Carboxylation of Acetophenone with Zinc(II) Alkoxides/CO_2 Systems: A Mechanistic Study

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Dedicated to Professor Dirk Walther on the occasion of his 60th birthday

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The crystal structures of the homoleptic dimer zinc(II) 2,6-di-*tert*-butylphenoxide (**1b**) and of the corresponding monomer **1b**/$(DMSO)_2$ are presented. The structural motif of **1b** is a Zn–O–Zn–O four-membered ring. The bulky phenoxide ligands led to a coordination number of only three for the zinc atom. Monomer **1b**/$(DMSO)_2$ crystallized as a four-coordinated monomer with a highly distorted tetrahedral geometry around the zinc center. ^{13}C NMR investigations reveal details for the reaction of CO_2 with a series of alkoxide zinc(II)/solvent systems [2,6-dimethylphenoxide zinc(II) (**1a**), zinc(II) 2,6-di-*tert*-butylphenoxide (**1b**), zinc(II) 2,6-diphenylphenoxide (**1c**), zinc(II) 4-*tert*-butylphenoxide (**1d**), and zinc(II) 2-pyridylcarbinolato (**2**)]. The interpretation of the ^{13}C NMR signals agree with ab initio calculations of a model zinc(II) phenoxide/CO_2 system. Experimentally, the carboxylation of acetophenone as a representative for CH-acidic substrates was carried out with specific zinc(II) phenoxide/CO_2 systems. The reactions resulted in yields of ca. 40% of benzoyl acetic acid. The role of the soluble zinc(II) phenylcarbonate intermediate is discussed with respect to the subsequent CO_2 transfer reaction.

Introduction

Several investigations intermediate into the mechanism of the activation of CO_2 by Zn^{II} complexes are documented.[1,2,5] Some of the fundamental understanding was obtained from the investigation of the mechanism of the copolymerization of CO_2 and epoxides.[1,3,5] However, the number of soluble zinc(II) compounds which are amenable to mechanistic investigations is limited. A synthesis first reported by Caulton allows for the preparation of soluble homoleptic zinc(II) alkoxide compounds (Figure 2).[4] The majority of the compounds prepared by this method are monomeric zinc(II) alkoxide structures.[4,5]

Darensbourg reported on the copolymerization process of cyclohexene oxide and CO_2 using zinc(II) phenoxides at 80 °C and a pressure of 55 bar.[5] NMR investigations revealed a shift of the carbon peak of CO_2 (170 ppm). This was demonstrated for the reaction of CO_2 with zinc(II) 2,4,6-trimethylphenoxide in pyridine at room temperature. The insertion of CO_2 into only one metal phenoxide group was proposed. This is in agreement with the X-ray structure of the dimeric $[Cd(S_2CO\text{-}2,6\text{-}Ph_2C_6H_3)]_2(\mu\text{-}O\text{-}2,6\text{-}Ph_2C_6H_3)_2$ obtained from the reaction of CS_2 with the corresponding cadmium(II) phenoxide (cf. Figure 7).[6]

In this paper new results concerning the activation and the transfer of CO_2 mediated by homoleptic zinc(II) alkoxide complexes are reported. The carboxylation of acetophenone to give benzoyl acetic acid at ambient temperature is described (Figure 1). This represents a novel application of easily accessible zinc complexes.

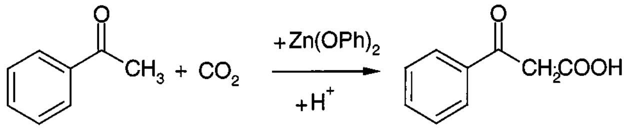

Figure 1. Carboxylation of acetophenone

Results and Discussion

1. Crystal Structure of Zinc(II) 2,6-Di-*tert*-butylphenoxide and Zinc(II) 2,6-Di-*tert*-butylphenoxide/$(DMSO)_2$

X-ray structures of zinc(II) phenoxides thus far reported indicate the preference of monomeric complexes which contain solvent molecules or phosphane ligands in the coordination polyhedron.[1,4,5,7] In the case of dimeric structures, there are heteroleptic compounds such as alkyl(alkyloxy) zinc(II), alkyl(aryloxy) zinc(II) compounds or $\{Zn[\mu\text{-}OCEt_3][N(SiMe_3)_2]\}_2$.[8] For the zinc(II) 2,4,6-tris-*tert*-butylphenoxide in THF solution, an aggregation to a stereochemically rigid dimer has been reported by Caulton by means of cryoscopic molecular weight determination.[4]

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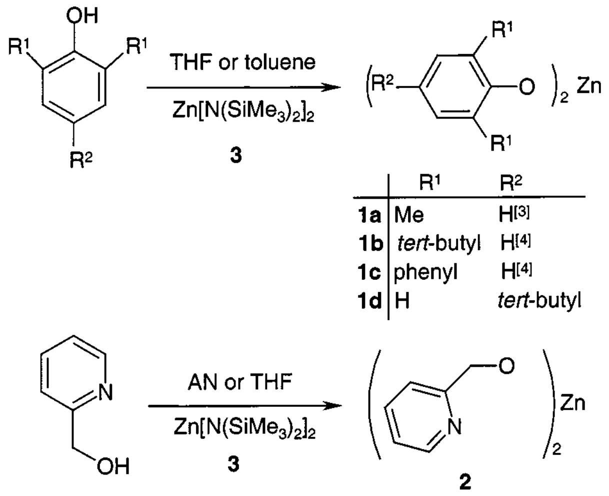
We now report on the X-ray structure of a homoleptic dimeric zinc(II) 2,6-di-*tert*-butylphenoxide complex crystallized from pentane (Figure 3).[9] The synthesis was performed in THF or toluene under an argon atmosphere, as previously described (Figure 2).[4,5]



	R1	R2
1a	Me	H[3]
1b	*tert*-butyl	H[4]
1c	phenyl	H[4]
1d	H	*tert*-butyl

Figure 2. Synthesis of zinc(II) alkoxides

This complex contains a central four-membered Zn−O−Zn−O ring (Figure 3). The metal cation is coordinated in a distorted trigonal planar geometry. The Zn−O bond lengths of the bridging Zn−O−Zn moiety [(Zn1−O2 (1.941(1) Å, Zn1−O4(1.975(1) Å, Zn2−O2(1.980(1) Å, Zn2−O4(1.949(1) Å] are significantly larger than the terminal bonds [Zn1−O1 1.831(1) Å) and Zn2−O3 1.839(1) Å].

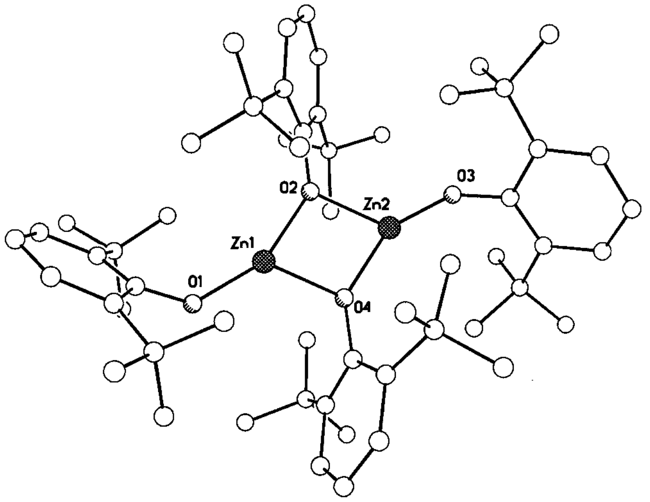


Figure 3. X-ray structure of the dimer of **1b**. Selected distances [Å] and bond angels [°]: Zn1−O1 1.831(2), Zn1−O2 1.941(2), Zn1−O4 1.975(2), Zn2−O3 1.839(2), Zn2−O2 1.980(2), Zn2−O4 1.949(2), Zn1−Zn2 2.9484(6), O1−C1 1.377(4), O3−C29 1.359(4), O2−C15 1.404(4), O4−C43 1.405(4), O1−Zn1−O2 150.5(1), O1−Zn1−O4 125.3(1), O2−Zn1−O4 82.6(1), O4−Zn2−O2 82.3(1)

The terminal zinc O(aryl) distances are equal within the experimental error to those found for the monomeric zinc complexes 2,6-di-*tert*-butylphenoxide−ZnL with L = $MePh_2$ and PCy_3 [Zn−O 1.845(4) and Zn−O 1.869 (3) Å].[7] In these complexes, the zinc atom is also coordinated in an analogous trigonal planar fashion. In the monomeric Zn^{II} phenoxide/(oxygen or nitrogen donor ligand)$_2$ structures which are reported, and also in the structure of **1b**/(DMSO)$_2$ (Figure 4), the zinc atom prefers a distorted tetrahedral coordination.[4,5,10] Also in these cases, the Zn−O bond lengths are in the range of Zn−O 1.846(11) [2,6-diisopropylphenoxide−zinc(II)/(THF)$_2$] to Zn−O 1.908(1) Å [**1b**/(DMSO)$_2$]. They are slightly longer than those of the bridged Zn−O bonds in the homoleptic dimeric structure. In heteroleptic dimeric zinc(II) compounds, the Zn−O distances [e.g. Zn−O 1.970(1) Å,[8a] 1.930(3) Å,[8b] 2.075(2) Å[8c]] are comparable to the bridging Zn−O bonds in **1b**. In general, the addition of solvent molecules to an unsolvated species leads to a ca. 0.1 Å shorter Zn−O(aryl) distance, which is easily understood in terms of electrostatic effects. In the dimeric structure, the oxygen interacts with two zinc centers.

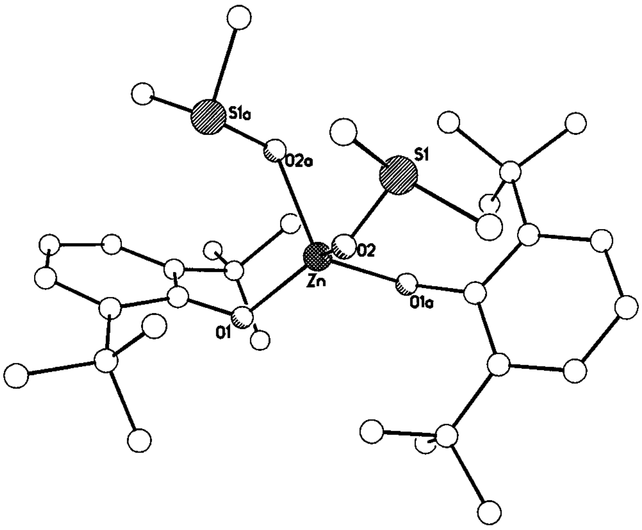


Figure 4. X-ray structure of the monomer of **1b**/(DMSO)$_2$. Selected distances [Å] and bond angels [°]: Zn−O1 1.907(1), Zn−O2 2.044(1), O1−C1 1.341(2), O1−Zn−O2 123.52(4), O1−Zn−O1a 108.77(6), O1−Zn−O2a 104.43(4), O2−Zn−O2a 93.04(7)

2. Reactivity of CO_2 with Zinc(II) Phenoxides in DMSO

The reaction of CO_2 with zinc(II) alkoxides has been studied by means of NMR spectroscopy in order to characterize the structure of a soluble phenoxide zinc(II)/CO_2 intermediate. Such an activated CO_2 is an essential prerequisite to enable the carboxylation of CH-acidic compounds at room temperature. We performed ^{13}C and ^{1}H NMR investigations in [D6]DMSO, [D7]DMF and [D5]pyridine before and after addition of CO_2. A typical NMR experiment is depicted in Figure 5 and 6 (see also Table 1).

After the addition of $^{13}CO_2$ and warming at 40 °C for 6 hours, the spectrum showed the ^{13}C chemical shifts of **1a.** Relative to these ^{13}C NMR signals, a downfield shift of the signals for the phenoxide *para*- and *ortho* carbons of 5.5 and 2.2 ppm (from $\delta = 113$ to $\delta = 119$ and from $\delta = 126$ to $\delta = 128$, respectively) was observed. This was accompanied by an upfield shift of the signal for the *ipso* carbon atom of 7.2 ppm (from $\delta = 163$ to $\delta = 155$). Physically dissolved $^{13}CO_2$ has a chemical shift of $\delta = 124$. Apart from the

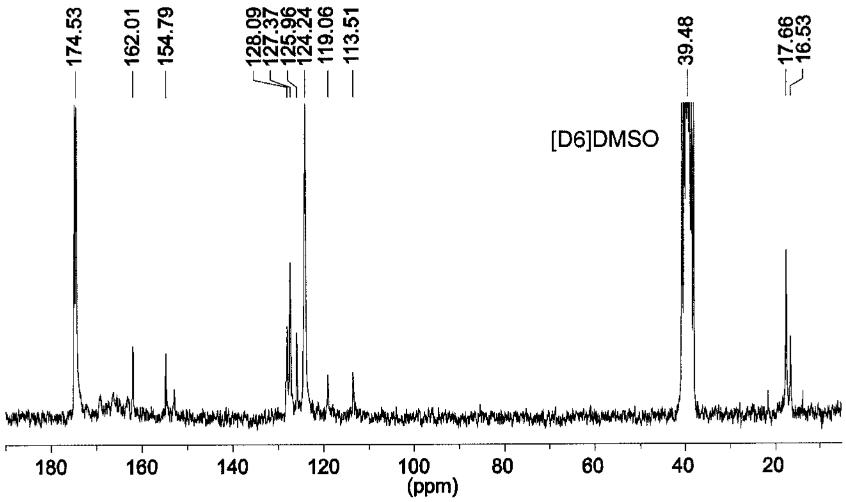


Figure 5. ^{13}C NMR spectra of **1a** in [D_6]DMSO after the addition of $^{13}CO_2$ and 6 h at 40 °C

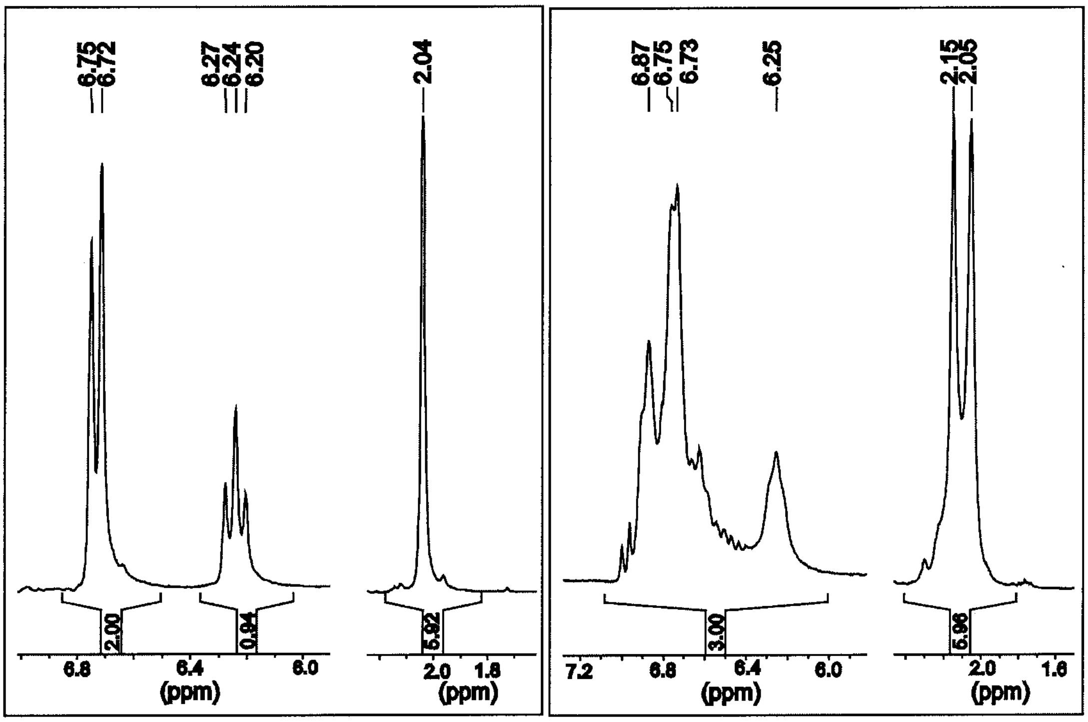


Figure 6. ^{1}H NMR spectra of **1a** in [D_6]DMSO and after the addition of $^{13}CO_2$ and 6 h at 40 °C

chemical shifts of the phenyl ring carbon atoms, an intense signal was detected at $\delta = 174.3$. After the addition of $^{13}CO_2$, the ^{1}H NMR spectrum showed a multiplet for the phenoxide hydrogen atoms and a signal at $\delta = 2.15$ in addition to the signal for the methyl hydrogen atom of **1a**. The integration of these two methyl signals suggests a 1:1 molar ratio. This is in agreement with the structure of a 2,6-diphenylphenoxide/CS_2 cadmium(II) complex and the results of the ^{13}C NMR investigations reported by Darensbourg (Figure 7).[5,6]

In contrast to Darensbourg's results, a reaction of the sterically hindered **1b** with CO_2 could be observed in DMSO.[4] The NMR spectrum is similar to that of 2,6-dimethylphenoxide zinc(II) (Table 1). Darensbourg proposed that the initiation process of the copolymer synthesis was the epoxide ring opening, because CO_2 showed no reactivity with sterically hindered zinc(II) phenoxide complexes. With our result we have found a new argument for a CO_2 insertion into the Zn−O bond as the first step of the mechanism of these reaction.

In agreement with the results of Darensbourg, **1a** and **1b** do not react with CO_2 in pyridine.[5] Also in the case of **1c** in various solvents (DMSO, DMF, pyridine, THF) and of **1d** in pyridine (**1d** is only soluble in pyridine) no such reactions were observed by ^{13}C NMR investigations. On further warming of **1d** to 60 °C, a white powder precipitated and an NMR experiment could not be performed. The product was isolated and washed with pentane. It was insoluble in

Table 1. Comparison of calculated and experimental ^{13}C chemical shifts of metal phenoxide systems

molecule	C_{CO2} δ values	C_{ipso} δ values	C_{para} δ values
I[a]		166.8	117.2
II[a]	135.2	169.7	120.9
III[a]	149.5	154.8	133.3
IV[a]	170.7	157.1	132.4
NaOPh[a]		180.4	113.5
NaO_2COPh[a]	173.5	163.0	129.7
NaOPh[b]		170.5	112.4
1a[b]		163.4	113.6
1a/$^{13}CO_2$ [c]	174.8	162.0/154.7	113.5/119.0
1b[b]		166.1	112.4
1b/$^{13}CO_2$ [c]	174.5	165.9/153.6	112.2/120.1
1c[b]		161.1	115.9
1d[d]		165.7	118.8

[a] GIAO-SCF (B3LYP/6−311+G*) calculated ^{13}C chemical shifts (δ, ppm relative to TMS = 0.0 ppm) on the Hartree−Fock optimized geometries (RHF/6−311+G*). − [b] Exp. in [D_6]DMSO. −[c] Exp. in [D_6]DMSO and 40 °C. − [d] Exp. in [D_5]pyridine.

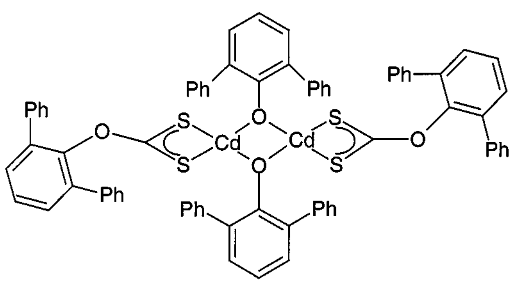


Figure 7. $[Cd(S_2CO\text{-}2,6\text{-}Ph_2C_6H_3)]_2(\mu\text{-}O\text{-}2,6\text{-}Ph_2C_6H_3)_2$ [6]

water and reacted with dilute HCl (gas evolution). In the MS measurement, both the phenol and CO_2 could be detected. We presumed that the complete reaction of CO_2 with both Zn−O(aryl) bonds of the phenoxide leads to an insoluble phenylcarbonate zinc(II). The formation of a soluble alkoxide zinc(II)/CO_2 complex is dependent on the solvent which is used and the steric demand of the phenol ligands.

In the case of the (2-pyridylcarbinolato)zinc(II) complex **2**, no signal was found in the region of δ = 170, but in pyridine a markedly broadened signal at δ = 156 was observed. Additionally, the broadened signals for the carbon atoms of the ring indicated an equilibrium reaction of the complex with CO_2. In order to get insight into the mechanism of this CO_2 insertion, quantum mechanical calculations on the model system zinc(II) phenoxide were carried out.

3. Ab initio Calculations

Darensbourg has shown a significant binding of various solvent molecules to the zinc center of phenoxide zinc(II) compounds in solution even at ambient temperature.[5] Unfortunately, computational limitations prevented us from considering the effects of microsolvation and thus explicit solvent molecules were not included in the model. However, as will be shown, our calculations agree well with the experimental data, thus verifying the validity of our approach. An analogous reaction mechanism for carbonic anhydrase was previously proposed for the activation of carbon dioxide.[11]

Due to the considerable size of the molecular geometry, optimizations were restricted to the HF/G-311+G* level of theory. All geometries were fully optimized and the nature of the stationary points characterized by harmonic frequency analysis. B3LYP/G-311+G* single point calculations were performed on the optimized geometries in order to introduce electron correlation into the energy calculation. The Gaussian94 set of programs was used.

The proposed mechanism is depicted in Figure 8. One of the electron lone pairs of the zinc-bonded oxygen interacts with the carbon of CO_2 to form the electrostatic encounter complex **II** (−2.79 kcal mol^{-1}). This facilitates the nucleophilic attack, leading to the intermediate product **III** (6.92 kcal mol^{-1}) which can rearrange to form the more stable insertion product **IV** (3.24 kcal/mol). This energy profile suggests a reversibility of the reaction.

The calculated stability of the encounter complex in solution must be questioned because electrostatic interactions in general decrease in the presence of solvent molecules.

The calculated Zn−O distance (1.78 Å) is found to be 0.15 Å shorter than the terminal Zn−O distances in the X-ray structure (cf. Figure 3). Considering the absence of dative solvent molecules in the calculated structure this fact is not surprising. In a previous study on the corresponding sodium compounds, the deviations from the experimental structures were in the range of 0.3−0.4 Å.[12] The choice of the model and the level of theory can therefore be considered to be satisfactory. The most important structural features are summarized in Figure 8. For the structures **I−IV**, we calculated the ^{13}C chemical shifts (Table 1). The RHF/6−311+G* level of theory on the formerly optimized geometries were used, following the guidelines reported by Chesseman et al.[13] Analogous results could be calculated in the case of the formation of the sodium phenyl carbonate.

These data allow for the verification of the ^{13}C NMR interpretation, summarized in the second part of this study. The peak at ca. 174 ppm can be assigned unambiguously to the inserted CO_2 carbon of the carbonate structure **IV**. There is also an upfield shift of the ^{13}C NMR signal of the *ipso* carbon atom and a downfield shift of the signal for the phenoxide *para* carbon, when following the reaction course from the zinc(II) phenoxide to zinc(II) phenylcarbonate.

In the case of the reaction of **2** with CO_2, the broadened signal at δ = 156 is an indicative of the existence of an equilibrium between the reactants and/or intermediate products such as **III** and **IV**.

4. Carboxylation of Acetophenone

The carboxylation of CH-acidic substrates (e.g. acetone or acetophenone) with an alkaline phenoxide solvent system was first carried out by Bottachio et al.[14] He postulated the formation of phenol and an enolate which is stabilized by the appropriate solvent in a very complex equilibrium. In a successive step, the enolate reacts with CO_2 to give the alkaline salt of the carboxylic acid. Walther et al.

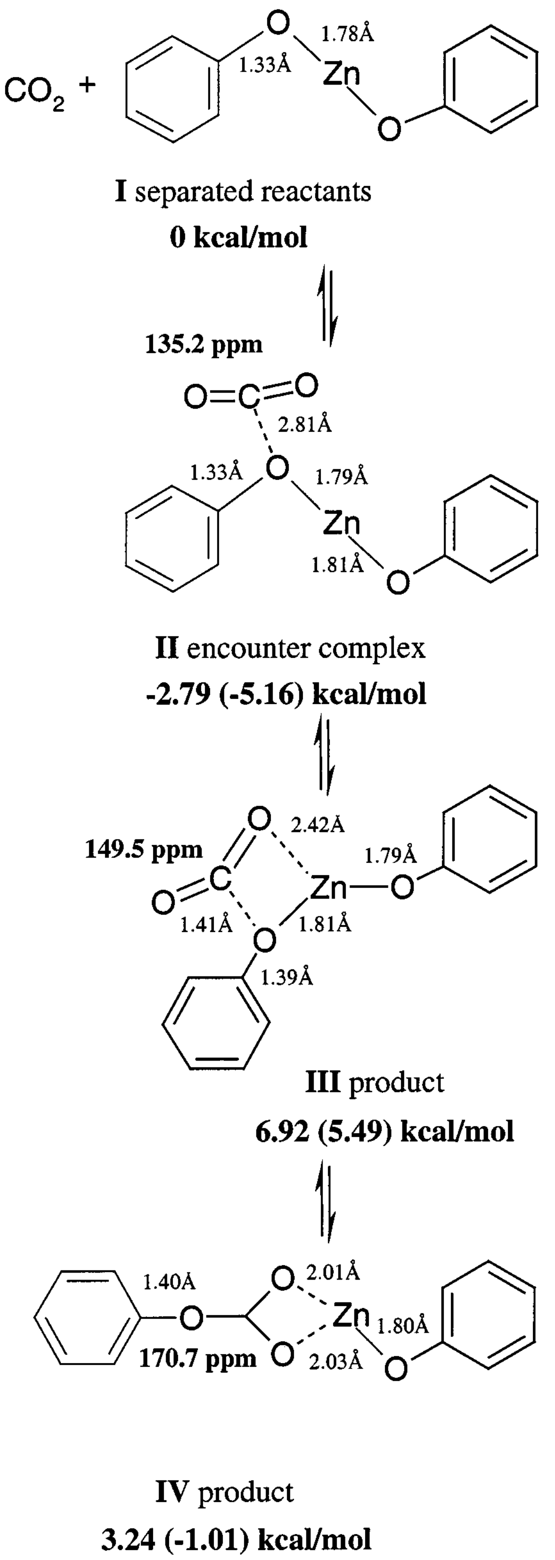


Figure 8. Quantum mechanical calculations on the model system phenoxide zinc(II)/CO_2 [geometries, relative energies, ^{13}C chemical shifts (δ, ppm relative to TMS) - B3LYP/6−311+G*//RHF/6−311+G* level of theory, HF results in parentheses]

postulated the activation of CO_2 by NaOPh/solvent complexes.[15] They obtained particularly high yields of carboxylic acids with a NaOPh/solvent ratio of 4−5:1 at room temperature. The use of magnesium enolates or carbamates had also been reported for these reactions.[16]

In our investigations, the carboxylation of acetophenone was carried out with zinc(II) alkoxide complexes (Table 2) The ligand, the solvent and the temperature were varied. Best results were obtained using **1a** and **1b** at a temperature of 40 °C in DMSO. Comparable yields resulted in cases for which a molar ratio of 3:1 of the zinc(II) complexes to acetophenone was applied. The lower yield of benzoyl acetic acid observed at a reaction temperature of 80 °C indicates a plausible but unwanted decarboxylation. A further explanation for the decreasing yield could be the formation of an insoluble phenylcarbonate zinc(II), which would limit the transfer of the CO_2 at this temperature.

Table 2. Yield of the carboxylation of acetophenone in DMSO to afford benzoyl acetic acid

Complex	Yield [%]		
	25 °C	40 °C	80 °C
Zinc(II) 2,6-dimethylphenoxide (**1a**)	33	46	32
Zinc(II) 2,6-di-*tert*-butylphenylphenoxide (**1b**)	24	37	25
Zinc(II) 2,6-diphenylphenoxide (**1c**)	4	23	<1
Zinc(II) 4-*tert*-butylphenoxide (**1d**)	0	0	0
(2-Pyridylcarbinolato)zinc(II) (**2**)	<1	<1	<1
Bis(trimethylsilylamido)zinc(II) (**3**)	5	4, 16[a]	8

[a] In THF.

The use of **1c** in DMSO for the reaction led to a lower yield of the benzoyl acetic acid. This can be explained both by a complete reaction of CO_2 to a zinc(II) 2,6-diphenylphenylcarbonate and by a poor solubility of the insertion product. In the case of **1d** dissolved in pyridine, the addition of CO_2 led to a precipitation of the previously described "white powder". After addition of acetophenone, no benzoyl acetic was detected.

Solvent dependence: For **1a**−**1c** dissolved in pyridine, the detection of a reaction with $^{13}CO_2$ in the NMR investigations and also the carboxylation failed. It worth noting that although the starting $Zn[N(SiMe_3)]_2$ **3** does not undergo an insertion reaction with CO_2, the amide **3** also enabled the carboxylation of acetophenone. The model reaction requires a zinc(II) complex which is soluble in the presence of CO_2. Reaction of the phenoxide zinc(II) complexes with acetophenone (i.e. without CO_2) was not observed in our NMR investigations. Our experiments revealed no indication of the formation of acetophenolate zinc(II) and phenol. The charge on the carbon of the activated complexes (natural charge of **III**: $q_c = 0.9974$ and of **IV**: $q_c = 0.9947$) allows no statement about the preference of the two product structures as a potential reactant towards acetophenone. At present we presume that the reaction of the zinc(II) complex, CO_2 and acetophenone is a concerted reaction, in which one of the structures **III** or **IV** plays a dominant role (cf. Figure 8).

On the other hand, (2-pyridylcarbinolato)zinc(II), (hydroxypyridinato)zinc(II) and (2,6-di-*tert*-butylbenzoato)-zinc(II) are inactive for the carboxylation of acetophenone (20 °C, 40 °C; DMSO, pyridine). Thus, the carboxylation of CH-acidic compounds requires a well optimized zinc(II) complex with a specific ligand design. An important property of this complex is an acceptable solubility (this requires bulky ligands). A relative low coordination number of the metal center is assumed to be decisive, too.

However, we have found a new reaction of zinc(II) alkoxides with CO_2 and acetophenone under remarkably mild conditions.

Experimental Section

The syntheses of **1a−1c** were performed under an argon atmosphere as previously described.[4,5]

Zinc(II) 2,6-Dimethylphenoxide {Zn[(OC_6H_3)(CH_3)$_2$]$_2$} (1a): The procedure was modified by adding Zn{N(Si(CH_3)$_3$)$_2$]}$_2$ (7.0 g, 18 mmol) in THF (80 mL) to a solution of sublimed 2,6-dimethylphenol (4.4 g, 36 mmol) in THF (100 mL). It was heated at reflux for 4 h. After cooling to room temperature, a white powder precipitated. The THF was removed in vacuo and the resulting solid was washed twice with pentane (50 mL) and dried in vacuo to yield a colorless powder. − Yield 5.7 g (83%), $C_{16}H_{18}O_2Zn$ (307.70): calcd. C 62.5, H 5.9; found C 60.55, H 6.20 (It is not possible to remove the ether ligand completely). − IR (KBr, disk): $\tilde{\nu}$ = 3026, 2918 [ν(C−H)], 1594, 1474, 1410 [ν(C=C)], 1200 [ν(C−O)], 760 cm^{-1} [δ(C−H)]. − ^1H NMR ([D$_6$]DMSO, 25 °C, TMS): δ = 2.03 (s, 6 H, C*H$_3$*), 6.22 (t, 1 H, C*H$_2$ para*), 6.82 (d, 2 H, C*H$_2$ meta*). − ^{13}C NMR ([D$_6$]DMSO, 25 °C, TMS): δ = 113.6 (*C*H, *para*), 125.9 (*C*H, *ortho*), 127.6 (*C*H, *meta*), 163.5 (*C*−O, *ipso*).

Zinc(II) 2,6-Di-*tert*-butylphenoxide {Zn[(OC_6H_3)(C(CH_3)$_3$)$_2$]$_2$} (1b): To a solution of sublimed 2,6-di-*tert*-butylphenol (7.5 g, 36 mmol) in THF or pentane (40 mL) was added a solution of Zn{N(Si(CH_3)$_3$)$_2$]}$_2$ (7.0 g, 18 mmol) in THF or pentane (80 mL). The solution was stirred for 4 h. The THF was then removed in vacuo and the resulting solid was washed twice with pentane (50 mL) and dried in vacuo to yield a colorless powder. After 3 days the product turned pale yellow. − Yield 6.2 (72%), $C_{28}H_{42}O_2Zn$ (476.02): calcd. C 70.65, H 8.89; found C 68.20, H 8.76. − IR (KBr, disk): $\tilde{\nu}$ = 3080, 2959 [ν(C−H)], 1468, 1426 [ν(C=C)], 1226 [ν(C−O)], 749 cm^{-1} [δ(C−H)]. − ^1H NMR ([D$_6$]DMSO, 25 °C, TMS): δ = 1.38, 1.40 (overlapping singlets, 19 H, C*H$_3$*), 6.27, 6.73 (t, 1 H, C*H$_2$ para*), 6.91, 7.07(d 2 H, C*H$_2$ meta*). − ^{13}C NMR ([D$_6$]DMSO, 25 °C, TMS): δ = 30.5, 31.3 (*C*H$_3$, *tert*-butyl) 34.7, 35.1 (*C*, *tert*-butyl) 112.4 (*C*H, *para*), 123.9, 124.4 (*C*H, *ortho*), 139.4 (*C*H, *meta*), 166.1 (*C*−O, *ipso*).

Zinc(II) 2,6-Diphenylphenoxide {Zn[(OC_6H_3)(C_6H_5)$_2$]$_2$} (1d): The synthesis and isolation are identical to those for the previous zinc phenoxides. Sublimed 2,6-diphenylphenol (8.9 g, 36 mmol) and Zn{N(Si(CH_3)$_3$)$_2$]}$_2$ (7.0 g, 18 mmol) were used for the reaction. Yield 9.3 g (93%), $C_{36}H_{26}O_2Zn(THF)_2$ (700.19): calcd. C 75.48, H 6.05; found C 73.89, H 5.73. − IR (KBr, disk): $\tilde{\nu}$ = 3050, 3023 [ν(C−H)], 1594, 1496, 1459, 1429 [ν(C=C)], 1224 [ν(C−O)], 762, 746, 703 cm^{-1}[δ(C−H)]. − ^1H NMR ([D$_4$]THF, 25 °C, TMS): δ = 7.1 (t, 1 H, C*H*), 7.3−7.7 (m, 1 H, C*H*). − ^{13}C NMR ([D$_4$]THF, 25 °C, TMS): δ = 115.9 (*C*H, *para*), 126.4 (*C*H, *para*), 126.4, 128.5, 129.0, 130.4, 132.9, (*C*H, *ortho*, *meta*), 142.5, 161.1 (*C*−O, *ipso*).

Zinc(II) 4-*tert*-Butylphenoxide {Zn[(OC_6H_3)(C(CH_3)$_3$)]$_2$} (1c): The synthesis and isolation are identical to those for the previous zinc phenoxides. After addition of Zn{N(Si(CH_3)$_3$)$_2$]}$_2$ (7.0 g, 18 mmol) in THF (30 mL) to a solution of sublimed 4-*tert*-butylphenol (5.4 g, 36 mmol) in THF (80 mL) a white powder precipitated directly. Yield 12.2 (93%), $C_{20}H_{26}O_2Zn$ (363.80): calcd. C 66.0, H 7.2; found C 64.9, H 7.3. − IR (KBr, disk): $\tilde{\nu}$ = 2964, 2870 [ν(C−H)], 1600, 1514, 1460 [ν(C=C)], 1244 [ν(C−O)], 828 cm^{-1}[δ(C−H)]. − ^1H NMR ([D$_6$]pyridine, 25 °C, TMS): δ = 1.2 (m, 9 H, C*H$_3$*), 7.2 (s, 4 H, C*H*). − ^{13}C NMR ([D$_6$]pyridine, 25 °C, TMS): δ = 31.9 (*C*H$_3$, *tert*-butyl) 33.7 (*C*, *tert*-butyl) 118.8 (*C*H, *para*), 126.6 (*C*H, *ortho*, *meta*), 165.7 (*C*−O, *ipso*).

(2-Pyridylcarbinolato)zinc(II) {Zn[(OCH_2)(C_5H_4N)]$_2$} (2): To a solution of 2-(hydroxymethyl)pyridine (2.8 g, 26 mmol) in acetonitrile (80 mL), a solution of Zn{N(Si(CH_3)$_3$)$_2$]}$_2$ (5.0 g, 13 mmol) in acetonitrile was added. From the stirred solution a white powder precipitated. The acetonitrile was removed by decanting and the resulting product washed twice with acetonitrile (50 mL), dried in vacuo to yield a colorless powder. Yield 3.3 g (90%), $C_{12}H_{12}N_2O_2Zn$ (281.62): calcd. C 51.18.0, N 9.95, H 4.29; found C 51.24, N 10.24, H 4.50. − IR (KBr, disk): $\tilde{\nu}$ = 3057, 2809, [ν(C−H)], 1607, 1568, 1483, 1441 [ν(C=C), ν(N=C)], 1094 cm^{-1} [ν(C−O)]. − ^1H NMR ([D$_3$]acetonitrile, 25 °C, TMS): δ = 3.7 (s, 2 H, C*H$_2$*), 6.32 (t, 1 H, C*H*), 6.48 (d, 1 H, C*H*), 6.85 (t, 1 H, C*H*), 7.54 (d, 1 H, C*H*). − ^{13}C NMR ([D$_3$]acetonitrile, 25 °C, TMS): δ = 64.3 (*C*H$_2$) 120.7 (*C*H, *meta*) 122.4 (*C*H, *ortho*), 137.2, 148.6 (*C*H, *para*), 161.0 (*C*−CH$_2$, *ipso*).

Crystallization of the Dimeric 1b and Monomeric 1b/(DMSO)$_2$: A saturated solution of zinc(II) 2,6-di-*tert*-butylphenoxide in pentane or DMSO, respectively, was allowed to cool to room temperature and then filtered to separate from crystallites. Colorless crystals suitable for X-ray structure determination were grown in the filtrate after a few days. − The intensity data were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption.[17] − The structures were solved by direct methods (SHELXS[18]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97[19]). For the compounds zinc(II) 2,6-di-*tert*-butylphenoxide/(DMSO)$_2$ the hydrogen atoms were located by difference Fourier synthesis and refined isotropically. The hydrogen atoms of the compound zinc(II) 2,6-di-*tert*-butylphenoxide were included at calculated positions with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.[20]

NMR Experiments: Samples of zinc(II) complexes (**1a−1c, 2, 3**) in aprotic polar solvents (0.1 M) were transferred into a NMR tube with a Young-valve system under an argon atmosphere. After measurement of both the ^{13}C NMR and the ^1H NMR spectrum, the solution was saturated thoroughly with CO_2 or $^{13}CO_2$ and reexamined. After this, the probe was heated for 6 h at 40 °C and the measurements were repeated at room temperature. A Bruker AC200 NMR spectrometer was used.

Carboxylation of Acetophenone: In a typical carboxylation run, {Zn[(CH_3)$_2$(OC_6H_3)]$_2$} (0.10 g, 0.3 mmol) was dissolved in the polar aprotic solvent (20 mL) and saturated with CO_2. Acetophenone (0.04 g, 0.3 mmol) was then added to the solution. Afterwards, CO_2 was passed through the solution for six hours at the reaction temperature. A 1:1 mixture of water/methanol (100 mL) was added to the reaction solution.

Separation and Quantitative Analysis of the Product Mixture: Phenol, acetophenone and benzoyl acetic acid were analyzed by HPLC (Gynkotec System): The method was developed by modifying a previously described procedure (Burtscher et al.).[21] Column: Nucleosil 5 C18, (Macherey−Nagel & Co.), injection volume: 20 µL, solvent A: 50% 0.01M phosphate buffer KH_2PO_4 (Merck analytical grade), solvent B: 50% acetonitrile, flow rate: 0.8 mL min^{-1}, isothermal at 298 K, program: isocratic, wavelength: 295 nm. The retention times are 4.2 min for benzoyl acetic acid and 7.0 min for acetophenone. The quantitative analysis was carried out by an external standard method. On the basis of a stock solution of acetophenone (6.1×10^{-4} g mL^{-1}) and benzoyl acetic acid (6.2×10^{-4} g mL^{-1}), a dilution series was measured. The calibration line was determined by linear regression (acetophenone: correction factor 1.051, variation coefficient 0.30%; benzoyl acetic acid: correction factor 1.108, variation coefficient 0.22%).

The carboxylation reaction was performed three times for each solvent and was analyzed twice via HPLC. The results, shown in Table 2, are averaged values of these three reactions.

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[1] D. J. Darensbourg, M. Holtcamp, *Coord. Chem. Rev.* **1996**, *153*, 155−174; M. Ruf, H. Vahrenkamp, *Chem. Ber.* **1997**, *130*, 975−980.

[2] R. Alsfasser, M. Ruf, S. Trofimenko, H. Vahrenkamp, *Chem. Ber.* **1993**, *126*, 703−710; R. Walz, K. Weis, M. Ruf, H. Vahrenkamp, *Chem. Ber.* **1997**, *130*, 975−980; E. Kimura, *Tetrahedron* **1992**, *48*, 6175−6217; E. Kimura, *Progress in Inorganic Chemistry*, edited by K. D. Karlin, John Wiley & Sons, **1994**, *41*, 443−491; E. Kimura, T. Koike, M. Shinoya, *Structure and Bonding,* **1997**, *89*, 1−28; K. Nakata, M. K. Uddin, K. Ogawa, K. Ichikawa, *Chemistry Letters* **1997**, 991−992; P. Ghosh, G. Parkin, J. Chem. Soc., *Dalton Trans.*, **1998**, 2281−2283.

[3] S. Inoue, M. Kobayashi, H. Koinuma, T. Tsuruta, *Macromol. Chem.* **1972**, *155*, 61−73; S. Inoue, M. Kobayashi, H. Koinuma, T. Tsuruta, *Macromol. Chem.* **1972**, *155*, 61−73; W. Kuran, S. Pasynkiewicz, J. Skupinska, *Macromol. Chem.* **1977**, *178*, 47−54; W. Kuran, S. Pasynkiewicz, J. Skupinska, *Macromol. Chem.* **1977**, *178*, 2149−2158; W. Kuran, T. Listos, *Macromol. Chem. Phys.* **1994**, *195*, 977−984; A. Rokicki, U.S. Patent, 4.782.445; H.-N. Sun, U.S. Patent, 4.789.727; H.-N. Sun, U.S. Patent, 4.783.445; M. Cheng, E. B. Lobkovsky, W. Kuran, T. Listos, *Macromol. Chem. Phys.* **1994**, *195*, 1011−1015; P. Gorecki, W. Kuran, *J. Polymer. Lett. Ed.* **1985**, *23*, 299; G. W. Coates, *J. Am. Chem. Soc.* **1998**, *120*, 11018−11019.

[4] R. L. Geerts, J. C. Huffman, K. G. Caulton, *Inorg. Chem.* **1986**, *25*, 1803−1805.

[5] D. J. Darensbourg, M. W. Holtcamp, *Macromolecules* **1995**, *28*, 7577−7579; D. J. Darensbourg, M. W. Holtcamp, G. E. Struck, M. S. Zimmer, S. A. Niezzgoda, P. R. Rainey, J. B. Robertson, J. D. Draper, J. H. Reibensies, *J. Am. Chem. Soc.* **1999**, *121*, 107−116.

[6] D. J. Darensbourg, S. A. Niezgoda, J. D. Draper, J. H. Reibenspies, *J. Am. Chem. Soc.* **1998**, *120*, 4690−4698.

[7] D. J. Darensbourg, M. S. Zimmer, P. Rainey, D. L. Larkins, *Inorg. Chem.* **1998**, *37*, 2852−2853.

[8] [8a] M. Parvez, G. L. Bergstresser, H. G. Richey, *Acta Cryst.* **1992**, *C48*, 641−644. − [8b] S. C. Goel, M. Y. Chiang, W. E. Buhro, *Inorg. Chem.* **1990**, *24*, 4646−4652. − [8c] J. T. B. H. Jastrzebski, J. Boersma, G. van Koten, W. J. J. Smeets, A. L. Spek, *Recl. Trav. Chim. Pays-Bas.* **1988**, *107*, 263−266. − [8d] P. A. Schaaf, E. Wissing, J. Boersma, W. J. J. Smeets, A. L. Spek, G. Koten, *Organometallics* **1993**, *12*, 3624−3629. − [8e] F. H. van der Steen, J. Boersma, A. L. Spek, G. van Koten, *Organometallics* **1991**, *10*, 2467−2480.

[9] Crystal data for 2,6 di-*tert*-butylphenoxide zinc(II): $C_{56}H_{84}O_4Zn_2 \times 0.5\ C_5\ H_{12}$, $M_r = 988.05$ $gmol^{-1}$, colorless prism, size $0.32 \times 0.30 \times 0.28$ mm^3, monoclinic, space group $P2_1/c$, $a = 22.8849(5)$, $b = 12.2669(4)$, $c = 21.7376(6)$ Å, $\beta = 114.162(1)°$, $V = 5567.7(3)$ Å^3, $T = -90$ °C, $Z = 4$, $\rho_{calcd.} = 1.179$ gcm^{-3}, μ (Mo-K_α) = 9.04 cm^{-1}, $F(000) = 2132$, 14729 reflections in $h(-25/25)$, $k(-13/0)$, $l(-24/24)$, measured in the range $2.05° \le \Theta \le 23.25°$, completeness $\Theta_{max} = 96.7\%$, 7969 independent reflections, $R_{int} = 0.0471$, 5715 reflections with $F_o > 4\ \sigma(F_o)$, 593 parameters, 4 restraints, $R1_{obs} = 0.043$, $wR^2{}_{obs} = 0.114$, $R1_{all} = 0.084$, $wR^2{}_{all} = 0.175$, GOOF = 0.914, largest difference peak and hole: 0.606/−0.502 e Å^{-3}.

[10] Crystal data for 2,6-di-*tert*-butylphenoxide zinc(II)/$(DMSO)_2$: **1b**/$(DMSO)_2$: $C_{32}H_{54}O_4S_2Zn$, $M_r = 632.24$ $gmol^{-1}$, colorless prism, size $0.36 \times 0.34 \times 0.32$ mm^3, monoclinic, space group $C2/c$, $a = 14.4358(2)$, $b = 14.7357(2)$, $c = 17.1059(3)$ Å, $\beta = 107.142(1)°$, $V = 3477.15(9)$ Å^3, $T = -90$ °C, $Z = 4$, $\rho_{calcd.} = 1.208$ gcm^{-3}, μ (Mo-K_α) = 8.58 cm^{-1}, $F(000) = 1360$, 4547 reflections in $h(-10/16)$, $k(-16/11)$, $l(-18/18)$, measured in the range $2.13° \le \Theta \le 23.28°$, completeness $\Theta_{max} = 96.2\%$, 2452 independent reflections, $R_{int} = 0.012$, 2377 reflections with $F_o > 4\ \sigma(F_o)$, 285 parameters, 0 restraints, $R1_{obs} = 0022$, $wR^2{}_{obs} = 0.065$, $R1_{all} = 0.023$, $wR^2{}_{all} = 0.071$, GOOF = 1.021, largest difference peak and hole: 0.227/−0.278 e Å^{-3}.

[11] S. Lindskog, J. E. Coleman, *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 2505; J. E. Coleman, J. *Biol. Chem.* **1967**, *242*, 5212; S. Lindskog, in *Carbonic Anhydrase*, Ed.: S. Lindskog, Wiley, New York **1983**, p. 77.

[12] T. Kremer, P. v. R. Schleyer, *Organometallics* **1997**, *16*, 737−746.

[13] J. R. Chesseman, G. W. Trucks, T. A. Keith, M. J. Frisch, *J. Chem. Phys.* **1996**, *104*, 5497−5509.

[14] G. Bottaccio, G. P. Chiusoli, *Chem. Commun.* **1966**, *24*, 618; G. Bottaccio, G. P. Chiusoli, M. Felicioli, *Gaz. Ch. Ital.* **1973**, *103*, 105−116; G. Bottaccio, G. P. Chiusoli, E. Alneri, M. Marchi, G. Lana, (Montedison S. p. A.) DE 2612577 C2, **1976**; G. Bottaccio, M. Marchi, G. P. Chiusoli, *Gaz. Ch. Ital.* **1976**, *106*, 831−841; G. Bottaccio, M. Marchi, *Gaz. Ch. Ital.* **1977**, *107*, 499−500.

[15] D. Walther, U. Ritter, S. Geßler, J. Sieler, M. Kunert, *Z. Anorg. Allg. Chem.* **1994**, *620*, 101−106; M. unert, M. Nauck, J. Sieler, E. Dinjus, *Chem. Ber.* **1997**, *130*, 1461−1465.

[16] M. Stiles, *J. Am. Chem. Soc.* **1959**, *81*, 2598−2599; H. L. Finkbeiner, G. W. Wagner, *J. Org. Chem*, **1963**, *28*, 215−217; N. M. Matsumura, Y. S. Sakaguchi, T. O. Ohba, H. Inoue, *J. Chem. Soc., Chem. Commun.* **1980**, 326−327.

[17] Z. Otwinowski, W. Minor, "Processing of X-ray Diffraction Data Collected in Oscillation Mode", in: Methods in Enzymology, vol. 276, *Macromolecular Crystallography, Part A*, edited by C.W. Carter & R.M. Sweet, pp. 307−326, Academic Press, **1997**.

[18] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467−473.

[19] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, **1993**.

[20] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary puplication no. CCDC-136058 and CCDC-136059. Copies of the data can be obtained free of Charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.)+44-1223/336.033; E-mail:deposit@ccdc.cam.ac.uk].

[21] E. Burtscher, H. Bider, R. Concin, O. Bobleter, *J. Chrom.* **1982**, *252*, 167−175.

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