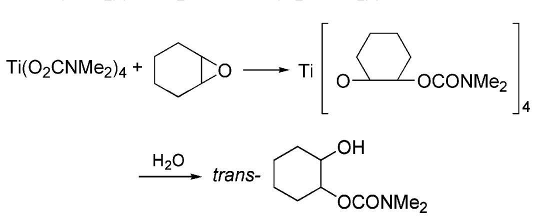


It is believed that the successful outcome of the reaction depends on (a) the activation of CO_2 by the amine and (b) activation of the olefin through complexation to the metal, promoting the nucleophilic attack by the carbamate anion.

4.2.3. With Epoxides

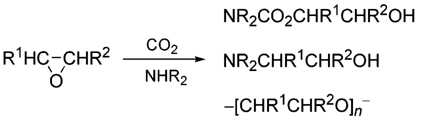
The reaction of $Ti(NMe_2)_4$ with CO_2 and 1,2-epoxycyclohexane, followed by hydrolysis of the reaction mixture, was reported to give 2-hydroxycyclohexyl-dimethylcarbamate in high yields.[243] The reaction was preferably carried out at 80 °C in benzene as medium under an elevated pressure (50 atm) of CO_2 for 210 h, followed by addition of water at atmospheric pressure. This led to *trans*-2-hydroxycyclohexyl dimethylcarbamate in a 50% yield, with respect to the titanium-bonded amido groups. Al-

Scheme 36



though $Ti(NMe_2)_4$ is known to react rapidly with CO_2 to give $Ti(O_2CNMe_2)_4$,[7b,8b,c] the formation of carbamic esters does not necessarily proceed through the intermediacy of alkyl-carbamato complexes of titanium(IV). Further work has in fact shown that even in the absence of titanium(IV), dimethylamine, 1,2-epoxycyclohexane and carbon dioxide give 2-hydroxycyclohexyl-dimethylcarbamate, under similar experimental conditions, in admixture with the corresponding amino-alcohol. Further studies have shown that carbamic esters can be prepared directly by reacting CO_2 and epoxides with a primary or a secondary aliphatic amine. Hydroxycarbamate of amino-alcohols, and/or oligomers of the epoxide were observed, the relative amounts depending on the nature of the reagents, and on reaction conditions.[244]

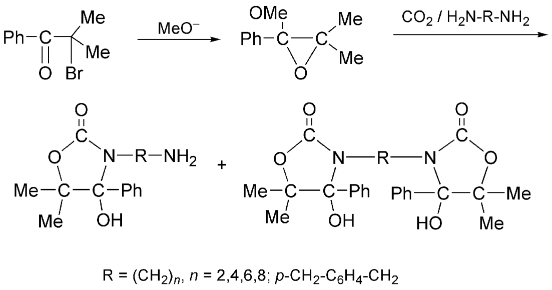
Scheme 37



Other transition metal amides such as $TiCp(NMe_2)_3$, and tungsten amides, $W_2(NMe_2)_6$ and $W(NMe_2)_6$, have been reported to be active in the formation of 2-hydroxylcyclohexyl-dimethylcarbamate from CO_2 and epoxycyclohexane.[245] Aromatic amines, in the presence of stoichiometric amounts of $ZnEt_2$, were reported to react with epoxycylohexane under CO_2 pressure to give 2-hydroxylcyclohexyl-diphenylcarbamate.[169]

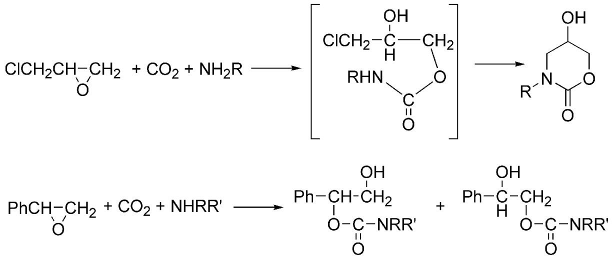
Reactions of 2-methoxy-3,3-dimethyl-2-phenyloxirane or α-bromoisobutyrophenone and CO_2 in the presence of α,ω-diamines afford cyclic carbamates (bis-2-oxazolidinones) according to Scheme 38. These reactions are catalyzed by methoxide.[246]

Scheme 38



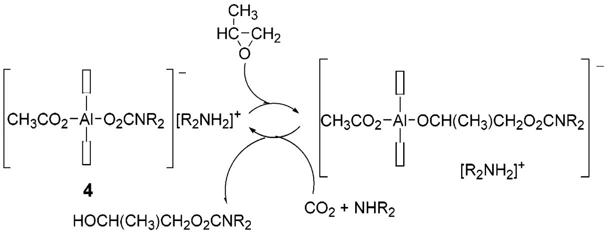
Cyclic carbamates (hydroxo-oxazinones) or hydroxycarbamates have been obtained under mild conditions by reacting chloromethyloxirane or phenyloxirane,[247] with carbon dioxide under pressure (10 atm) and a primary or a secondary amine, respectively, see Scheme 39.

Scheme 39



The acetate of (5,10,15,20-tetraphenylporphinato)aluminum(III), $Al(TPP)(O_2CCH_3)$, was found to catalyze the formation of dialkylcarbamic esters from CO_2, a secondary amine and an epoxide.[248] For example, in the reaction of 100 equiv of diethylamine and 1,2-epoxypropane, in the presence of 1 equiv of the aluminum complex, a turnover of 47 of the diethylcarbamic ester $NEt_2CO_2CH_2CH(Me)OH$ was obtained at 60 °C under a pressure of 50 atm of carbon dioxide. In the case of a secondary amine and 1,2-epoxypropane, the catalytic formation of 2-hydroxypropyl dialkylcarbamate is considered to proceed by the insertion of the epoxide between the aluminum−oxygen bond of the (porphinato)aluminum carbamate **4** to form an aluminum alkoxide, followed by cleavage by diethylcarbamic acid (from carbon dioxide and diethylamine) to give the product and regenerating the active aluminum carbamato group (Scheme 40).[248]

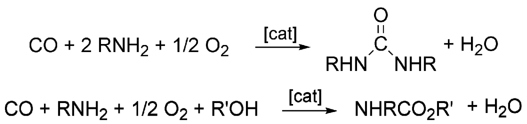
Scheme 40



4.2.4. Carbamic Esters by Oxidative Carbonylation of Amines

Oxidative carbonylation of primary amines into ureas[249] and the related conversion to carbamic acid esters, [250] see Scheme 41, have been the subject of several reports. Catalysts based on metal complexes of group 6[251] and of manganese,[249c,252] ruthenium,[249a,250d] cobalt,[249d,250f] rhodium,[250g,l] nickel,[249b] palladium,[249e,250] gold,[253] and polymer-supported palladium/manganese bimetallic systems [54] have been demonstrated to assist this reaction.

Scheme 41

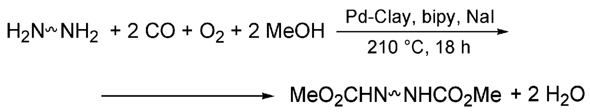


$$CO + 2\,RNH_2 + 1/2\,O_2 \xrightarrow{[cat]} RHN\text{–}C(=O)\text{–}NHR + H_2O$$

$$CO + RNH_2 + 1/2\,O_2 + R'OH \xrightarrow{[cat]} NHRCO_2R' + H_2O$$

Carbamate esters are also produced in good yields by using a heterogeneous catalyst consisting of a metal of the platinum group and an ammonium- or an alkali-metal iodide.[255] Carbamic acid esters [250a] have also been obtained by using catalytic amounts of Pd−Clay, a nitrogen-containing donor ligand and NaI as promoter under severe conditions of temperature and pressure (p_{CO} = 70 atm; p_{O2} = 11 atm). The following scheme shows the reaction occurring with a diamine, for example, $H_2N(CH_2)_8NH_2$.

Scheme 42



$$H_2N{\sim}NH_2 + 2\,CO + O_2 + 2\,MeOH \xrightarrow[210\ °C,\ 18\ h]{Pd\text{-}Clay,\ bipy,\ NaI} MeO_2CHN{\sim}NHCO_2Me + 2\,H_2O$$

4.2.5. Carbamic Esters by Electrochemical Syntheses

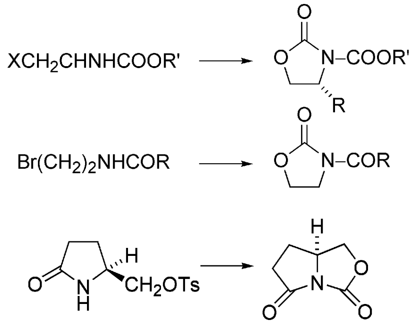
The radical anion of carbon dioxide, $CO_2^{-}\bullet$, reacts with aromatic or aliphatic amines, under mild conditions, affording the corresponding carbamates in high to excellent yields based on the amine.[256] For example, with benzylamine,[256a] $NHBzCO_2Et$, see Scheme 43, is obtained.

Scheme 43

$$NH_2Bz + CO_2 + EtI \xrightarrow{e^-} HI + NHBzCO_2Et$$

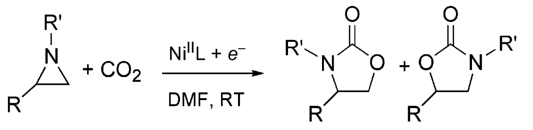
The electrochemically generated carbon dioxide radical anion was found to give reaction with *N*-acyl or *N*-alkoxycarbonyl alkylamines yielding the appropriate carbamates, see Scheme 44.[257,258,259]

Scheme 44

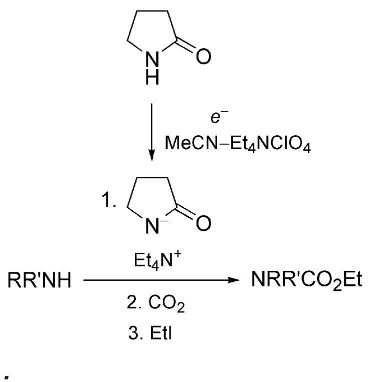


Electrochemistry has been used to prepare cyclic carbamates from aziridines and CO_2 [260] or from the electrogenerated base of 2-pyrrolidone after addition of both carbon dioxide and ethyl iodide,[261] see Schemes 45 and 46.

Scheme 45



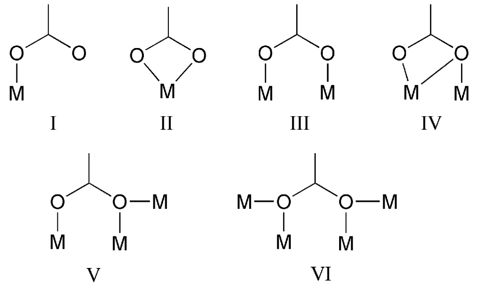
Scheme 46



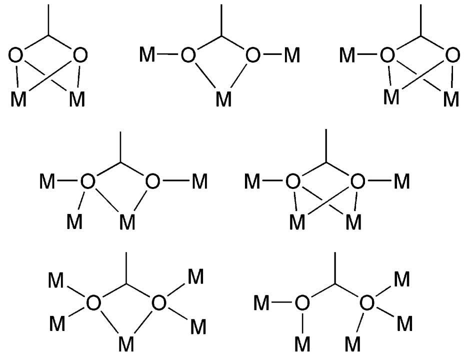
5. Conclusions

The class of carbamato metal complexes entered the chemical literature at a rather late stage, mainly due to the initial difficulties in their preparation. Several new synthetic routes, avoiding the formation of the amido complexes, have been discovered in the last three decades. In this connection, it is to be noted[130,131] that $SiClMe_3$, a primary amine RNH_2, and CO_2 in the presence of $NH(SiMe_3)_2$ had been disclosed at an early stage to produce the trimethylsilylcarbamates $Si(O_2CNHR)Me_3$. Although the details of this reaction have not been investigated, this is presumably the first time a carbamato derivative has been prepared without the intermediacy of the preformed alkylamido precursor.

Scheme 47



Scheme 48



Most of the work reported in this review-article has been carried out on *N*,*N*-dialkylcarbamato metal complexes, as obtained from secondary amines. These complexes are usually more soluble in organic solvents than the unsubstituted or monosubstituted compounds and therefore are more easily purified by conventional methods, and studied by the usual physicochemical techniques. In fact, the metal complexes of this class derived from primary amines tend to be associated both in solution and in the solid state through hydrogen bonding. At variance with metal carboxylates, which are characterized by a relatively low reactivity, carbamato metal complexes are strongly affected by electrophilic reagents, and several examples have been reported in this review-article. On the other hand, carbamato and carboxylato metal complexes are related chemical species from a structural viewpoint.

Scheme 47 shows the structural arrangements which are common to both classes of compounds and which have been found on the basis of X-ray crystallographic work. Scheme 48 shows the structural arrangements which have been found for carboxylato metal derivatives, and have no counterpart, until now, within carbamato derivatives. It is to be expected that in the coming years there will a transfer of some bonding arrangements from Scheme 48 to Scheme 47. The all-monodentate arrangement of the coordinated groups has been found for both the carbamato and carboxylato derivatives of silicon, namely $Si(O_2CNEt_2)_4$ [85] and $Si(O_2CMe)_4$, respectively.[262] As frequently noted in this article, the monodentate type of bonding in some cases is characterized by an IR stretching vibration around 1700 cm^{-1}. Instructive in this connection is the inspection of the IR table in the Appendix, where the *N*,*N*-dialkylcarbamato derivatives are mostly arranged according to the criterion of isostructural groups.

In principle, all chemical elements known to possess stable positive oxidation states can form carbamato complexes. It is important to realize that the most convenient route to these derivatives is the chloride/carbamato exchange, which amounts to reacting a metal chloride or a metal halide in general with an amine in the presence of carbon dioxide. The earlier synthetic methodology from amido derivatives is limited by the stability of the starting materials or by the difficulties connected with their preparation, particularly for transition d and f elements. It is to be noted that the (metal chloride)/amine/CO_2 route was systematically introduced only at a later stage, when carbamato derivatives of nontransitional or early transitional elements had already been prepared by the classical amido route. A fundamental aspect of this chemistry derives from the carbonation of amines. In fact, it has been shown conclusively that the basic equilibria involve the formation of ammonium carbamates and, in some cases, carbamic acids. In this connection, it is interesting to note that carbonation of a few secondary amines to the appropriate carbamic acid is a favorable process in the neat amine or in media of low polarity. On the other hand, preliminary recent results[75,76] show that carbonation of some *primary* amines favors the formation of the corresponding carbamic acid also in solution. Earlier work on the amine/CO_2 system has mostly been carried out in aqueous solution, as extensively outlined in section 2 of the review. On the other hand, the study of the interaction between amines and carbon dioxide in non aqueous systems has not been studied to an extensive extent and much therefore remains to be investigated on this point.

6. List of Acronyms and Abbreviations

18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane
2,2′-Npy_2	2,2′-dipyridylaminato
Ar	substituted aryl
Bu	*n*-butyl
Bz	benzyl
CCDC	Cambridge Crystallographic Data Centre
CN	Coordination number
Cp	η^5-cyclopentadienyl anion
Cp*	η^5-pentamethylcyclopentadienyl anion
CSD	Cambridge Structural Data Base
Cy	cyclohexyl
Cymene	4-*iso*-propyltoluene
DEA	diethanolamine, $HN(CH_2CH_2OH)_2$
DGA	diglycolamine, $HO(CH_2)_2O(CH_2)_2NH_2$
DIPA	di-2-propanolamine, $HN(CH_2CHOHCH_3)_2$
Diphos	bis(dialkylphosphino)ethane
DME	1,2-dimethoxyethane
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
EAN	effective atomic number
en	ethylenediamine
Et	ethyl
FIZ	Fachinformationszentrum, Karlsruhe, Germany
H_3heidi	*N*-(2-hydroxyethyl)-iminodiacetic acid, HO-$(CH_2)_2N(CH_2COOH)_2$
HMPA	hexamethylphosphoramide
^{i}Bu	*iso*-butyl
^{i}Pr	*iso*-propyl
MDEA	methyldiethanolamine
Me	methyl
MEA	monoethanolamine
NBD	norbornadiene
PCTFE	poly(chlorotrifluoroethylene)
Ph	phenyl
pip	piperidyl
Pr	*n*-propyl
R	alkyl group
^{s}Bu	*sec*-butyl
sc-CO_2	supercritical carbon dioxide
^{t}Bu	*tert*-butyl
Tf	triflato anion, $CF_3SO_3^-$
Thex	2,3-dimethyl-2-butyl
THF	tetrahydrofuran
TMEDA	tetramethylethylenediamine

7. Acknowledgments

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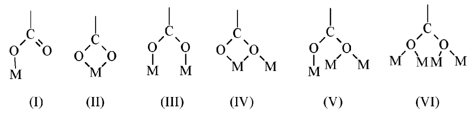
8. Appendix

Table Coordination Modes and IR Spectra of *N,N*-Dialkylcarbamato Metal Complexes (1750−1300 cm^{-1})[a]



compound	coordination mode	IR bands (cm^{-1}) [b]	ref
$W(O_2CNMe_2)_3(NMe_2)_3$	(I)	1636vs, 1580w, 1568w	8c
$Ru(O_2CN^iPr_2)_2(PPh_3)_2(CO)_2$	(I)	1594s, 1570s, 1529w, 1485s, 1434s, 1425s,1370s, 1337s	177
trans-$Pd(O_2CNEt_2)_2(NHEt_2)_2$*	(I)[c]	1590m, 1555s, 1475s, 1455m, 1440w, 1410s, 1375s, 1325m	71b
trans-$Pt(O_2CNEt_2)_2(NHEt_2)_2$*	(I)[c]	1586m, 1563s, 1474s, 1458m, 1436w, 1411s, 1374s, 1326m	105

Table (Continued)

compound	coordination mode	IR bands (cm^{-1}) [b]	ref
trans-$Cu(O_2CNBz_2)_2(NHBz_2)_2$	(I)[c]	1570s, 1496m, 1462s, 1452s, 1408s, 1377m, 1311s	62b
$Au(O_2CNEt_2)(PPh_3)$	(I)	1601s, 1580m, 1569m, 1478m, 1468m, 1457w, 1435s, 1407ms, 1371ms	104a
$Si(O_2CN^iPr_2)_4$	(I)	1705s, 1475sh, 1465sh, 1440sh, 1430ms, 1380mw, 1370m, 1320ms,1300s[d]	85
$Ti(O_2CNMe_2)_2(NMe_2)_2$	(II)	1705w, 1597sh, 1575vs 1496s, 1410vs	8d
$Ti(O_2CN^iPr_2)_4$*	(II)	1550vs, 1500s, 1460m, 1320vs	92
$Zr(O_2CN^iPr_2)_4$*	(II)[e]	1535vs, 1500vs, 1380s, 1360vs	92
$Hf(O_2CN^iPr_2)_4$*	(II)	1540vs, 1510vs, 1480m, 1350s	92
$Sn(O_2CN^iPr_2)_4$*	(II)	1550s, 1515s, 1480ms, 1450ms, 1360s,br	86
$Zr(O_2CNEt_2)_4$*	(II)	1565s, 1505s, 1450s, 1380m, 1325s	88
$Nb(O_2CNEt_2)_4$*	(II)	1558s, 1505s, 1483s, 1441s, 1377s, 1348m	93
$Sn(O_2CNEt_2)_4$*	(II)	1567s, 1523s, 1483s, 1458s, 1440s, 1384s, 1377s, 1349m	86a, 87
$Cr_2(O_2CNEt_2)_4(\mu\text{-}NEt_2)_2$	(II)	1485s, 1378m, 1337m, 1322s (1500−1300 cm^{-1})	96a
$[Ru(O_2CNMe_2)(PMe_2Ph)_4]^+$	(II)	1565vs, 1465s, 1412s	164
$[Ru(O_2CN^iPr_2)(PPh_3)_2(CO)_2]^+$	(II)	1556s,1460s. 1438s. 1380s	181
$Ru((O_2CN^iPr_2)_2(PPh_3)_2$	(II)	1588w, 1574w, 1505vs, 1465s, 1436s, 1378s, 1366m,1352s,1314w	177
$Ag(O_2CNEt_2)(PPh_3)_2$	(II)	1585w,1571w, 1529s, 1478m,1456w, 1434s, 1414ms, 1368m	104a
$Mo_2(O_2CNEt_2)_4$	(III)	1510vs, 1460w, 1435ms, 1380m, 1315s[d]	96b
$Cr_2(O_2CNEt_2)_4(NHEt_2)_2$*	(III)	1578s, 1560sh, 1510sh, 1498s, 1460m, 1433s, 1378m, 1318s[d]	96
$Cu_2(O_2CNEt_2)_4(NHEt_2)_2$*	(III)	1575s, 1550s, 1480s, 1460m, 1420s, 1375m, 1300s	95
$Zn_4(\mu_4{-}O)(O_2CNMe_2)_6$	(III)	1689sh, 1538br,vs, 1461s, 1402s	178b
$Zn_4(\mu_4{-}O)(O_2CNEt_2)_6$	(III)	1570vs, 1510vs, 1460s, 1430s, 1380s, 1320s	178c
$Zn_4(\mu_4{-}O)(O_2CNBu_2)_6$	(III)	1570s, 1504s, 1430s, 1378m, 1326s	*f*, 62b
$Ag(O_2CNMe_2)$	(V)	1554sh, 1520s, 1466sh, 1386s	104
$Mn_6(O_2CNEt_2)_{12}$*	(II), (V), (VI)	1596s, 1532m,1515vs, 1489vs, 1460m, 1430s, 1374s, 1346m, 1317vs	98, 99
$Fe_6(O_2CNEt_2)_{12}$*	(II), (V), (VI)	1593s, 1522s, 1485s, 1460s,1429s, 1375s, 1314s	173b
$Co_6(O_2CNEt_2)_{12}$*	(II), (V), (VI)	1590s, 1520s, 1480s, 1455m, 1420s, 1370m, 1340m, 1310s	83d
$Nd_4(O_3CN^iPr_2)_{12}$*	(II), (III), (V)	1592s, 1529s, 1484s, 1449s, 1383s, 1353s	*g*, 110
$Eu_4(O_3CN^iPr_2)_{12}$*	(II), (III), (V)	1597s, 1533m, 1488s, 1450s, 1385s, 1354s	*h*, 110
$Gd_4(O_3CN^iPr_2)_{12}$*	(II), (III), (V)	1598m, 1537s, 1485s, 1451s, 1385s, 1355s	*h*, 110
$Ho_4(O_3CN^iPr_2)_{12}$*	(II), (III), (V)	1601s, 1538m, 1489s, 1462s, 1450s, 1385s, 1354s	*g*, 110
$Er_4(O_3CN^iPr_2)_{12}$*	(II), (III), (V)	1600s, 1535m, 1490s, 1470s, 1460s, 1450s, 1380m, 1350s	*i*, 109b
$Yb_4(O_3CN^iPr_2)_{12}$*	(II), (III), (V)	1605s, 1535s, 1490s, 1460s, 1370s, 1350s	109a,b
$Fe_8(\mu_4{-}O)_2(O_2CN^iPr_2)_{12}$*	(II), (V), (VI)	1568s, 1551s, 1485s, 1466s, 1449s, 1386s, 1355s	173b
$Co_8(\mu_4{-}O)_2(O_2CN^iPr_2)_{12}$*	(II), (V), (VI)	1623w,1568s, 1520s, 1461s, 1379s, 1354s	175
$Ni_8(\mu_4{-}O)_2(O_2CN^iPr_2)_{12}$*	(II), (V), (VI)	1625w,1566s, 1526s,1455s,1385s,1358s	*l*, 175
$Ni_6Zn_2(\mu_4{-}O)_2(O_2CN^iPr_2)_{12}$*	(II), (V), (VI)	1570s, 1530m, 1480sh, 1460vs, 1380s,1360s	71c, 174

[a] Unless otherwise stated, the molecular structures of the compounds in this Table have been established by X-ray diffractometry. When ligand composition is the same, the asterisk defines an isostructural series. [b] Nujol and/or PCTFE mull, unless otherwise stated. [c] The uncoordinated oxygen is involved in hydrogen-bonding. [d] C_2Cl_4 solution. [e] Solid-state structure unknown. [f] Farnocchi, S. Tesi di laurea in Chimica, Università di Pisa, Pisa, Italy, 2002. [g] Merigo, A. Tesi di Dottorato in Scienze Chimiche, Università di Pisa, Pisa, Italy, 2000. [h] Merigo, A. Tesi di laurea in Chimica, Università di Pisa, Pisa, Italy, 1995. [i] Baisch, U. Diplomarbeit, Universität Tübingen, Tübingen, Germany, 2001. [l] Bradicich, C. Tesi di laurea in Chimica, Università di Pisa, Pisa, Italy, 2001.

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