N,N-Dialkylcarbamato Complexes of the d^{10} Cations of Copper, Silver, and Gold

by **Rocco Alessio**[a]), **Daniela Belli Dell'Amico**[a])*, **Fausto Calderazzo**[a]), **Ulli Englert**[b]), **Alessandro Guarini**[c]), **Luca Labella**[a]), and **Peter Strasser**[a])

[a]) Università di Pisa, Sezione di Chimica Inorganica, Dipartimento di Chimica e Chimica Industriale,
Via Risorgimento, 35, I-56126 Pisa

[b]) Institut für Anorganische Chemie der Rheinisch-Westfälischen Technischen Hochschule Aachen,
Professor-Pirlet-Strasse 1, D-52074 Aachen

[c]) *I.G.D.-EniChem*, Via G. Fauser, 4, I-28100 Novara

The reaction of CuO^{t}Bu with CO$_2$ and ^{i}Pr$_2$NH in the presence of PPh$_3$ gives the dialkylcarbamato complex [Cu(O$_2$CN^{i}Pr$_2$)(PPh$_3$)$_2$] (**1**). The CO$_2$/R$_2$NH system (R = Me, Et) in an appropriate organic medium reacts with Ag$_2$O giving the corresponding *N,N*-dialkylcarbamato complexes of analytical formula [Ag(O$_2$CNR$_2$)] (R = Me, **2**; R = Et, **3**). The methyl derivative **2** was characterized by X-ray diffraction methods. Crystal data of **2**: for [Ag$_2$(O$_2$CNMe$_2$)$_2$], C$_6$H$_{12}$Ag$_2$N$_2$O$_4$, mol. wt. 391.9; monoclinic, space group $P2_1/c$, a = 12.08(1), b = 3.797(2), c = 11.316(7) Å, β = 113.37(6)°, V = 476.3 Å^3, Z = 2, D_c = 2.732 g cm^{-3}; μ(MoK_α) = 40.64 cm^{-1}, F(000) = 376.0; R = 0.059, R_w = 0.067; g.o.f. 1.27. The structure consists of dinuclear [Ag$_2$(O$_2$CNMe$_2$)$_2$] units with slightly distorted linearly two-coordinated Ag-atoms containing bridging carbamato groups to form a substantially planar eight-membered ring with an intra-annular Ag–Ag distance of 2.837(2) Å; the dinuclear units are further joined by Ag–O bonds to form an infinite array. Compound **3**, which is presumably dinuclear, as suggested by cryoscopic measurements in benzene, undergoes a structural fission with PPh$_3$, giving the mononuclear triphenylphosphine derivative [Ag(O$_2$CNEt$_2$)(PPh$_3$)$_2$] (**4**). The amine-catalyzed conversion of Ag$_2$O into Ag$_2$CO$_3$, in the presence of the ^{i}Pr$_2$NH/CO$_2$ system, is also reported. Cl-Exchange from [AuCl(PPh$_3$)] with [Ag(O$_2$CNEt$_2$)] (**3**) gives the first *N,N*-dialkylcarbamato complex of gold, namely [Au(O$_2$CNEt$_2$)(PPh$_3$)] (**5**), which crystallizes in the monoclinic system: C$_{23}$H$_{25}$AuNO$_2$P · 0.5 C$_7$H$_{16}$, mol. wt. 625.5, space group $P2_1/c$; a = 13.212(5), b = 12.25(1), c = 16.795(6) Å, β = 109.09(2)°, V = 2568(2) Å^3, Z = 4, D_c = 1.618 g cm^{-3}; μ(AgK_α) = 31.40 cm^{-1}, F(000) = 1236.0; R = 0.058; R_w = 0.064; g.o.f. 2.121. The compound contains two-coordinated Au-atom, namely to the P-atom and to the O-atom of the monodentate carbamato group, the P–Au–O bond angle being 174.7(3)°. The reaction with MeI showed these compounds to react predominantly at the carbamato O-atom giving the corresponding urethanes R$_2$NCO$_2$Me. Evidence was gathered for the transient coordination of CO to Ag in **3**.

---

1. Introduction. – Among O-ligated complexes of metal cations of Group 11, of electronic configuration d^{10}, *N,N*-dialkylcarbamato complexes are still in their infancy. Although *N,N*-dialkylcarbamato complexes of Cu^{II} [1] are well-established and easily prepared from copper(II) chloride with R$_2$NH/CO$_2$, the corresponding Cu^I derivatives are rather elusive and have been only briefly mentioned in the literature [2] as intermediates in the synthesis of alkylurethanes. O-Ligated Ag^I complexes are of considerable interest for both organic [3] and inorganic [4] syntheses and for their use in catalysis (for ethylene epoxidation, see [5]). In this connection, it is of interest that silver oxide Ag$_2$O is exceptional among metal oxides in having a relatively high ΔG_f° of -11.2 kJ mol^{-1} [6]. Recently, an O-ligated Ag^I precursor has allowed the isolation of the first crystallographically established carbonyl derivative of this cation [7], namely [Ag(CO)(OTeF$_5$)$_2$-B(OTeF$_5$)$_2$]. Even less frequent are Au^I complexes with O-donor ligands [8].

Our interest in *N*,*N*-dialkylcarbamato complexes of transition- and main-group [9] elements urged us to synthesize the still unknown derivatives of Group 11 metal cations containing this ligand. This paper reports the first homoleptic¹) *N*,*N*-dialkylcarbamato complexes of Ag^I and Au^I and compares their properties with those of the corresponding Cu^I derivatives. A preliminary report on part of this work has appeared [10].

2. Results and Discussion. – 2.1. *Product Characterization.* Copper(I) *tert*-butoxide²) [11] is the preferred starting material³) for the preparation of the corresponding *N*,*N*-dialkylcarbamato derivatives of formula $[Cu(O_2CNR_2)]$. Compounds of the same formula containing an additional ligand L (R = Et, Bu, ^tBu; L = ^tBuNC, PBu_3, $P(OMe)_3$) were reported years ago by *Tsuda* and coworkers [2]. We have confirmed their preliminary data and isolated the isopropyl derivative (see *Eqn. 1*) and its PPh_3 adduct **1** (see *Eqn. 2*) which are new compounds.

$$CuO^tBu + {}^iPr_2NH + CO_2 \rightarrow {}^tBuOH + [Cu(O_2CN^iPr_2)] \quad (1)$$

$$[Cu(O_2CN^iPr_2)] + 2\,PPh_3 \rightarrow \underset{\mathbf{1}}{[Cu(O_2CN^iPr_2)(PPh_3)_2]} \quad (2)$$

It is possible that the PPh_3 adducts of the *N*,*N*-dialkylcarbamato complexes have a molecular structure similar to that reported for $[Cu(O_2CMe)(PPh_3)_2]$ [12] and $[Cu(O_2CCF_3)(PPh_3)_2]$ [13]. In these compounds, the Cu-atom has a pseudo-tetrahedral geometry with a bidentate carboxylato ligand. The IR spectra of our Cu^I compounds with intense bands below 1550 cm^{-1} support the presence of bidentate carbamato groups.

In a preliminary survey of preparative methods leading to *N*,*N*-dialkylcarbamato derivatives of Ag^I, silver halides, $AgBF_4$, and $[Ag(MeCN)_4]BF_4$ were reacted individually, without success, with the R_2NH/CO_2 system. Attempts were also made to prepare silver *tert*-butoxide in solution and use it *in situ* for the preparation of the required products, by analogy with the earlier findings with Cu^I. On the other hand, no reaction occurred between AgCl and KO^tBu. We also verified that the acetonitrile complex $[Ag(MeCN)_4]BF_4$, as obtained [14a] from Ag-metal and $NOBF_4$ in MeCN, reacted promptly with KO^tBu yielding a black precipitate of Ag. This agrees with the literature data [14b] concerning the low stability of silver alkoxides.

The most appropriate starting material for the preparation of the *N*,*N*-dialkylcarbamato complexes of Ag^I is the oxide Ag_2O: *N*,*N*-dialkylcarbamic acid (see *Eqn. 3*) or the dialkylammonium cation (see *Eqn. 4*) are believed to be the electrophilic reagents interacting with the oxide. The formation of the ethyl and methyl derivatives is represented by the stoichiometry of *Eqn. 5*.

$$R_2NH + CO_2 \rightleftharpoons R_2NC(O)OH \quad (3)$$

$$2\,R_2NH + CO_2 \rightleftharpoons (R_2NH_2)(O_2CNR_2) \quad (4)$$

---

[1] Throughout this paper, the term homoleptic denotes a compound formed by anionic ligands of the same type.

[2] Tetrahydrofuran solutions of CuO^tBu, as prepared from cuprous chloride and KO^tBu [11a], are indefinitely stable at room temperature under exclusion of air and moisture [11b].

[3] No reaction was found to occur between cuprous chloride and the R_2NH/CO_2 system.

$$Ag_2O + 2\,CO_2 + 2\,R_2NH \rightarrow 2\,[Ag(O_2CNR_2)] + H_2O \qquad (5)$$

$$\mathbf{2}\ R = Me$$

$$\mathbf{3}\ R = Et$$

The preparation of the methyl derivative **2** is best carried out in dry MeCN, the H_2O produced in the reaction being subtracted by solvation. For the ethyl derivative **3**, which is more susceptible to hydrolysis than **2**, heptane is preferred as a reaction medium, and H_2O is subtracted by molecular sieves. In both cases a possible competitive reaction is the formation of the dialkylammonium hydrogencarbonate, according to *Eqn. 6*.

$$(R_2NH_2)(O_2CNR_2) + H_2O \rightarrow R_2NH + (R_2NH_2)(O_2COH) \qquad (6)$$

In an earlier preliminary communication [10], the ethyl derivative **3** was proposed to be dinuclear on the basis of cryoscopic measurements in benzene solution, and by analogy to the dinuclear structure reported for $[Ag_2(O_2CCF_3)_2]$ [15]. IR Bands just below 1550 cm^{-1}, normally associated with bridging carbamato groups, further suggest a dinuclear structure. This suggestion is now substantiated by the single-crystal X-ray diffraction study of the methyl derivative **2**.

Compound **2** forms an infinite chain of $[Ag_2(O_2CNMe_2)_2]$ units containing eight-membered Ag–O–C–O–Ag–O–C–O rings (see *Fig. 1*) held together by Ag–O bonds at interannular Ag–O distances of 2.600(8) Å, with intra-annular Ag–O bond lengths of 2.156(9) and 2.219(8) Å (av. 2.19(1) Å) (see *Table 1*).

Relevant to the present findings is the molecular structure of the glutarato complex of silver [16] showing similar intra-annular Ag–O distances of 2.20(1) Å (av.). Also the succinato derivative of silver [17] is based on an infinite array of O-coordinated Ag-atoms

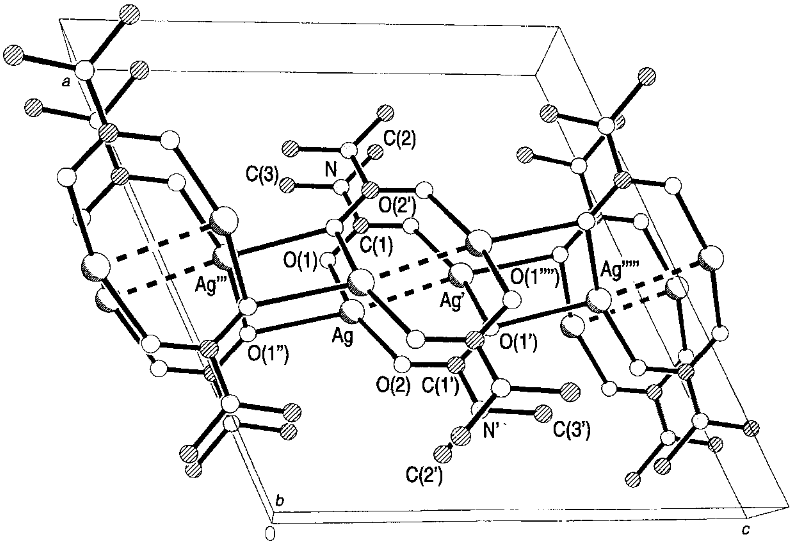


Fig. 1. *Crystal packing of* $[Ag(O_2CNMe_2)]$ (**2**), *with the numbering scheme used.* ' = 1 − *x*, −*y*, 1 − *z*; '' = 1 − *x*, 1/2 + *y*, 1/2 − *z*; ''' = 1 − *x*, *y* − 1/2, 1/2 − *z*; '''' = *x*, −1/2 − *y*, *z* + 1/2; ''''' = *x*, 1/2 − *y*, *z* + 1/2.

Table 1. *Selected Bond and Contact Distances* [Å] *and Angles* [deg] *for Compound* **2**[a])

Ag–O(2)	2.156(9)	Ag–O(1)	2.219(8)
Ag–O(1'')	2.600(8)	Ag ··· Ag'	2.837(2)
O(1)–Ag–O(2)	161.6(3)	Ag'''–O(1)–C(1)	141.8(7)
O(1'')–Ag–O(2)	104.3(3)	Ag'''–O(1)–Ag	99.0(2)
Ag'–Ag–O(2)	78.4(2)	Ag–O(2)–C(1')	130.6(8)
Ag'–O(1)–C(1)	117.8(8)		

[a]) Numbers in parentheses are estimated standard deviations in the last significant figure. The superscripts have the same meanings as in *Fig. 1*.

in a slightly distorted linear coordination, although the structural motif in this case is different from ours.

The crystal and molecular structure of $[\mathrm{Ag(O_2CNEt_2)(PPh_3)_2}]$ (**4**) [10] consists of mononuclear $[\mathrm{Ag(O_2CNEt_2)(PPh_3)_2}]$ units with a bidentate carbamato group around the Ag-atom in a distorted tetrahedral geometry. The details of this structure do not need to be repeated here, except for noting that similar structural data for the formato complex $[\mathrm{Ag(O_2CH)(PPh_3)_2}]$ have in the meanwhile appeared in the literature [18]. The silver complexes are both monoclinic and crystallize in the same space group *C2/c*; the bidentate carbamato ligand and the formato group are at Ag–O distances of 2.429(7) and 2.425(3) Å, respectively, *i.e.*, at the same distance, within experimental error.

The triphenylphosphine adduct **5** of *N,N*-diethylcarbamatogold(I) was obtained by the reaction of $[\mathrm{AuCl(PPh_3)}]$ with $[\mathrm{Ag(O_2CNEt_2)}]$ in toluene (*Eqn. 7*). The driving force of this reaction is evidently the formation of AgCl.

$$[\mathrm{AuCl(PPh_3)}] + [\mathrm{Ag(O_2CNEt_2)}] \rightarrow \mathrm{AgCl} + \underset{\mathbf{5}}{[\mathrm{Au(O_2CNEt_2)(PPh_3)}]} \qquad (7)$$

Although this seems unlikely, it is possible that a carbamato complex with a $\mathrm{PPh_3/Au}$ ratio > 1 may exist. In this connection, it should be noted that $\mathrm{Au^I}$ forms three adducts with triphenylphosphine, corresponding to linear two-coordination [19] in $[\mathrm{AuCl(PPh_3)}]$ (P–Au–Cl, 179.63(8)°), trigonal planar coordination in $[\mathrm{AuCl(PPh_3)_2}] \cdot 0.5\ \mathrm{C_6H_6}$ [20] (P–Au–P, 132.1(1)°), and distorted tetrahedral coordination in $[\mathrm{AuCl(PPh_3)_3}]$ [21].

To the best of our knowledge, compound **5** is the first *N,N*-dialkylcarbamato complex of $\mathrm{Au^I}$ to be reported in the literature. Also, carboxylato complexes of $\mathrm{Au^I}$ are rare, and only a few have been investigated crystallographically, namely the acetate [22], the benzoate [23], the isobutyrate and lactate [24], and the hippurate [25], all of them as the 1:1 adducts with triphenylphosphine. It was, therefore, worthwhile to perform an X-ray diffraction experiment to determine the molecular and crystal structure of **5**, and to compare the data with those reported in the literature for the carboxylato complexes. *Fig. 2* shows the molecular structure of compound **5**: the Au-atom is almost linearly coordinated to the P-atom and to the O-atom of the monodentate carbamato group, the P–Au–O(1) angle being 174.7(3)° (see *Table 2*). The monodentate nature of the carbamato group is in agreement with the IR spectroscopic data, showing a strong band at a relatively high wavenumber value (1601 $\mathrm{cm^{-1}}$), associated with a stretching vibration of the carbamato ligand. Although the Et groups of the carbamato ligand and the atoms

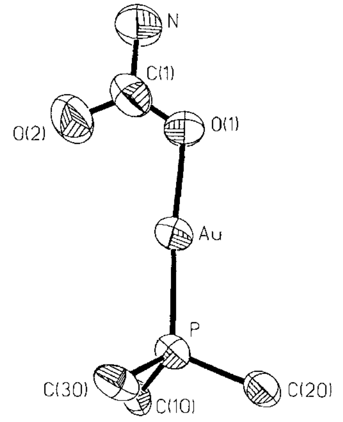


Fig. 2. *Partial view of* $[Au(O_2CNEt_2)(PPh_3)]$ (**5**) · *0.5* C_7H_{16} *with the atom-numbering scheme.* Ellipsoidal boundaries at the 50% probability level.

Table 2. *Selected Bond Distances* [Å] *and Angles* [deg] *for Compound* **5** · *0.5* C_7H_{16}[a])

Au–P	2.212(2)	Au–O(1)	2.047(7)
P–Au–O(1)	174.7(3)	P–Au–C(1)	162.2(2)
O(1)–Au–C(1)	22.5(2)	Au–P–C(10)	113.2(3)
Au–P–C(20)	112.3(2)	Au–P–C(30)	112.8(4)
Au–O(1)–C(1)	117.9(7)		

[a]) Numbers in parentheses are estimated standard deviations in the last significant figure.

of the clathrated heptane exhibit anisotropic displacement parameters indicating considerable disorder, it was possible to obtain reliable bonding parameters for the atoms of interest in this context. It is, therefore, possible to compare the bond distances of compound **5** with those of the known carboxylato complexes. The Au–O distance of 2.047(7) Å in **5** compares quite well with the Au–O distances in the corresponding triphenylphosphine adducts of the carboxylato complexes $[Au(O_2CR)(PPh_3)]$: 2.063(6) Å in the acetate [22], 2.033(6) Å in the benzoate [23], 2.047(6) and 2.038(6) Å in the isobutyrate and the lactate [24], respectively, and 2.077(5) Å in the hippurate [25].

Our new metrical data on the carbamato complexes of Ag^I and Au^I can contribute to the problem concerning the ionic radius of univalent cations of Group 11, recently raised in the literature [26a–c]. *Table 3* compares the metrical parameters of some relevant carboxylato and carbamato complexes of Cu^I, Ag^I, and Au^I, all of them containing PPh_3 as additional ligand. The data for the chloro-PPh_3 complexes [19–21] indicate that an increase of *ca.* 10% in the bond distance between the metal and the anionic ligand is to be expected by increasing the coordination number (CN) by one unit between 2 and 4. An increase of the ionic radius upon increasing the coordination number is well-established in the literature [27]. If one uses this criterion, it can be seen that the metal–O distance within the carbamato complexes follows the trend: $Cu < Ag \approx Au$. If the metal–P distances are considered in the $[AuCl(PPh_3)_n]$ series, a reduction by *ca.* 5% of the Au–P distance is expected on decreasing the coordination number by one unit. Here

Table 3. *Structural Parameters of Copper(I), Silver(I), and Gold(I) Complexes*

	Space group	CN	M-L [Å][a])	M-P [Å]	Ref.
$[Cu(O_2CMe)(PPh_3)_2]$	monoclinic, $P2_1/a$	4	2.210(3)	2.236(3)[b])	[12]
$[Cu(O_2CCH_2F)(PPh_3)_2]$	monoclinic, $P2_1/a$	4	2.225(3)	2.227)(3)[b])	[13]
$[Cu(O_2CH)(PPh_3)_2]$	monoclinic, $C2/c$	4	2.226(3)	2.247(1)[b])	[26d]
$[Ag(O_2CH)(PPh_3)_2]$	monoclinic, $C2/c$	4	2.425(3)	2.426(1)[b])	[18]
$[Ag(O_2CNEt_2)(PPh_3)_2]$	monoclinic, $C2/c$	4	2.429(7)	2.426(2)[b])	[10]
$[AuCl(PPh_3)]$	orthorh., $P2_12_12_1$	2	2.279(3)	2.235(1)	[19]
$[AuCl(PPh_3)_2]$	triclinic, $P1$	3	2.500(4)	2.231(4)[b])	[20]
$[AuCl(PPh_3)_3]$	monoclinic, $P2_1/n$	4	2.710(2)	2.413(2)[b])	[21]
$[Au(O_2CNEt_2)(PPh_3)]$	monoclinic, $P2_1/c$	2	2.047(7)	2.212(2)	this work
$[Au(O_2CPh)(PPh_3)]$	monoclinic, $P2_1/n$	2	2.033(6)	2.213(3)	[23]
$[Au(O_2CMe)(PPh_3)]$	orthorh., $P2_12_12_1$	2	2.063(6)	2.207(3)	[22]

[a]) L = Anionic ligand. [b]) Average.

again, the comparison of the known metrical data suggests that the M–PPh_3 distance follows the same trend as above, namely $Cu < Ag \approx Au$. *Schmidbaur* and coworkers [26a] have recently pointed out that Au^I is smaller than Ag^I by *ca.* 0.08 Å on the basis of the M–P metrical data in the isostructural ionic compounds $[M(Pmes_3)_2]BF_4$ (mes = 1,3,5-$C_6H_2Me_3$, M = Ag, Au). Although a contraction of Au^I could be expected on the basis of relativistic effects [26b,c], this does not appear to be substantiated by the data on the O-containing anionic donor ligands.

2.2. *Reactivity.* The reaction of methyl iodide with the *N*,*N*-dialkylcarbamato complexes reported in this paper gave *N*,*N*-dialkylmethylurethane in all cases (*Eqn. 8*).

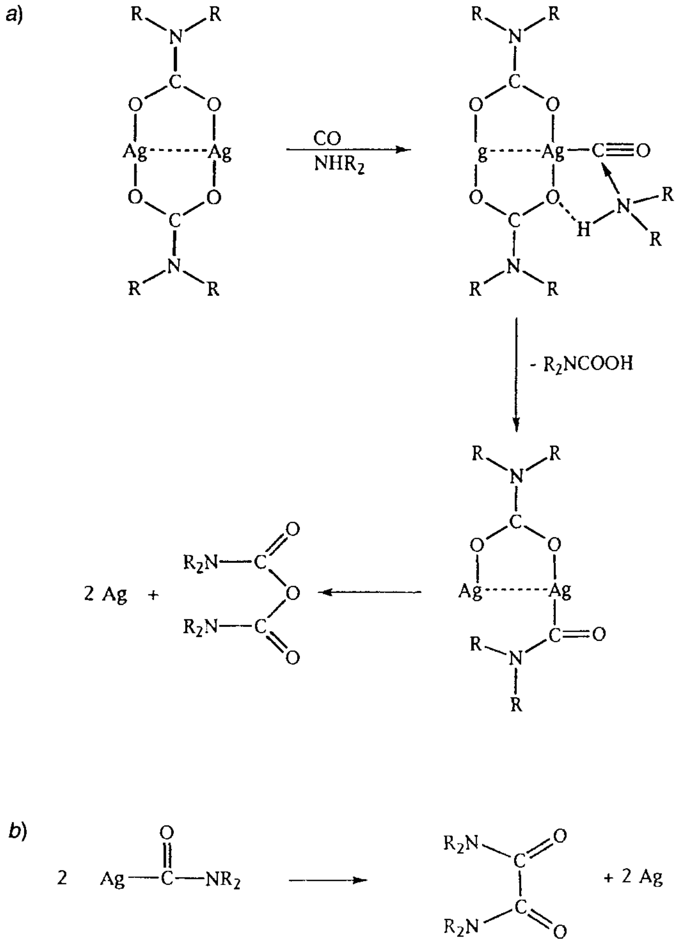
$$[M(O_2CNR_2)L_x] + MeI \rightarrow [MIL_x] + R_2NCO_2Me \qquad (8)$$

$$\begin{aligned} &L = PPh_3 \\ &M = Ag,\ R = Et;\ x = 0,2 \\ &M = Au,\ R = Et;\ x = 1 \end{aligned}$$

Tsuda and coworkers [2] have reported the formation of urethanes from *N*-alklyl- or *N*,*N*-dialkylcarbamato complexes of Cu^I and RI; the presence of an additional ligand was claimed to be necessary for the reaction to proceed. We found that in the case of $[Cu(O_2CN^iPr_2)]$, urethane formation took place in the absence of any ligand. Urethanes arise from the electrophilic attack at the carbamato O-atom, with retention of the carbon dioxide moiety in the organic fragment. The more frequently observed case is electrophilic attack on the carbamato N-atom, with evolution of CO_2 (M = Co^{II} [28], Cu^{II} [29], Ni^{II} [30], Pd^{II} [29], Si^{IV} [29]). With *N*,*N*-dialkylcarbamato complexes of monovalent cations, urethanes are produced by reaction of an alkyl halide with $[M][O_2CNR_2]$, with M being Na^+ or K^+ complexed by a cryptand or a crown ether [31], or with the $R'R''NH/CO_2$ system (R' = alkyl, R'' = H, alkyl) [32]. In the latter case, yields and selectivity can be improved in the presence of *a*) a relatively strong, sterically hindered organic base [33] or *b*) a crown ether [34]. To a first approximation, charge density on the cation appears to be a relevant factor in determining the nucleophilic character of the carbamato O-atoms and, therefore, their reactivity with alkyl halides.

The reactivity of [Cu(O$_2$CN^{i}Pr$_2$)], [Ag(O$_2$CNEt$_2$)] (**3**), and [Ag(O$_2$CNEt$_2$)(PPh$_3$)$_2$] (**4**) towards carbon monoxide was also studied. The Cu^I complex reversibly absorbs CO over short times giving a carbonyl derivative of unknown nuclearity showing a band at 2092 cm^{-1} in dimethoxyethane and at 2080 cm^{-1} in THF. These values are typical of carbonyl copper(I) complexes; *e.g.*, [Cu(O$_2$CCF$_3$)(CO)]$_n$ [35], [Cu(O^{t}Bu)(CO)]$_4$ [36], and [CuCl(CO)] [37] show $\tilde{\nu}$(CO) at 2120 (solid state), 2063 (toluene), and 2120 (solid state) cm^{-1}, respectively. The dependence of the CO uptake on temperature was studied by measuring the CO absorption in the range 269–298 K. When the system was allowed to react with CO over some days at room temperature, decomposition occurred, and metallic Cu was formed.

Scheme



To detect possible carbonyl adducts of Ag^I in solution, the carbamatosilver complex [Ag(O$_2$CNEt$_2$)] (**3**) was reacted with CO in MeCN. Although no direct spectroscopic evidence of carbonyl complexes in solution was obtained, formation of a silver mirror was observed, accompanied by the production of organic carbonyl-containing products. When deliberately added amine (Et_2NH) was present in solution, the oxamide $(CONEt_2)_2$ was formed; otherwise, the main product was the carbamic anhydride $(Et_2NCO)_2O$ together with minor quantities of the corresponding oxamide. The formation of these products is presumably due to a primary interaction of CO with the (*N*,*N*-diethylcarbamato)silver complex, producing a transient carbonyl complex, followed by attack of Et_2NH, deliberately added or deriving from fortuitous hydrolysis of the starting silver complex, to the C-atom of the coordinated CO (see *Scheme a*). According to this hypothesis, the carbamoyl silver derivative **A** (R = Et) so obtained reductively eliminates metallic silver and carbamic anhydride. When the amine concentration is higher, silver reduction can proceed with oxamide formation (*Scheme b*). The two paths correspond to a bi-electronic and a mono-electronic oxidation of CO, respectively. The latter one has to be compared with the production of oxamides by secondary amines and CO assisted by silver acetate, as reported by *Saegusa et al.* [3a].

The coordinatively saturated $[Ag(O_2CNEt_2)(PPh_3)_2]$ (**4**) neither reacts with CO nor gives the above mentioned organic products: this is a further evidence that pre-coordination of CO is an essential step in the observed reactions.

We gratefully acknowledge the support by the *Consiglio Nazionale delle Ricerche* (*C.N.R.*, Roma), by the *Ministero dell'Università e della Ricerca Scientifica e Tecnologica* (*M.U.R.S.T.*), and by an exchange visiting programme between the Technische Hochschule of Aachen and the University of Pisa (Vigoni Exchange Programme) which made the collaboration possible. We also thank *Chimet S.p.A.*, 52041 Badia al Pino, Arezzo, Italy, for a loan of gold.

Experimental Part

1. *General.* All reactions and manipulations were carried out under CO_2 or an inert gas (N_2 or Ar). Solvents and reagents used for the preparation of all the *N*,*N*-dialkylcarbamato complexes were carefully dried before use. The triphenylphosphine derivative $[AuCl(PPh_3)]$ was prepared from [AuCl(CO)] and the stoichiometric amount of PPh_3 in CH_2Cl_2. IR Spectra: *Perkin-Elmer-FT-1725* instrument; PCTFE = polychlorotrifluoroethylene; in cm^{-1}. NMR Spectra: *Varian Gemini 200 BB* spectrometer; δ in ppm rel. to $SiMe_4$, J in Hz. GC/MS: *Varian-3400* gas chromatograph equipped with a *SPB-5* capillary column (30 m × 0.22 mm) and coupled to a *Finnigan-TSQ-700* mass spectrometer operated in the electron-impact mode (70 eV).

2. *Syntheses (*N,N*-Diisopropylcarbamato)copper(I)* ($[Cu(O_2CN^iPr_2)]$). This compound was prepared according to the procedure outlined by *Tsuda et al.* for compounds of this class [2]. As no exper. details are available, the synthesis is described in detail. A soln. of KO^tBu (10.66 g, 95.0 mmol) in THF (200 ml) was added dropwise to a suspension of CuCl (9.68 g, 97.8 mmol) in the same solvent (100 ml). The soln. became gradually yellow. After stirring for 1 d at r.t., the suspension was filtered and the solid washed (3 × 20 ml). The filtrate was treated with $^iPr_2NH$ (50 ml, 354 mmol) and with CO_2. After stirring for 1 d, no further absorption of CO_2 was observed; the yellow soln. was evaporated, and the resulting solid was dried *in vacuo* at 50° to remove ^tBuOH and the excess of amine. To the solid residue, heptane (400 ml) was added and stirring continued for 1 d. Then the suspension was filtered and the colorless solid dried *in vacuo* (11.71 g, 59%). $[Cu(O_2CN^iPr_2)]$ is slightly soluble in the common org. solvents. IR (nujol): 1654*m*, 1601*m*, 1559*m*, 1509*s*, 1469*s*, 1384*s*, 1354*s*, 1315 (sh), 1262*m*, 1215*m*, 1206*m*, 1161*s*, 1135*m*, 1122*m*, 1092*w*, 1066*m*, 1031*m*, 923*w*, 899*w*, 870*w*, 840*w*, 800*m*, 790*m*, 777*m*, 723*w*, 666*w*, 652*w*, 635*m*, 609*w*, 563*w*, 507*m*. Anal. calc. for $C_7H_{14}CuNO_2$ (207.74): CO_2 21.2, Cu 30.6; found: CO_2 20.4, Cu 29.6.

*(*N,N*-Diisopropylcarbamato)bis(triphenylphosphine)copper(I)* ($[Cu(O_2CN^iPr_2)(PPh_3)_2]$; **1**). Triphenylphosphine (2.85 g, 10.9 mmol) was added to 100 ml of toluene together with $[Cu(O_2CN^iPr_2)]$ (1.09 g, 5.3 mmol). The colorless soln. was stirred for 24 h and then concentrated to *ca.* 30 ml under vacuum. Heptane (50 ml) was added, and the resulting colorless precipitate was collected by filtration and dried *in vacuo*: 0.9 g (23%) of **1**. IR (PCTFE mull): 1602*m*, 1585*w*, 1528*m*, 1494*w*, 1477*m*, 1452*m*, 1434*s*, 1371*w*, 1360*w*, 1343*m*. ^1H-NMR (C_6D_6, 25°): 7.6 (*m*); 7.0 (*m*); 4.3 (*sept.*); 1.45 (*d*). ^{31}P-NMR (C_6D_6, 25°, H_3PO_4): −4.00. Anal. calc. for $C_{43}H_{44}CuNO_2P_2$ (732.32): C 70.5, H 6.1, N 1.9; found: C 69.5, H 5.8, N 1.8.

*Bis(*N,N*-dimethylcarbamato)disilver(I)* ([$Ag_2(O_2CNMe_2)_2$]; **2**). Into MeCN (200 ml) cooled to *ca.* −60° under CO_2 (500-ml flask) Me_2NH (20.4 g, 452 mmol) was introduced through a syphon. When no more gas absorption was observed, Ag_2O (10.30 g, 44.5 mmol) was added at r.t. under magnetic stirring; Ag_2O rapidly disappeared, and the mixture was stirred for *ca.* 3 h at r.t. The light brown precipitate was filtered off and dried *in vacuo* affording 14.23 g (82%) of **2**. Complex **2** is not decomposed upon exposure to air over short periods of time. By cooling in the refrigerator, the mother liquor gave a further crop of the crystalline **2** (0.51 g, total yield 85%). IR (nujol and PCTFE mulls): 1554 (sh), 1520*s*, 1466 (sh), 1386*s* (carbamato group). Anal. calc. for $C_3H_6AgNO_2$ (195.96): C 18.4, H 3.1, N 7.1, CO_2 22.5; found: C 17.6, H 3.1, N 6.8, CO_2 22.1.

*(*N,N*-Diethylcarbamato)silver(I)* ([$Ag(O_2CNEt_2)$]; **3**). To a soln. of $(Et_2NH_2)(O_2CNEt_2)$ in heptane (400 ml) obtained by reacting Et_2NH (22.6 ml, 16.0 g, 219 mmol) with CO_2 at 1 atm, 4-Å molecular sieves (10 g) were added and, in small portions, Ag_2O (10.13 g, 43.7 mmol; Et_2NH/Ag molar ratio 2.51). After 12 h stirring under CO_2, the suspension was filtered and the resulting soln. evaporated. The solid was dissolved in 75 ml of heptane under N_2 and the soln. thus obtained cooled down to *ca.* −80°. The colorless precipitate was dried *in vacuo*: The compound was found to be approximately dinuclear by cryoscopy in benzene (found: mol. wt. 401). IR (nujol and PCTFE mulls): 2965*m–s*, 2924*m–s*, 2866*m*, 1506 (sh), 1482*s*, 1453*m*, 1428*s*, 1372*m*. ^1H-NMR (C_6D_6, 25°): 3.48 (*q*); 1.22 (*t*). ^{13}C-NMR (C_6D_6, 25°): 164.0 (O_2CN); 43.2 (CH_2); 14.7 (Me). Anal. calc. for $C_5H_{10}AgNO_2$ (224): Ag 48.2, CO_2 19.6; found: Ag 48.2, CO_2 19.1.

Treatment of Ag_2O with Diisopropylamine. Conversion to Ag_2CO_3. To a soln. obtained from $^iPr_2NH$ (9.1 ml, 6.60 g, 64.5 mmol) and CO_2 at 1 atm in heptane (100 ml), Ag_2O (3.00 g, 6.52 mmol) was added corresponding to a $^iPr_2NH/Ag$ molar ratio of 2.5. By stirring at r.t., the black Ag_2O gradually disappeared and was substituted by a colorless solid, which, after 48 h stirring, was filtered off and dried under reduced pressure; 3.5 g (*ca.* quant.) Ag_2CO_3. IR: mainly 1418*s*, 1339*s*; identical to the IR of an authentic sample prepared from $AgNO_3$ and Na_2CO_3 in H_2O.

No significant conversion of Ag_2O into Ag_2CO_3 was observed under the following conditions: *a*) Ag_2O suspended in heptane under CO_2 at 1 atm; *b*) Ag_2O suspended in MeCN under CO_2 at 1 atm; *c*) Ag_2O suspended in an aq. alkaline soln. of NaOH (pH *ca.* 11) under CO_2; *d*) Ag_2O suspended in H_2O in the presence of Et_3N under CO_2 at 1 atm. On the other hand, a fast conversion of Ag_2O into Ag_2CO_3 was observed when Ag_2O was suspended in H_2O in the presence of an equimolar quantity of Et_2NH under CO_2 at 1 atm.

*(*N,N*-Diethylcarbamato)bis(triphenylphosphine)silver(I)* ([$Ag(O_2CNEt_2)(PPh_3)_2$]; **4**). Complex **3** (1.26 g, 5.6 mmol) was dissolved in toluene (100 ml) and treated with PPh_3 (3.02 g, 11.5 mmol) under stirring and exclusion of light. The voluminous precipitate was collected by filtration and dried *in vacuo*. IR (nujol, PCTFE mulls): 1585*w*, 1571*w*, 1529*s*, 1478*m*, 1456*w*, 1434*s*, 1414*m–s*, 1368*m*. ^1H-NMR (C_6D_6, 25°): 7.55 (*m*); 6.95 (*m*); 3.75 (*q*); 1.35 (*t*). ^{31}P-NMR (toluene/C_6D_6, H_3PO_4): 7.2 (br., temp.-dependent multiplicity, *i.e. s* at + 30° and −20°, br. *d* at −80°, $J(P, Ag) = 447$[4])). Anal. calc. for $C_{41}H_{40}AgNO_2P_2$ (748.59): C 65.8, H 5.4, N 1.9, CO_2 5.9; found: C 66.0, H 5.8, N 1.7, CO_2 5.7.

*(*N,N*-Diethylcarbamato)triphenylphosphinegold(I)* ([$Au(O_2CNEt_2)PPh_3$]; **5**). The complex was prepared by a metathetical reaction between [$Ag(O_2CNEt_2)$] and [$AuCl(PPh_3)$]: The Au^I complex (2.05 g, 4.1 mmol) was added to a soln. of [$Ag(O_2CNEt_2)$] (0.91 g, 4.1 mmol) in toluene (100 ml), and the mixture was stirred at r.t. for several days. The precipitate of AgCl thus obtained was filtered off and the soln. concentrated to 30 ml. By addition of heptane and cooling to *ca.* −30°, **5** was obtained as a deep brown precipitate. The compound was recovered by filtration, and dried *in vacuo*: 1.86 g (78%). IR (nujol, PCTFE mulls): 1601*s*, 1580*m*, 1569*m*, 1478*m*, 1468*m*, 1457*w*, 1435*s*, 1407*m–s*, 1371*m–s*. ^1H-NMR (C_6D_6, 25°): 7.2 (*m*); 6.9 (*m*); 3.6 (*q*); 1.3 (*t*). ^{31}P-NMR (C_6D_6, 25°, H_3PO_4): 29.4. Anal. calc. for $C_{23}H_{25}AuNO_2P$ (606.37): C 48.0, H 4.3, CO_2 7.6; found: C 49.3, H 4.4, CO_2 6.3.

3. *X-Ray Crystallography of Compounds* **2** *and* **5**. Compound **2** was recrystallized from MeCN by cooling a sat. soln. to *ca.* −18°. Compound **5** was recrystallized from a toluene soln. by slow addition of heptane, thus obtaining crystals having the composition [$Au(O_2CNEt_2)PPh_3$] · 0.5 C_7H_{16}. The X-ray data were collected with an *Enraf-Nonius-CAD4* diffractometer equipped with a graphite monochromator. An empirical absorption correction on the basis of azimuthal scans [39] was applied before averaging over symmetry-equivalent reflections. Crystal data, parameters of data collection, and convergence results are given in *Table 4*. Both structures were solved with *Patterson* and subsequent difference *Fourier* syntheses. All non-H-atoms of the carbamato complexes were refined [40] with anisotropic displacement parameters; H-atoms were calculated (C–H 0.98 Å, $U_{iso(H)} = 1.3 \cdot U_{eq(C)}$) and treated as riding atoms. Crystals of the gold complex **5** clathrate disordered heptane close

---

[4]) Silver NMR-active nuclei: ^{107}Ag ($I = 1/2$, isotopic abundance 51.8%), ^{109}Ag ($I = 1/2$, isotopic abundance 48.2%), see [38].

Table 4. *Crystal Data, Parameters of Data Collection and Convergence Results for Compounds* **2** *and* **5** $\cdot$ *0.5* C_7H_{16}

	2	**5** $\cdot$ 0.5 C_7H_{16}
Formula	$C_6H_{12}Ag_2N_2O_4$	$C_{26.5}H_{33}AuNO_2P$
Formula weight	391.9	625.5
Cryst. size/mm^3	0.2 × 0.08 × 0.08	0.4 × 0.4 × 0.3
Space group	$P2_1/c$ No. 14	$P2_1/c$ No. 14
a/Å	12.08(1)	13.212(5)
b/Å	3.797(2)	12.25(1)
c/Å	11.316(7)	16.795(6)
β/°	113.37(6)	109.09(2)
V/Å^3	476.3(6)	2568(2)
Z	2	4
T/K	253	293
Radiation	MoK_α	AgK_α
λ/Å	0.7107	0.5594
D_c/g cm^{-3}	2.732	1.618
Scan mode	ω	$\theta - 2\theta$
Absorption correction	Ψ scans	Ψ scans
$2\theta_{max}$/°	54	48
Measured reflections	1244	13415
Unique reflections	1187	8499
Observed reflections	634 with $I > 2\sigma(I)$	2853 with $I > 3\sigma(I)$
No. of parameters	64	269
Resid. electron density/e Å^{-3}	1.9 at 1.1 Å from Ag	2.5 at 0.9 Å from Au
Absorption coefficient/cm^{-1}	40.65	31.40
R_{int}	0.049	0.0408
R	0.059	0.058
$R_w(w^{-1} = \sigma^2(F_o)$	0.067	0.064
G.o.f	1.27	2.121

to a crystallographic inversion centre. Simple *van-der-Waals* calculations[5] [41] show that the complex molecules alone leave a big void (*ca.* 100 Å^3) in the unit cell; inside this void, the solvent C-atoms show up clearly in a difference *Fourier* map. These peaks were assigned isotropic displacement parameters in the refinement. The ethyl C-atoms in **5**, especially C(2) and C(5), show pronounced anisotropic displacement parameters indicating a certain degree of disorder. *Fig. 1* was elaborated by SHELXTL-Plus Program [42]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication.

4. *Reactivity. Reaction of* [$Cu(O_2CN^iPr_2)$] *with MeI.* [$Cu(O_2CN^iPr_2)$] (0.29 g, 1.4 mmol) was added to 10 ml of MeI. From the suspension, the solid CuI was recovered by filtration and dried (*ca.* quant. yield). The filtrate showed an IR band at 1703 cm^{-1} due to $MeOC(O)N^iPr_2$.

Reaction of [$Ag(O_2CNR_2)$] *with MeI. a)* [$Ag(O_2CNEt_2)$] (**3**; 0.29 g, 1.3 mmol) was added to 15 ml of MeI, giving immediately a suspension. The solid, separated by filtration and dried, was AgI (95% yield). The colorless filtrate showed an IR band at 1701 cm^{-1} due to $MeOC(O)NEt_2$. *b)* [$Ag(O_2CNEt_2)$] (**3**; 0.10 g, 0.45 mmol) was added to a soln. of MeI (0.44 ml, 7.1 mmol) in THF (10 ml). AgI precipitated. The liquid phase showed the IR band due to $MeOC(O)NEt_2$ at 1707 cm^{-1} with A = 0.60 (ε = 1350 M^{-1} cm^{-1}, cell path 0.0104 cm) corresponding to a *ca.* quant. yield. *N,N*-Diethylmethylurethane was obtained by treating [$Ag(O_2CNEt_2)(PPh_3)_2$] (**4**) with MeI in THF. *c)* The methyl derivative **2** (0.171 g, 0.87 mmol) with neat MeI (3.0 ml) gave a 30% yield of $MeOC(O)NMe_2$.

Reaction of [$Au(O_2CNEt_2)(PPh_3)$] (**5**) *with MeI.* [$Au(O_2CNEt_2)(PPh_3)$] (**5**; 0.13 g, 0.22 mmol) was added to a soln. of MeI (0.15 ml, 2.41 mmol) in THF (5 ml). After some minutes, the supernatant liquid showed an IR

---

[5] Local programs essentially based on *Gavezzotti*'s algorithm in OPEC [41].

band at 1707 cm^{-1}, due to $MeOC(O)NEt_2$ ($A = 0.34$, $\varepsilon = 1350\ M^{-1}\ cm^{-1}$, cell path 0.0104 cm; corresponding to 57% yield).

Reaction of $[Cu(O_2CN^iPr_2)]$ with CO. A suspension of $[Cu(O_2CN^iPr_2)]$ (0.17 g, 0.82 mmol) in dimethoxyethane (25 ml) absorbed CO at r.t. and 1 atm producing a light yellow soln. which showed an IR band at 2092 cm^{-1} (a similar behavior was observed in THF, $\tilde{\nu}$(CO) 2080 cm^{-1}). By reducing the CO partial pressure, a reduction of the band intensity was observed. Gas-volumetric CO uptake measurements carried out at different temp. till the equilibrium conditions were reached, gave the following values of the molar ratio between the absorbed CO and Cu^I: 0.623 (269 K), 0.442 (278 K), 0.249 (290 K), 0.165 (298 K).

Reaction of $[Ag(O_2CNEt_2)]$ (**3**) *with CO.* Under CO, **3** (1.15 g, 5.13 mmol) was added to MeCN (25 ml). Slowly an Ag mirror deposited on the reactor walls, and CO uptake was observed. After 11 d stirring at r.t., the liquid phase showed, besides the IR band at 2337 cm^{-1} due to CO_2, two strong bands at 1751 and 1707 cm^{-1}, due to $(NEt_2CO)_2O$, and weak bands at 1652 and 1637 cm^{-1} due to $(Et_2NCO)_2$. The suspension was filtered and the filtrate evaporated. The residue was treated with Et_2O (20 ml) and the resulting suspension filtered; the filtrate, which did not contain Ag^I, was analyzed by GC/MS. The molecular and fragment ions of $(Et_2NCO)_2O$ and $(Et_2NCO)_2$ were observed, the major component being $(Et_2NCO)_2O$. In a similar experiment, carried out using ^{13}CO, IR bands at 1740 and 1676 cm^{-1} observed for the soln. were attributed to $Et_2N^{13}C(O)OC(O)NEt_2$.

Reaction of $[Ag(O_2CNEt_2)]$ (**3**) *with Et_2NH and CO.* Under CO **3** (0.86 g, 3.8 mmol) and Et_2NH (5 ml, 48 mmol) (molar ratio Ag/Et_2NH 1:13) were added to MeCN (25 ml). A slow deposition of an Ag mirror on the reactor walls was observed together with CO uptake. After 7 d stirring at r.t., the mixture was filtered. The filtrate showed IR bands at 1652 and 1637 cm^{-1} due to the oxamide $(Et_2NCO)_2$. The filtrate was evaporated and the residue treated with Et_2O (10 ml) and with an aq. sat. NaCl soln. (10 ml). The org. layer was separated and analyzed by GC/MS: the molecular and fragment ions of $(Et_2NCO)_2$ were observed.

Treatment of $[Ag(O_2CNEt_2)(PPh_3)_2]$ (**A**) *with CO.* A suspension of **4** (0.38 g, 0.5 mmol) in heptane (50 ml) was saturated with CO and stirred 3 d at r.t. No reaction was observed, and the unreacted **4** was nearly quantitatively recovered by filtration.

REFERENCES

[1] E. Agostinelli, D. Belli Dell'Amico, F. Calderazzo, D. Fiorani, G. Pelizzi, *Gazz. Chim. Ital.* **1988**, *118*, 729.

[2] T. Tsuda, H. Washita, K. Watanabe, M. Miwa, T. Saegusa, *J. Chem. Soc., Chem. Commun.* **1978**, 815.

[3] a) T. Saegusa, T. Tsuda, K. Isayama, K. Nishijima, I. Isegawa, *Tetrahedron Lett.* **1968**, 1641; b) N. J. Bunce, N. G. Murray, *Tetrahedron* **1971**, *27*, 5323; c) J. March, 'Advanced Organic Chemistry', 3rd edn., J. Wiley, New York, 1985, p. 654.

[4] S. Song, W. C. Trogler, *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 770.

[5] R. A. Van Santen, H. P. C. E. Kuipers, *Adv. Catal.* **1987**, *35*, 265, and ref. cit. therein.

[6] 'Handbook of Chemistry and Physics', 73rd edn., Ed. D. R. Lide, C. R. C. Press, Boca Raton, Florida, 1992–1993.

[7] P. K. Hurlburt, O. P. Anderson, S. H. Strauss, *J. Am. Chem. Soc.* **1991**, *113*, 6277; P. K. Hurlburt, J. J. Rack, S. F. Dec, O. P. Anderson, S. H. Strauss, *Inorg. Chem.* **1993**, *32*, 373.

[8] R. J. Puddephatt, in 'Comprehensive Coordination Chemistry', Vol. 5, Eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon Press, Oxford, 1987, p. 871.

[9] D. Belli Dell'Amico, F. Calderazzo, '*N,N*-Dialkylcarbamates of Transition and Non-Transition Elements', in 'Advanced Syntheses and Methodologies in Inorganic Chemistry', Vol. 5, Eds. S. Daolio, M. Fabrizio, P. Guerriero, E. Tondello, and P. A. Vigato, Bressanone, December 2–7, 1991, p. 1.

[10] R. Alessio, D. Belli Dell'Amico, F. Calderazzo, U. Englert, *Gazz. Chim. Ital.* **1993**, *123*, 719.

[11] a) T. Tsuda, T. Hashimoto, T. Saegusa, *J. Am. Chem. Soc.* **1972**, *94*, 658; b) G. M. Whitesides, J. S. Sadowski, J. Lilburn, *ibid.* **1974**, *96*, 2829.

[12] H. G. B. Drew, A. H. bin Othman, D. A. Edwards, R. Richards, *Acta Crystallogr., Sect. B* **1975**, *31*, 2695.

[13] R. D. Hart, P. C. Healy, G. A. Hope, D. W. Turner, A. H. White, *J. Chem. Soc., Dalton Trans.* **1994**, 773.

[14] a) A. S. Morkovnik, Z. S. Morkovnik, V. V. Bessonov, *Zh. Neorg. Khim.* **1987**, *32*, 3106 (*CA*: **1988**, *108*, 105251 j); b) R. C. Mehrotra, *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 269.

[15] R. G. Griffin, J. D. Ellett, Jr., M. Mehring, J. G. Bullitt, J. S. Waugh, *J. Chem. Phys.* **1972**, *57*, 2147.

[16] A. Michaelides, S. Skoulika, V. Kiritsis, A. Aubry, *J. Chem. Soc., Chem. Commun.* **1995**, 1415.

[17] A. Michaelides, V. Kiritsis, S. Skoulika, A. Aubry, *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1495.

[18] G. A. Bowmaker, Effendy, J. V. Hanna, P. C. Healy, G. J. Millar, B. W. Skelton, A. H. White, *J. Phys. Chem.* **1995**, *99*, 3909.

[19] N. C. Baenziger, W. E. Bennett, D. M. Soboroff, *Acta Crystallogr., Sect. B* **1976**, *32*, 962.

[20] N. C. Baenziger, K. M. Dittemore, J. R. Doyle, *Inorg. Chem.* **1974**, *13*, 804.

[21] P. G. Jones, G. M. Sheldrick, J. A. Muir, M. M. Muir, L. Bird Pulgar, *J. Chem. Soc., Dalton Trans.* **1982**, 2123.

[22] P. G. Jones, *Acta Crystallogr., Sect. C* **1984**, *40*, 1320.

[23] P. G. Jones, *Acta Crystallogr., Sect. C* **1985**, *41*, 905.

[24] J. P. Fackler, Jr, Md. N. I. Khan, C. King, R. J. Staples, R. E. P. Winpenny, *Organometallics* **1991**, *10*, 2178.

[25] P. G. Jones, R. Schelbach, *J. Chem. Soc., Chem. Commun.* **1988**, 1338.

[26] a) A. Bayler, A. Schier, G. A. Bowmaker, H. Schmidbaur, *J. Am. Chem. Soc.* **1996**, *118*, 7006; b) P. Pyykkö, J.-P. Desclaux, *Acc. Chem. Res.* **1979**, *12*, 276; c) K. S. Pitzer, *ibid.* **1979**, 12, 271; d) N. Marsich, A. Camus, G. Nardin, *J. Organomet. Chem.* **1982**, *239*, 429.

[27] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751.

[28] D. Belli Dell'Amico, F. Calderazzo, B. Giovannitti, G. Pelizzi, *J. Chem. Soc., Dalton Trans.* **1984**, 647.

[29] D. Belli Dell'Amico, F. Calderazzo, unpublished results.

[30] A. Bacchi, D. Belli Dell'Amico, F. Calderazzo, U. Giurlani, G. Pelizzi, R. Rocchi, *Gazz. Chim. Ital.* **1992**, *122*, 429.

[31] A. Belforte, F. Calderazzo, *J. Chem. Soc., Dalton Trans.* **1989**, 1007; M. Aresta, E. Quaranta, *J. Org. Chem.* **1988**, *53*, 4153; M. Aresta, E. Quaranta, *J. Chem. Soc., Dalton Trans.* **1992**, 1893.

[32] Y. Yoshida, S. Ishii, M. Watanabe, T. Yamashita, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1534 and ref. cit. therein.

[33] W. D. McGhee, Yi Pan, D. P. Riley, *J. Chem. Soc., Chem. Commun.* **1994**, 699; W. McGhee, D. Riley, K. Christ, Y. Pan, B. Parnas, *J. Org. Chem.* **1995**, *60*, 2820, and ref. cit. therein.

[34] M. Aresta, E. Quaranta, *Tetrahedron* **1992**, *48*, 1515.

[35] A. F. Scott, L. L. Wilkening, B. Rubin, *Inorg. Chem.* **1969**, *8*, 2533; P. F. Rodesiler, E. L. Amma, *J. Inorg. Nucl. Chem.* **1977**, *39*, 1227.

[36] T. Tsuda, H. Habu, S. Horiguchi, T. Saegusa, *J. Am. Chem. Soc.* **1974**, *96*, 5930; R. L. Geerts, J. C. Huffman, K. Folting, T. H. Lemmen, K. G. Caulton, *ibid.* **1983**, *105*, 3503.

[37] M. Pasquali, C. Floriani, A. Gaetani-Manfredotti, *Inorg. Chem.* **1981**, *20*, 3382; M. Håkansson, S. Jagner, *ibid.* **1990**, *29*, 5241.

[38] R. K. Harris, B. E. Mann, 'NMR and Periodic Table', Academic Press, London, 1978.

[39] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

[40] *ENRAF-Nonius*, 'SDP Version 5.0', 1989.

[41] A. Gavezzotti, *J. Am. Chem. Soc.* **1983**, *105*, 5220.

[42] G. M. Sheldrick, 'SHELXTL-Plus, Rel 5.03', *Siemens Analytica X-Ray Instruments Inc.*, Madison, Wisconsin, 1995.

Received July 9, 1997