Zirconium(II)- and Hafnium(II)-Assisted Reductive Coupling of Coordinated Carbonyl Groups Leading to Ketenylidene Complexes of Zirconium(IV) and Hafnium(IV)

Fausto Calderazzo, Ulli Englert, Alessandro Guarini, Fabio Marchetti, Guido Pampaloni,* Annalaura Segre and Giovanna Tripepi

Abstract: The biscyclopentadienyldicarbonyl derivatives of zirconium(II) and hafnium(II) ($[\mathrm{MCp_2(CO)_2}]$; M = Zr, Hf) promote the reductive coupling of coordinated carbon monoxide to give, in the presence of *N,N*-dialkylcarbamates of the tetravalent metals $[\mathrm{M(O_2CNR_2)_4}]$, the ketenylidene complexes $[\mathrm{M_3Cp_2(\mu_2\text{-}CCO)(\mu_3\text{-}O)(O_2CNR_2)_6}]$ (**1a**: M = Zr, R = Et; **1b**: M = Zr, R = *i*Pr; **2**: M = Hf, R = *i*Pr). The yields of the isolated zirconium complexes are as high as 60%, while that of the hafnium derivative is 40%. The X-ray crystal structure analysis of **1b** shows that it consists of trinuclear molecules, with the three zirconium atoms held together by the bidentate $\mathrm{C_2O}$ ligand, by the tridentate bridging oxide and by the bidentate carbamato groups. Labelling experiments with $[\mathrm{ZrCp_2(^{13}CO)_2}]$ show that the ketenylidene ligand originates from the coordinated CO groups. These ketenylidene complexes, which are rare examples of compounds containing a CCO but no CO ligand, are characterized by an intense IR band at about 2015 cm^{-1}, associated with the bridging $\mathrm{C_2O}$ ligand. The ketenylidene group of **1b** was readily removed and replaced by a bidentate μ-oxo ligand of the same hapticity by reaction with carbon dioxide or acetone or by thermal decomposition. The resulting product $[\mathrm{Zr_3Cp_2(\mu\text{-}O)(\mu_3\text{-}O)(O_2CN\mathit{i}Pr_2)_6}]$ (**3**) crystallizes in the same space group as **1b** and with similar cell constants and bond parameters.

Keywords
carbon–carbon coupling · carbonyl complexes · hafnium complexes · ketenylidene complexes · zirconium complexes

Introduction

Carbon–carbon bond formation is the most important elementary process in the Fischer–Tropsch reaction catalyzed by transition metals.[1] Reductive coupling of CO can also be triggered by strong reducing agents such as alkali metals. This leads to the formation of a series of oxocarbon anions of general formula $\mathrm{C}_n\mathrm{O}_n^{\,2-}$ (n = 2, 3, 4, 5 and 6), all of which are cyclic except for the acetylendiolate $[\mathrm{O\text{-}C{\equiv}C\text{-}O}]^{2-}$ (n = 2).[2] Carbon monoxide C–C coupling has been reported to occur with some zirconium(IV)[3] and tungsten(IV)[4] derivatives under mild conditions, by reductive elimination and by reductive coupling, respectively. It has, in addition, been reported that $[\mathrm{SmCp^*_2(THF)_2}]$ reacts with CO under pressure at room temperature to give $[\mathrm{Sm_2Cp^*_4(O_2CCCO)(THF)_2}]$,[5] where the ketenecarboxylato ligand is formed by reductive coupling of three CO molecules followed by further coupling and rearrangement.

The ketenylidene ligand $\mathrm{C_2O^{2-}}$, containing carbon in an average oxidation state of zero, is known in several transition metal complexes. It can be formed by the following routes: a) reductive dehalogenation or simple dehalogenation of a metal-coordinated $\mathrm{C{-}X}_n$ fragment, such as the reaction of $[\mathrm{Co_3(CO)_9C\text{-}Cl}]$ with $\mathrm{AlCl_3}$ in the presence of CO to give $[\mathrm{Co_3(CO)_9CCO]AlCl_4}$;[6] b) reductive cleavage (by an external reducing agent such as an alkali metal) in a trinuclear or tetranuclear metal cluster of a C–O bond, obtained by electrophilic activation of a metal-coordinated carbonyl group;[7] c) reaction of a low-valent metal complex with $\mathrm{C_3O_2}$.[8] Furthermore, metal ketenides of general formula $\mathrm{M_2CCO}$ have been prepared[9] from copper, silver or gold salts and ketene or ketene precursors.

To the best of our knowledge, only one case has been reported where the ketenylidene ligand is obtained directly from CO (presumably metal coordinated) through a metal-assisted reduction: Wolczanski and co-workers[10] treated the tantalum(III) complex $[\mathrm{Ta(OSi\mathit{t}Bu)_3}]$ with CO and thus obtained both the oxo and the ketenylidene complexes of tantalum(V). The idealized stoichiometry of this reaction is shown in Equation (1). The ketenylidene complex was identified spectroscopically and sug-

$$2[\mathrm{Ta(OSi\mathit{t}Bu)_3}] + 2\,\mathrm{CO} \longrightarrow [\mathrm{Ta(O)(OSi\mathit{t}Bu)_3}] + [\mathrm{Ta(CCO)(OSi\mathit{t}Bu)_3}] \quad (1)$$

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0947-6539/96/0204-0412 $ 15.00+.25/0

gested to be mononuclear. Presumably this four-electron process requires the concerted action of at least two metal centres; this suggests that the products of Equation (1) are the ultimate result of more complicated ligand modification and ligand transfer processes, which could not be identified under the conditions used in the tantalum(III) system.

In the course of our research into redox reactions involving early transition elements,[11] we have found that the dicarbonyl complexes of zirconium(II) and hafnium(II), $[MCp_2(CO)_2]$, but not $[TiCp_2(CO)_2]$, undergo rather selective redox processes leading to the formation of trinuclear complexes of the formally tetravalent metals and the ketenylidene ligand, which arises from the reductive coupling of coordinated CO. The presence of the *N,N*-dialkylcarbamate of the tetravalent metal $[M(O_2CNR_2)_4]$ is essential in this process; it does not apparently take part in the redox process, but simply cooperates in the assembly of the molecular fragments around the metal-coordinated ketenylidene ligand. We report the molecular structure of the zirconium(IV) ketenylidene derivative $[Zr_3Cp_2(\mu_2\text{-}CCO)(\mu_3\text{-}O)(O_2CN\mathit{i}Pr_2)_6]$ (**1b**) and of its reaction product with CO_2 or acetone $[Zr_3Cp_2(\mu_2\text{-}O)(\mu_3\text{-}O)(O_2CN\mathit{i}Pr_2)_6]$ (**3**). Part of this work has been communicated in a preliminary form.[12]

Results and Discussion

When $[ZrCp_2(CO)_2]$ was treated with one equivalent of $[Zr(O_2CNR_2)_4]$ (R = Et or *i*Pr) at room temperature, no reaction was observed after 15 h of stirring. The photochemical irradiation of the toluene solution resulted in the complete decomposition of the Zr^{II} carbonyl compound and the carbamato complex was recovered unchanged. In contrast, at reflux with exclusion of light a rapid colour change from red to deep brown was observed together with evolution of CO (monitored by IR spectroscopy[13]). A colourless crystalline material separated out when the reaction mixture was cooled down to room temperature. An IR spectrum of the solution revealed a sharp absorption band at 2016 cm^{-1}. The yield of isolated product, based on the zirconium(II) complex introduced, ranged from 30 to 60% both in the case of R = Et (**1a**) and R = *i*Pr (**1b**).

The product did not evolve carbon monoxide upon contact with a saturated solution of iodine in pyridine; it was thus ruled out that the absorption at 2016 cm^{-1} (slightly dependent on the solvent; 2013 cm^{-1} in the solid state) was due to a CO stretching vibration. The compound was found to be diamagnetic and characterized by IR absorptions typical of carbamato[14] and cyclopentadienyl derivatives.

The structure of the isopropyl compound **1b** was established unambiguously by X-ray crystal structure analysis. Figure 1 shows the molecular structure of $[Zr_3Cp_2(\mu_2\text{-}CCO)(\mu_3\text{-}O)(O_2CN\mathit{i}Pr_2)_6]$ (**1b**). It consists of an oxygen-centred triangle of zirconium atoms [Zr···Zr distance (mean value), 3.597(1) Å]. One of the zirconium atoms (Zr 1) is coordinated to four bridging carbamato groups and to the unique bidentate carbamato group; the other two atoms (Zr 2 and Zr 3) are each coordinated to three bridging carbamato ligands, to one cyclopentadienyl ring and to the bridging ketenylidene group. If the centroid of the Cp ligands is thought of as occupying one coordination site, the Zr 2 and Zr 3 atoms are in a distorted octahedral environment. The coordination around Zr 1 can be envisaged as being a capped, distorted octahedron, where the capping atom is one of the two oxygens of the unique "terminal" bidentate carbamato ligand (containing the C 11 carbon atom). Table 1 contains a selected list of bond lengths and angles.

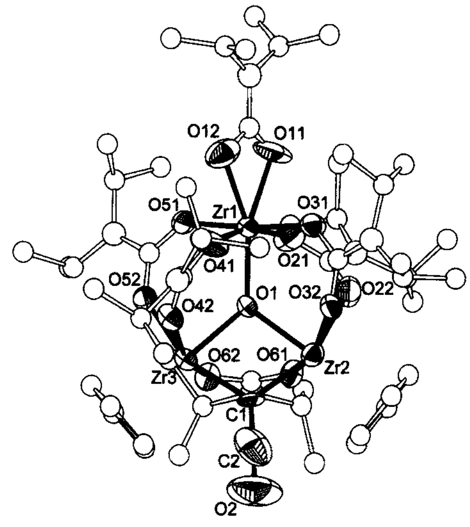


Fig. 1. ORTEP [41] projection of the molecular structure of $\mathbf{1b}\cdot0.5\,C_7H_8$ (thermal ellipsoids at the 50% probability level). The atoms of the carbamato and of the cyclopentadienyl ligands are represented by spheres of arbitrary radii.

Table 1. Selected bond lengths (Å) and angles (°) of $\mathbf{1b}\cdot0.5\,C_7H_8$ (estimated standard deviations in parentheses refer to the least significant digit).

Zr 1–O 1	2.049(5)	Zr 3–O 62	2.162(6)
Zr 1–O 11	2.237(7)	Zr 3–C 1	2.138(8)
Zr 1–O 21	2.163(7)	Zr 1–O 12	2.260(7)
Zr 1–O 41	2.121(7)	Zr 1–O 31	2.093(5)
Zr 1–C 11	2.61(1)	Zr 1–O 51	2.054(5)
Zr 2–O 22	2.193(7)	Zr 2–O 1	2.140(5)
Zr 2–O 61	2.149(6)	Zr 2–O 32	2.165(6)
Zr 3–O 1	2.126(5)	Zr 2–C 1	2.122(8)
Zr 3–O 42	2.108(6)	O 2–C 2	1.24(1)
Zr 3–O 52	2.203(6)	C 1–C 2	1.31(2)
O 1–Zr 1–O 11	149.7(3)	O 12–Zr 1-O 51	85.7(2)
O 1-Zr 1-O 12	152.2(3)	O 21-Zr 1-O 31	93.9(3)
O 1-Zr 1-O 21	80.1(2)	O 21-Zr 1-O 41	161.8(2)
O 1-Zr 1-O 31	93.9(2)	O 21-Zr 1-O 51	87,9(3)
O 1-Zr 1-O 41	81.8(2)	O 31-Zr 1-O 41	85.2(3)
O 1-Zr 1-O 51	91.3(2)	O 31-Zr 1-O 51	174,7(2)
O 1-Zr 1-C 11	177.4(4)	O 11-Zr 1-O 12	58.0(3)
O 11-Zr 1-O 21	69.7(3)	O 11-Zr 1-O 31	86.4(2)
O 11-Zr 1-O 41	128.3(3)	O 11-Zr 1-O 51	89.6(3)
O 12-Zr 1-O 21	127.3(3)	O 12-Zr 1-O 31	89.2(2)
O 12-Zr 1-O 41	70.9(3)	O 1-Zr 2-O 22	83.4(2)
O 1-Zr 2-O 32	84.0(2)	O 1-Zr 2-O 61	82,3(2)
O 1-Zr 2-C 1	73.7(2)	O 1-Zr 3-O 42	82,9(2)
O 1-Zr 3-O 52	83.8(2)	O 1-Zr 3-O 62	82,6(2)
O 1-Zr 3-C 1	73.6(2)	Zr 2-C 1-C 2	126,8(8)
Zr 3-C 1-C 2	128.1(8)	O 2-C 2-C 1	179.0(1)

The essentially planar $Zr_3(\mu_3\text{-}O)$ fragment [Zr 1–O 1 2.049(5), Zr 2–O 1 2.140(5), Zr 3–O 1 2.126(5) Å; Zr 1-O 1-Zr 2 125.0(2), Zr 1-O 1-Zr 3 130.0(3), Zr 2-O 1-Zr 3 103.8(2)°] has been observed in other zirconium(IV) complexes, for example, in $[Zr_3Cp_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)(\mu_2\text{-}PhCOO)_3]^+PhCOO^-\cdot Et_2O$[15] and $[Zr_3Cp^{\ddagger}_3Cl_3(\mu\text{-}Cl)_4(\mu_3\text{-}O)]$.[16] The cyclopentadienyl rings are essentially planar [Zr–C average distance = 2.60(1) Å] with an average C–C bond length of 1.38(2) Å.

The ketenylidene ligand is close to linear [C 1-C 2-O 2, 179(1)°], and the C 1–C 2 [1.31(2) Å] and the C 2–O 2 [1.24(1) Å] bond lengths are similar to the values reported for the structurally characterized μ_3-ketenylidene carbonyl complexes reported in the literature.[17] It is noteworthy that compound **1b** represents the first example of a structurally characterized μ_2-CCO complex. Other complexes of this type for which the structure has been inferred on the basis of spectroscopic and analytical data are $\{(C_8H_{14})(CO)Rh(\mu_2\text{-}CCO)Cl\}_n$ [18] and $\{(C_2H_4)(acac)(CO)Rh(\mu_2\text{-}CCO)\}_2$.[19]

The surprising formation of **1** can be represented by Equation (2) (**1a**, R = Et; **1b**, R = *i*Pr). In the case of **1b** the reaction

$$3[ZrCp_2(CO)_2] + 3[Zr(O_2CNR_2)_4] \longrightarrow \underset{\mathbf{1}}{2[Zr_3Cp_2(\mu_2\text{-}CCO)(\mu_3\text{-}O)(O_2CNR_2)_6]} + 2CO + 2Cp^{\bullet} \qquad (2)$$

was studied in detail and the following facts were established:

1) GC-MS analysis of the crude solution after separation of the zirconium complex and exposure to air showed the presence of dicyclopentadiene, probably formed by hydrogen addition to $Cp^{\bullet}$ followed by dimerization.
2) The reaction in mesitylene (1,3,5-$Me_3C_6H_3$) begins at around 100 °C and is fast at 139 °C (see Experimental Procedure).
3) The quantity of gas evolved in the reaction corresponds to a $CO/[ZrCp_2(CO)_2]$ molar ratio of 1.00. The higher value with respect to the theoretical one [0.67, see Eq. (2)] is due to the thermal decomposition of $[ZrCp_2(CO)_2]$. In a blank experiment conducted with $[ZrCp_2(CO)_2]$ in the absence of the *N,N*-diisopropylcarbamato complex, CO was produced corresponding to a $CO/[ZrCp_2(CO)_2]$ molar ratio of 0.41. The $CO/[ZrCp_2(CO)_2]$ molar ratio due to reaction (2) in the first experiment is therefore actually 0.59.
4) Complex **1b** is not stable under the reaction conditions. The maximum concentration of the ketenylidene complex **1b** is achieved after approximately 30 min (see Fig. 2).

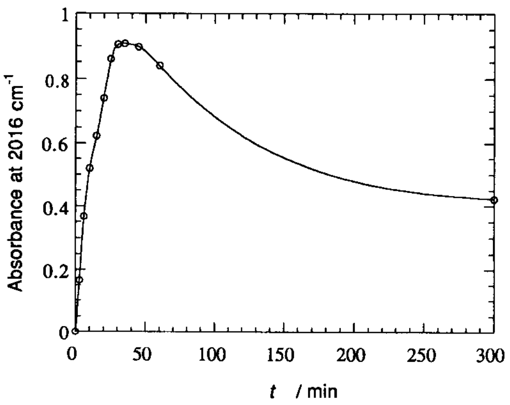


Fig. 2. Reaction of $[ZrCp_2(CO)_2]$ with $[Zr(O_2CN\textit{i}Pr_2)_4]$ in refluxing toluene. Plot of the absorbance of the stretching vibration of the ketenylidene ligand at 2016 cm^{-1} ($\varepsilon = 1294\ cm^{-1}\,M^{-1}$, $b = 0.01$ cm) as a function of time.

$[ZrCp^{*}_{2}(CO)_2]$ was found to be unchanged after heating in the presence of an equimolar amount of $[Zr(O_2CN\textit{i}Pr_2)_4]$ in toluene solution. Since the formation of **1b** requires M–Cp dissociation, the higher stability of the M–Cp* bond with respect to the unsubstituted ligand[20] may account for this observation.

In order to throw some light onto the mechanism of formation of the ketenylidene group, we carried out some experiments using the ^{13}C-labelled compounds $[ZrCp_2(^{13}CO)_2]$ or $[Zr(O_2{}^{13}CN\textit{i}Pr_2)_4]$. With an equimolar mixture of $[ZrCp_2(CO)_2]$ and $[Zr(O_2{}^{13}CN\textit{i}Pr_2)_4]$, $[Zr_3Cp_2(\mu_2\text{-}CCO)(\mu_3\text{-}O)(O_2{}^{13}CN\textit{i}Pr_2)_6]$ was formed; this was deduced from the fact that the absorption band at $\tilde{\nu} = 2016\ cm^{-1}$ was not shifted, while the bands due to the C=O and C=N stretching vibrations of the carbamato ligand shifted from 1530, 1510 and 1360 cm^{-1} in the unlabelled compound to 1495, 1460 and 1335 cm^{-1}, respectively, in the labelled compound. A similar shift of the carbamato absorptions is observed on going from $[Zr(O_2CN\textit{i}Pr_2)_4]$ (1535, 1500, 1360 cm^{-1})[21] to $[Zr(O_2{}^{13}CN\textit{i}Pr_2)_4]$ (1505, 1465, 1335 cm^{-1}).

The reaction of $[ZrCp_2(^{13}CO)_2]$ with $[Zr(O_2CN\textit{i}Pr_2)_4]$ under comparable conditions afforded a solution with a strong absorption at 1951 cm^{-1} ($\Delta\tilde{\nu} = 62\ cm^{-1}$). This result shows that the labelled ketenylidene complex $[Zr_3Cp_2(\mu_2\text{-}{}^{13}C^{13}CO)(\mu_3\text{-}O)(O_2CN\textit{i}Pr_2)_6]$ ([^{13}C]**1b**) had been formed. The $^{13}C\{^1H\}$ spectrum of the product in solution shows two doublets at $\delta = 181.5$ and 112.4 ($J_{CC} = 78.9$ Hz), attributed to the α and β ketenylidene carbon atoms, respectively. Similar values have been reported for other ketenylidene complexes described in the literature.[17]

In conclusion, the labelling experiments have shown that the μ_2-ketenylidene ligand in **1** is formed by reductive coupling of the zirconium-coordinated carbonyl groups; the four equivalents of electrons required by Equation (3) for each ketenylidene

$$2CO \longrightarrow \text{“}\mu_2\text{-CCO”} + \text{“}\mu_3\text{-O”} \qquad (3)$$

ligand formed are provided by zirconium(II) and by the homolytic cleavage of the M–Cp bond [see Eq. (2)].

In the case of hafnium, the reaction between equimolar quantities of $[HfCp_2(CO)_2]$ with $[Hf(O_2CN\textit{i}Pr_2)_4]$ proceeded slowly at the reflux temperature of the solution. This is consistent with the lower reactivity generally observed for 5d elements when compared to their 4d congeners.[22] The product **2** was isolated

$$[Hf_3Cp_2(\mu_2\text{-}CCO)(\mu_3\text{-}O)(O_2CN\textit{i}Pr_2)_6] \quad \mathbf{2}$$

as crystalline material in an average yield of 40%. The somewhat lower yield compared to the zirconium analogue is due to the slower rate of formation; in spite of the higher thermal stability of **2** under the reaction conditions, the net result is a lower concentration of the product in solution. One way of improving yields is to recover the less soluble reaction product by filtration after 24 h of refluxing in toluene, and to reflux the resulting solution for an additional 24 h in order to convert more starting material. A GC-MS analysis of the solution from the reaction, after exposure to air, showed the presence of dicyclopentadiene and 1,1'-dihydrofulvalene as major products; this suggests that the reaction proceeds in a similar way to the zirconium case. In Table 2, the main spectroscopic data of **1b** and **2** are reported: their similarity leaves little doubt that the hafnium ketenylidene complex **2** has the same overall structure as **1b**.

Table 2. Spectroscopic data of **1b** and **2**.

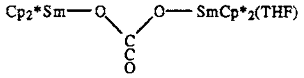
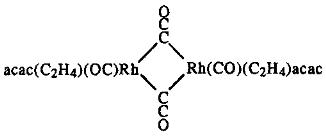
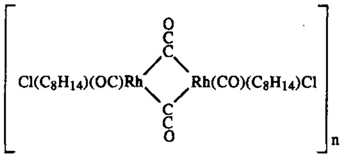
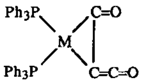
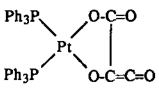
	1b	**2**
IR [a]		
$\tilde{\nu}$(Cp)	3110	3107
$\tilde{\nu}$(CCO)	2013	2021
$\tilde{\nu}(O_2CN)$	1580, 1530, 1510, 1385, 1360	1584, 1538, 1515, 1385, 1360
^1H NMR [b]		
$\delta(CH_3)$	1.2	1.2
δ(CH)	3.8	3.8
δ(Cp)	6.7	6.7

[a] Nujol or polychlorotrifluoroethylene mulls; $\tilde{\nu}/cm^{-1}$. [b] $[D_6]$benzene, 20 °C, δ (ppm with TMS as reference).

The IR spectra in the 2100–2000 cm^{-1} region of the ketenylidene compounds of zirconium and hafnium as well as those reported in the literature, deserve some comment. Owing to the fact that the CCO ligand absorbs in the same region as metal-bonded carbonyl groups, the assignment is not straightforward when carbonyl ligands are also present.[23] Unfortunately, until now, no solid-state X-ray data have been available for complexes where the carbonyl groups were absent[10] or where the carbonyl stretching vibrations were easily assigned.[18, 19] Compound **1b** therefore represents the first case where both the solid-state structure is known and carbonyl ligands are absent; it is also the first time the ketenylidene IR stretching vibration can be assigned unequivocally in a well-defined coordination geometry of the ligand.

Table 3 reports the IR spectra in the 2100–2000 cm^{-1} region for some compounds containing the C_2O sequence of atoms. The ketenylidene absorption bands lie within a range of around 200 cm^{-1} and are almost independent of the substituent on the β-carbon atom. For example, the tantalum(III) compound $[(tBuSiO)_3Ta\text{-}CCO]$, thought to be mononuclear,[10] shows a stretching vibration at 2076 cm^{-1}, while the silver ketenide Ag_2CCO, containing "rod-like" CCO groups interacting with four silver atoms,[9c, d] absorbs at 2060 cm^{-1}. Moreover, it is important to note that ketene derivatives show a strong absorption at 2151 cm^{-1} in the gas phase,[25] which is not strongly affected by the substitution at the β-carbon atom.[28] These data, which are at variance with the conclusions of Wolczanski and co-workers,[10] suggest that the coupling between the C–O and the C–C stretching vibrations within the C_2O ligand is *not strong*.

Table 3. Selected IR data in the 2200–1900 cm^{-1} region of compounds containing the C_2O group.

Compound	CCO Coordination Mode	IR Spectrum (cm^{-1}) [a]	Reference
CCO		1969 (argon matrix)	[24]
H_2CCO		2151 (gas phase)	[25]
Ag_2CCO	μ_4-CCO [b]	2060 (nujol mull)	[9c,d]
Au_2CCO		2015 (nujol mull)	[9b]
Cu_2CCO		2030 (nujol mull)	[9a]
$Zr_3Cp_2[\mu_2\text{-}CCO](\mu_3\text{-}O)(O_2CN^iPr_2)_6$	μ_2-CCO [c]	2016 (toluene)	This work
$Hf_3Cp_2[\mu_2\text{-}CCO](\mu_3\text{-}O)(O_2CN^iPr_2)_6$	μ_2-CCO [c]	2024 (toluene)	This work
$(Bu^t_3SiO)_3TaCCO$	terminal CCO [d]	2076 (cyclohexane)	[10b]
$(CO)(PR_3)_2Rh(CCO)SiMe_3$	μ_2-CCO [d]	2020, 1953 (CO) (benzene)	[26]
$Rh(Al_2O_3)/CCO$	[e]	2155	[27]
	μ_2-CCO [d]	2100 (KBr)	[5]
	μ_2-CCO [d]	2080, 2010 (CO) (KBr)	[19]
	μ_2-CCO [d]	2080, 2015 (CO) (KBr)	[18]
	[d]	M=Ni, 2086 (CH_2Cl_2) M=Pt, 2080 (CH_2Cl_2)	[18]
	[d]	2080 (CH_2Cl_2)	[18]

[a] Unless otherwise stated, the wavenumbers refer to the absorption of the ketenylidene ligand. [b] Coordination mode deduced from X-ray powder diffraction data. [c] Coordination mode from X-ray single-crystal structure analysis. [d] Coordination mode proposed on the basis of analytical and spectroscopic properties. [e] Coordination mode proposed on the basis of analytical and spectroscopic properties of the adsorbed species.

The isolation and characterization of compounds **1** and **2** allows us to speculate on the reactions of CO adsorbed at metal surfaces. If the dicarbonyl complexes of zirconium(II) and hafnium(II) are taken as model compounds, CO chemisorption at metal surfaces or reduced metal oxides might be expected to lead to surface-coordinated ketenylidene groups as intermediates or as final products.[29] The proximity of metal atoms in **1** and **2** may represent a situation similar to that of exposed atoms on a metal surface. Moreover, the strong IR absorption of the CCO ligand in the same spectral region as that of terminally bonded metal-coordinated carbonyl groups may be leading to misinterpretation of the spectroscopic data for heterogeneous systems. Some years ago, Shriver and co-workers proposed that the CCO fragment may exist on a "carbide closest-packed metal surface in the presence of CO" and that "the surface carbide species on a Fischer–Tropsch catalyst may be present as CCO".[23] In addition, it has been suggested that IR-active CCO sequences absorbing around 2100 cm^{-1} form when MgO is exposed to carbon monoxide.[30] In an IR spectroscopic study on the decomposition of carbon suboxide on an alumina-supported rhodium surface,[27] Pei and Worley suggested that CCO groups were present.

CO_2 or acetone reacted rapidly with the ketenylidene complex **1b** to replace the C_2O ligand with a bridging oxide. The same product was obtained by thermal decomposition. A similar reaction with CO_2 was observed with the hafnium derivative **2**. The inorganic product of the reaction with CO_2 and the organic substances obtained in the reaction with acetone were studied in detail and are described below.

The reaction of **1b** with carbon dioxide in toluene at or below room temperature gave a deep orange solution within minutes; an IR spectrum of the solution did not show any absorption in the 2100–2000 cm^{-1} region. By layering the toluene solution with heptane, crystalline **3** was obtained in 48% yield, and characterized by analytical and spectroscopic methods. The mass spectrum of **3** contains a peak at $m/z = 1297$ attributed to the protonated molecular ion $[Zr_3Cp_2(O)_2(O_2CN\textit{i}Pr_2)_6H]^+$; this suggests that **3** is of the same nuclearity as **1b**.

A single-crystal X-ray structure analysis of **3** (Fig. 3, Table 4) confirmed its molecular structure. The main structural

$[Zr_3Cp_2(\mu_2\text{-}O)(\mu_3\text{-}O)(O_2CN\textit{i}Pr_2)_6]$ **3**

difference to **1b** is that the ketenylidene group has been replaced by a bridging oxide of the same hapticity and in the same position. Like **1b**, **3** also contains an oxo-centred triangle of zirconium atoms, two of which are bound to cyclopentadienyl rings, bridging carbamates and the μ_2-oxo group; the third zirconium atom is linked to bridging carbamato ligands and to the unique terminal carbamato ligand. Again, the Zr1 ··· Zr2 and

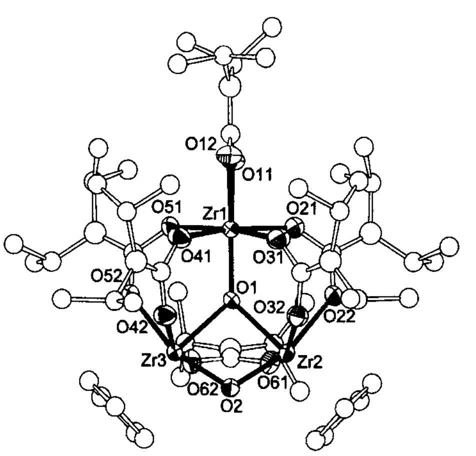


Fig. 3. ORTEP [41] projection of the molecular structure of **3** (thermal ellipsoids at the 50% probability level). The atoms of the carbamato and of the cyclopentadienyl ligands are represented by spheres of arbitrary radii.

Table 4. Selected bond lengths (Å) and angles (°) of **3** (estimated standard deviations in parentheses refer to the least significant digit).

Zr1–O1	1.993(2)	Zr1–O11	2.286(3)
Zr1–O12	2.253(3)	Zr1–O21	2.125(3)
Zr1–O31	2.145(3)	Zr1–O41	2.150(3)
Zr1–O51	2.110(3)	Zr1–C11	2.658(4)
Zr2–O1	2.161(2)	Zr2–O2	1.953(3)
Zr2–O22	2.207(3)	Zr2–O32	2.151(3)
Zr2–O61	2.163(3)	Zr3–O1	2.189(2)
Zr3–O2	1.955(3)	Zr3–O42	2.138(3)
Zr3–O52	2.187(3)		
O1-Zr1-O11	140.2(1)	O2-Zr3-O42	95.4(1)
O1-Zr1-O12	162.6(1)	O2-Zr3-O62	91.8(1)
O1-Zr1-O21	87.6(1)	O42-Zr3-O62	158.0(1)
O1-Zr1-O31	88.0(1)	O41-Zr1-O51	81.3(1)
O1-Zr1-O41	89.0(1)	O1-Zr2-O2	76.5(1)
O1-Zr1-O51	88.1(1)	O1-Zr2-O22	84.7(1)
O11-Zr1-O12	57.2(1)	O1-Zr2-O32	82.6(1)
O11-Zr1-O21	70.6(1)	O1-Zr2-O61	79.4(1)
O11-Zr1-O31	120.1(1)	O2-Zr2-O22	161.2(1)
O11-Zr1-O41	120.0(1)	O12-Zr1-O51	100.8(1)
O11-Zr1-O51	71.9(1)	O21-Zr1-O31	82.6(1)
O12-Zr1-O21	102.3(1)	O21-Zr1-O51	113.3(1)
O12-Zr1-O31	79.2(1)	O31-Zr1-O41	82.5(1)
O12-Zr1-O41	77.7(1)	O2-Zr2-O32	95.9(1)
O21-Zr1-O41	164.9(1)	O22-Zr2-O32	82.0(1)
O31-Zr1-O51	163.4(1)	O1-Zr3-O42	82.7(1)
O2-Zr2-O61	92.3(1)	O1-Zr3-O62	79.0(1)
O22-Zr2-O61	83.6(1)	O2-Zr3-O52	160.2(1)
O32-Zr2-O61	157.9(1)	O42-Zr3-O52	84.0(1)
O1-Zr3-O2	75.8(1)	Zr1-O1-Zr3	129.5(1)
O1-Zr3-O52	84.6(1)	Zr2-O2-Zr3	110.0(1)

Zr1 ··· Zr3 distances are very similar (3.72 and 3.76 Å, respectively), and the Zr2 ··· Zr3 distance somewhat shorter (3.36 Å). It should be noted that the *R* value for **3** is 0.038 while the corresponding parameter for **1b** is 0.064. The difference may be related to the presence of disorder in the clathrated toluene and in one of the carbamato ligands in **1b**.

The reaction of **1b** with CO_2 is fast even in the absence of solvents, and **3** can be obtained in analytically and spectroscopically pure form by recrystallization from toluene/heptane mixtures with yields ranging from 50 to 60%. It is important to note that, based on gas-volumetric experiments, **1b** in toluene absorbs CO_2 in a CO_2/**1b** molar ratios of up to 0.86.

Similar observations were made in the case of the hafnium analogue. Compound **2** in toluene absorbed CO_2 in a CO_2/**2** molar ratio of up to 0.80. Complex **4** was isolated on a preparative scale in 54% yield and characterized by analytical and spectroscopic methods. It was again possible to detect the protonated molecular ion $[Hf_3Cp_2(O)_2(O_2CN\textit{i}Pr_2)_6H]^+$ at *m*/*z* = 1563.

$[Hf_3Cp_2(\mu_2\text{-O})(\mu_3\text{-O})(O_2CN\textit{i}Pr_2)_6]$ **4**

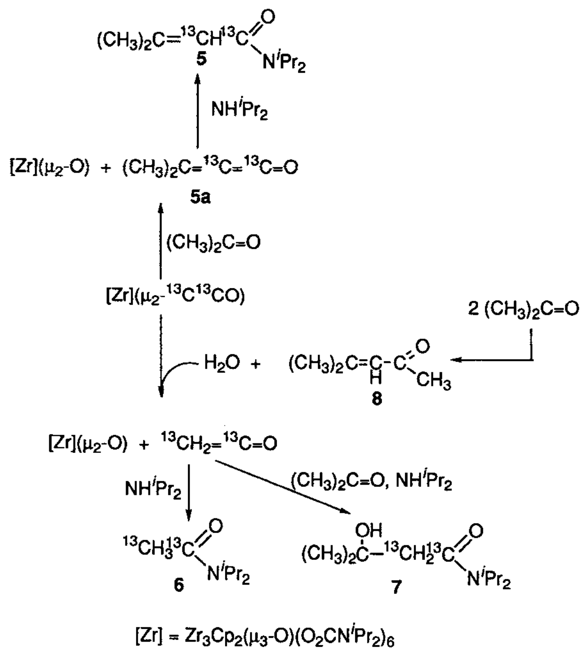
Although the inorganic compounds formed in the reaction of **1b** and **2** with carbon dioxide have been isolated and characterized, we have not been able to follow the fate of the CCO group. In agreement with the nucleophilic character of the α-carbon atom of organic ketenes,[31] a reaction such as that shown in Equation (4) might be taking place, but we do not, as yet, have

$$[M_3Cp_2(\mu_2\text{-CCO})(\mu_3\text{-O})(O_2CN\textit{i}Pr_2)_6] + CO_2 \longrightarrow [M_3Cp_2(\mu_2\text{-O})(\mu_3\text{-O})(O_2CN\textit{i}Pr_2)_6] + \text{“}C_3O_2\text{”} \qquad (4)$$

any evidence for the formation of carbon suboxide or any of its derivatives.[31a, 32]

The formation of the μ-oxo derivatives **3** and **4** shows that the ketenylidene fragment can be readily displaced. We decided to carry out a detailed investigation of the deep yellow solution obtained in the reaction of **1b** with acetone. An IR spectrum of the solution recorded shortly after dissolution of **1b** in neat acetone showed no absorption in the 2100–1900 cm^{-1} region. After removal of the volatiles, the residue had the same analytical and spectroscopic properties as **3**, after recrystallization from toluene/heptane.

The GC-MS analysis of the distillate collected from a reaction of the labelled compound $[^{13}C]$**1b** with acetone revealed the presence of **5**, **6**, **7** and **8** (Scheme 1). Compound **5** contains the fragments derived from acetone and the ketenylidene ligand plus an N*i*Pr₂ residue, and is probably formed by reaction of dimethylmethyleneketene (**5a**)[31c] with diisopropylamine. The presence of adventitious water, or water produced in the zirconium-assisted dehydration of acetone to give **8**, leads to the formation of free amine and compounds **6** and **7**. In this connection, ^{13}C NMR spectroscopy has demonstrated that **1b** reacts with water at low temperature to give acetic acid with the intermediate formation of ketene. In fact, the $^{13}C\{^1H\}$ NMR spectrum of



Scheme 1. Reaction pathways proposed in the reaction of $[^{13}C]$**1b** with acetone.

$[Zr_3Cp_2(\mu_2\text{-}^{13}C^{13}CO)(\mu_3\text{-}O)(O_2CN\mathit{i}Pr_2)_6]$ ([^{13}C]**1b**) at −80 °C shows the two doublets due to the labelled carbon atoms at 180.9 and 112.4. In the presence of air, immediate appearance of a doublet at $\delta \approx 2$ ($J_{C-C} = 100.6$ Hz) assigned to the methylenic carbon atom of ketene is observed. This assignment was confirmed by recording a ^{1}H-coupled ^{13}C spectrum: a doublet of triplets ($J_{C-H} = 166.8$ Hz) due to the coupling of ^{13}C with hydrogen was present at $\delta \approx 2$. On warming the solution, the ketene peak disappeared, and the proton-coupled ^{13}C NMR spectrum showed a doublet at $\delta = 179.1$ ($J_{C-C} = 70.4$ Hz) and a doublet of quartets at $\delta = 24.8$ characteristic of acetic acid. These experimental observations are summarized in Scheme 1.

Conclusions

This study has shown that CO precoordinated to zirconium or hafnium can be converted to a C_2O ligand in a trinuclear zirconium or hafnium complex. The ketenylidene ligand is formally a dianion, and the metal cations in these complexes are therefore in the IV oxidation state. Dicarbon monoxide is an unstable molecule that can be produced from CO [Eq. (5)], for example,

$$2CO \longrightarrow C_2O + O \tag{5}$$

by pulse radiolysis in the gas phase.[33] The enthalpy of the reaction has been estimated[34] to be 206 ± 5 kcal mol^{-1}. At least part of the driving force for the formation of C_2O within the zirconium amd hafnium complexes evidently originates from the formation of the triply bridging oxo ligand. The transformation of CO to C_2O is therefore made possible by the presence of highly electrophilic elements. It should be noted in this context that the only other system known to trigger the reductive coupling of CO to give a metal-bonded dicarbon monoxide ligand is a tantalum(III) complex.[10]

Experimental Procedure

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified nitrogen or argon. Solvents were dried by conventional methods prior to use. IR spectra of solutions or mulls (nujol and/or polychlorotrifluoroethylene) prepared under rigorous exclusion of moisture and air were measured on Perkin-Elmer 283 and FT-1725X instruments. ^{1}H and ^{13}C NMR spectra were measured on Varian Gemini 200BB and Bruker AM 200 instruments. Mass spectra (desorption chemical ionization with isobutane as the reagent gas) were measured on a Finnigan MAT 8400 double-focusing reverse geometry instruments. GC-MS analyses were performed on a Finnigan INCOS 50 quadrupole instrument operated in the electron impact mode at 70 eV. Gas analyses were performed on a DANI 3200 gas chromatograph equipped with a molecular sieve 5A column. The zirconium and hafnium content of the complexes was obtained by ICP-AES analysis or by gravimetric determination as ZrO_2 or HfO_2. ^{13}CO (Merck, Sharp and Dohme, 99.5% enrichment) was used without purification. $^{13}CO_2$ was obtained by treatment of $Ba^{13}CO_3$ (Aldrich, 99.5% enrichment) with concentrated sulfuric acid. Commercial $ZrCl_4$ (Fluka) and $HfCl_4$ (Cezus Chemie, zirconium content < 0.2%) were treated in refluxing $SOCl_2$ and dried at 200 °C under reduced pressure. $[ZrCp_2Cl_2]$ [35], $[HfCp_2Cl_2]$ [35] and $[M(O_2CNR_2)_4]$ (R = Et, *i*Pr; M = Zr, Hf) [21] were prepared according to literature procedures. $[Zr(O_2{}^{13}CN\mathit{i}Pr_2)_4]$ was obtained [21] by using ^{13}C-labelled carbon dioxide [IR (nujol and polychlorotrifluoro ethylene, wavenumbers in italics shift in labelled compound): $\tilde{\nu}$ = 2980 (m–s), 2960 (m), 2940 (m–w), *1505* (vs), *1465* (vs), 1380 (m), 1370 (m–w), *1335* (vs), 1200 (m), 1160 (m–s), 1140 (m), 1060 (m–s), 810 (s), *770* (s), 620 (s) and 515 (m) cm^{-1}]. The dicarbonyl derivatives $[MCp_2CO_2]$ (M = Zr, Hf) were prepared by modifying the published procedure [36], by using a CO pressure of ca. 5 atmosphere in the reductive carbonylation of $[MCp_2Cl_2]$. $[ZrCp_2(CO)_2]$, 67% yield [IR (toluene): $\tilde{\nu}$ (ε, cm^{-1} M^{-1}) = 1969 (2537), 1876 (4330) cm^{-1}]; $[HfCp_2(CO)_2]$, 46% yield [IR (toluene): $\tilde{\nu}$ (ε, cm^{-1} M^{-1}) = 1959 (2293), 1862 (4024) cm^{-1}]. $[ZrCp_2(^{13}CO)_2]$ [IR (THF): $\tilde{\nu}$ = 1921 (s) and 1828 (s) cm^{-1}; IR (heptane): $\tilde{\nu}$ = 1930 (s) and 1844 (s) cm^{-1}] was prepared in a 40% yield at atmospheric pressure of ^{13}CO by a similar procedure.

Synthesis of $[Zr_3Cp_2(\mu_2\text{-}CCO)(\mu_3\text{-}O)(O_2CNR_2)_6]$ (**1a**: R = Et; **1b**: R = *i*Pr): The preparation of **1b** is described in detail; **1a** was prepared by the same procedure. A solution of $[ZrCp_2(CO)_2]$ (1.89 g, 6.8 mmol) and $[Zr(O_2CN\mathit{i}Pr_2)_4]$ (4.83 g, 7.2 mmol) in toluene (30 mL) was refluxed for 35 min. After the reaction had cooled to room temperature, an IR spectrum of the solution showed a strong absorption at 2016 cm^{-1}. The IR spectrum of the gas phase had absorptions at 2173 and 2117 cm^{-1} typical of carbon monoxide [13]. Colourless crystals separated out from the brown solution on standing. They were collected by filtration, washed with heptane (3 × 5 mL) and dried in vacuo at room temperature (1.97 g) The solution was evaporated to dryness under reduced pressure at room temperature, and heptane (30 mL) added; the resulting suspension was filtered, and the colourless solid dried in vacuo (1.39 g). The diamagnetic, colourless solid was identified as **1b**.

1b: total yield 56%; spectroscopic yield 80%. Anal. found: C 48.4, H 7.2, N 6.1, CO_2 19.0, Zr 20.1. Calcd for $C_{54}H_{94}N_6O_{14}Zr_3$: C 48.9, H 7.1, N 6.3, CO_2 19.9, Zr 20.6%. IR (nujol and polychlorotrifluoroethylene): $\tilde{\nu}$ = 3110 (m–w), 2970 (m–s), 2930 (m), 2870 (w), 2013 (s), 1964 (w), 1580 (w), 1530 (vs), 1510 (vs), 1385 (s), 1360 (vs), 1210 (m), 1160 (m–w), 1135 (w), 1075 (m), 1020 (m–w), 900 (w), 870 (w), 820 (m), *800* (m–s), 785 (vs), 730 (m–w), *680* (m–s), *660* (w), *600* (m–s), *570* (m–s), 530 (m–s) and 470 (m–w) cm^{-1}. IR (THF): $\tilde{\nu}$ = 2015 cm^{-1}; IR (CH_2Cl_2): $\tilde{\nu}$ = 2010 cm^{-1}; IR (toluene): $\tilde{\nu}$ (ε, cm^{-1} M^{-1}) ≈ 2016 (1788) cm^{-1}. ^{1}H NMR (200 MHz, [D$_6$]benzene, 25 °C): δ = 6.7 (s, 10H; Cp), 3.8 (multiplet, 6H; CH), 1.2 (multiplet, 72H; CH_3); ^{13}C NMR ([D$_8$]toluene, 25 °C): δ = 181.5 (C*C*O); 169.5, 162.4, 161.0 (*C*O$_2$); 112.4 (*C*CO); 114 (Cp); 46.9, 45.7 [*C*H(CH$_3$)$_2$]; 22 (*C*H$_3$, partial overlap with solvent signals). The reaction was repeated several times, with reproducible yields of around 60%. The mass spectrum of the filtrate showed the presence of *i*Pr$_2$NCOCH$_3$ (m/z = 143) and dicyclopentadiene (m/z = 132).

1a: pale brown, 30–60% yield. Anal. found: C 42.9, H 6.1, N 7.4, CO_2 22.4, Zr 21.4. Calcd for $C_{42}H_{70}N_6O_{14}Zr_3$: C 43.6, H 6.1, N 7.3, CO_2 23.6, Zr 22.8%. IR (nujol and polychlorotrifluoroethylene): $\tilde{\nu}$ = 3110 (m–w), 2990 (m), 2940 (m), 2880 (w), 2013 (s), 1964 (w), 1580 (s), 1530 (vs), 1460 (vs), 1440 (vs), 1380 (s), 1320 (vs), *1215* (m–s), *1095* (m), *1070* (m), *1010* (m), *970* (m), *935* (m–w), *830* (m), *820* (m), 800 (s), 795 (s), 785 (s), 670 (m–s), 630 (m–s), 540 (w) and 430 (m) cm^{-1}. ^{1}H NMR (200 MHz, [D$_6$]benzene, 25 °C): δ = 6.6 (s, 10H; Cp), 3.12 (multiplet, 12H; CH_2), 0.94 (multiplet, 18H; CH_3).

Both compounds are slightly soluble in aliphatic hydrocarbons, and soluble in aromatic hydrocarbons and THF; they react slowly with CH_2Cl_2 and instantaneoulsly with acetone (vide infra).

$[Zr_3Cp_2(\mu_2\text{-}CCO)(\mu_3\text{-}O)(O_2{}^{13}CN\mathit{i}Pr_2)_6]$ was prepared by reaction of $[ZrCp_2(CO)_2]$ with $[Zr(O_2{}^{13}CN\mathit{i}Pr_2)_4]$ and characterized by ^{13}C NMR and IR spectroscopy. IR (nujol and polychlorotrifluoroethylene mulls; wavenumbers in italics shift in labelled compound): $\tilde{\nu}$ = 3110 (m–w), 2970 (m–s), 2930 (m), 2870 (w), 2013 (s), 1964 (w), *1495* (vs), *1460* (vs), 1385 (s), *1335* (vs), 1210 (m), 1160 (m–w), 1135 (w), 1075 (m), 1020 (m–w), 900 (w), 870 (w), 815 (m–s), 790 (s), 775 (m), 760 (m), 730 (m–w), 680 (m–s), 660 (w), 600 (m–s), 570 (m–s), 530 (m–s) and 470 (m–w) cm^{-1}.

$[Zr_3Cp_2(\mu_2\text{-}^{13}C^{13}CO)(\mu_3\text{-}O)(O_2CN\mathit{i}Pr_2)_6]$ ([^{13}C]**1b**) was obtained by reaction of $[ZrCp_2(^{13}CO)_2]$ with $[Zr(O_2CN\mathit{i}Pr_2)_4]$. The IR spectrum in toluene shows a strong absorption at 1951 cm^{-1}. The IR spectrum in nujol/ polychlorotrifluoroethylene is superimposable on that of the unlabelled compound, except for the strong absorption at 2013 cm^{-1} which was shifted to 1951 cm^{-1}. The ^{13}C NMR (50.31 MHz, [D$_6$]benzene, 25 °C) spectrum shows two doublets at δ = 181.5 (C*C*O) and 112.4 (*C*CO) (J_{CC} = 78.9 Hz).

Gas-volumetric study of the reaction of $[ZrCp_2(CO)_2]$ with $[Zr(O_2CN\mathit{i}Pr_2)_4]$: A solution of $[ZrCp_2(CO)_2]$ (0.154 g, 0.55 mmol) and $[Zr(O_2CN\mathit{i}Pr_2)_4]$ (0.521 g, 0.78 mmol) in mesitylene (9 mL) was saturated with CO. The temperature was slowly raised from 19.5 to 129 °C. The volume readings were corrected for the expansion with increasing temperature during the experiment by performing separate experiments under identical conditions but without the zirconium complexes. The corrected volumes of gas evolved were measured as a function of temperature and time; Figure 4 shows the CO/Zr^{II} molar ratios as a function of temperature (top) and reaction time (bottom). After ca. 2 h the heating was interrupted and the reaction mixture allowed to cool down to 19.5 °C. It was found that 5.56×10^{-4} mol of gas were produced (CO by gas chromatography) corresponding to a CO/$[ZrCp_2(CO)_2]$ molar ratio of 1.00.

Gas-volumetric study of the thermal stability of $[ZrCp_2(CO)_2]$: A solution of $[ZrCp_2(CO)_2]$ (0.115 g, 0.41 mmol) in mesitylene (8 mL) was saturated with CO. The temperature was slowly raised from 21 to 139 °C: the volume of gas, corrected as described above, was measured as a function of time and temperature. The volume difference at room temperature, at the end of the experiment, corrected for the vapour pressure of the solvent gave the CO/$[ZrCp_2(CO)_2]$ molar ratio. In the time between 44 and 135 min and in the range of temperatures $98 \leq T \leq 120$ °C, as for the synthesis of **1b**, 0.17 mmol of CO were produced corresponding to a CO/$[ZrCp_2(CO)_2]$ molar ratio of 0.41.

Gas-volumetric study of the thermal stability of 1b: A suspension of **1b** (0.103 g, 0.077 mmol) in mesitylene (10 mL) was saturated with CO. The temperature was slowly raised from 21 to 139 °C. The variation of the volume of gas evolved, correct-

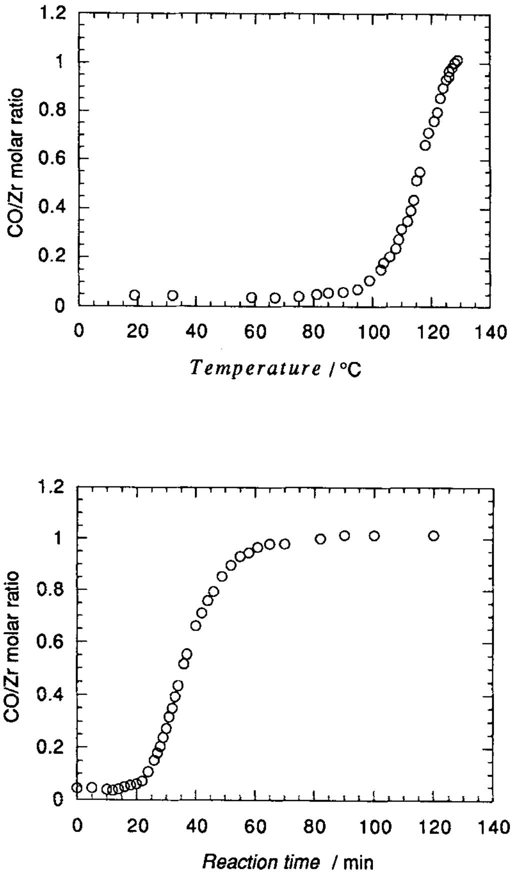


Fig. 4. Reaction of $[ZrCp_2(CO)_2]$ with $[Zr(O_2CN\textit{i}Pr_2)_4]$ in mesitylene under an atmosphere of CO. Plot of the $CO/[ZrCp_2(CO)_2]$ molar ratio as a function of temperature (top) and time (bottom). For details, see text.

ed as described above, showed that the thermal decomposition took place without gas evolution.

Synthesis of $[Hf_3Cp_2(\mu_2\text{-}CCO)(\mu_3\text{-}O)(O_2CN\textit{i}Pr_2)_6]$ (2): A solution of $[HfCp_2(CO)_2]$ (3.03 g, 8.3 mmol) and $[Hf(O_2CN\textit{i}Pr_2)_4]$ (6.43 g, 8.5 mmol) in toluene (75 mL) was heated at reflux for 24 h and then allowed to cool to room temperature. An IR spectrum of the brown solution revealed a strong absorption at 2024 cm^{-1}. Pale colourless crystals separated out at −30 °C. They were collected by filtration, washed with toluene (2 × 4 mL) and dried in vacuo at room temperature (2.94 g). GC-MS analysis of the filtrate revealed the presence of $\textit{i}Pr_2NCOCH_3$ (m/z = 143), dicyclopentadiene (m/z = 132) and cyclopentadiene (m/z = 66). The solution, still containing unchanged $[HfCp_2(CO)_2]$ (2.11 mmol) and $[Hf(O_2CN\textit{i}Pr_2)_4]$, was heated again at reflux for 24 h and then allowed to cool to room temperature. The volume of the solution was reduced in vacuo: a colourless solid separated at −30 °C and was collected by filtration, washed with toluene (4 mL) and dried in vacuo (0.56 g). The diamagnetic, colourless solid was identified as **2** (total yield 40%). Anal. found: C 39.9, H 5.6, N 4.5. Calcd for $C_{54}H_{94}N_6O_{14}Hf_3$: C 40.9, H 5.9, N 5.3%. IR (nujol and polychlorotrifluoroethylene): $\tilde{\nu}$ = 3107 (m−w), 2021 (s), 1967 (w), 1584 (w), 1538 (vs), 1515 (vs), 1385 (s), 1206 (m), 1162 (m−w), 1137 (w), 1024 (m), 971 (w), 900 (w), 871 (w), 823 (m), 790 (m−s), 741 (vs), 690 (m−s), 672 (w), 654 (w), 606 (m−s), 585 (m−s) cm^{-1}. IR (toluene): $\tilde{\nu}$ = 2024 cm^{-1}. ^{1}H NMR (200 MHz, [D$_6$]benzene, 25 °C): δ = 6.7 (s, 10H; Cp), 3.8 (m, 6H; CH), 1.2 (m, 72H; CH$_3$). The reaction was repeated several times; the yields were around 40%. A GC-MS analysis of the filtrate showed $\textit{i}Pr_2NCOCH_3$ (m/z = 143), dicyclopentadiene (m/z = 132) and 1,1′-dihydrofulvalene (m/z = 130) to be present.

Synthesis of $[Zr_3Cp_2(\mu_2\text{-}O)(\mu_3\text{-}O)(O_2CN\textit{i}Pr_2)_6]$ (3): A suspension of **1b** (3.36 g, 2.5 mmol) in toluene (50 mL) was treated with an excess of CO_2. An immediate change in the colour of the solution was observed from pale yellow to deep yellow to red. This was accompanied by the disappearance of the IR absorption at 2013 cm^{-1}. The volume of the solution was reduced to 10 mL, and heptane was layered on top of the toluene solution. A red powder together with colourless crystals formed. The crystals were decanted, washed with heptane (2 × 10 mL) and dried. Colourless crystals (0.535 g) were obtained. The solution was filtered and cooled to −78 °C, affording a second crop (0.884 g) of a microcrystalline, colourless solid. The compound was identified as **3** (total yield 48%). Anal. found: C 48.1, H 7.3, N 6.5, Zr 20.8. Calcd for $C_{52}H_{94}N_6O_{14}Zr_3$: C 48.0, H 7.3, N 6.5, Zr 21.0%. IR (nujol and polychlorotrifluoroethylene): $\tilde{\nu}$ = 3110 (w), 2970 (m−s), 2930 (m−s), 2870 (w), 1580 (s), 1500 (vs), 1450 (m−s), 1385 (m−s), 1350 (s), 1260 (w), 1210 (m−s), 1160 (s), 1135 (m−w), 1070 (s), 1035 (w), 1020 (m−w), 900 (m), 870 (w), 810 (w), 790 (s), 780 (s), 670 (m−s), 620 (w), 600 (m−s), 560 (m), 530 (m), 510 (w), 445 (w) and 370 (m) cm^{-1}. ^{1}H NMR (200 MHz, [D$_6$]benzene, 25 °C): δ = 6.7 (m, 10H; Cp), 3.8 (m, 6H; CH), 1.2 (m, 72H; CH$_3$). ^{13}C NMR (50.31 MHz, [D$_6$]benzene, 25 °C): δ = 166.5, 162.4, 161.0 (CO_2); 115.1, 114.3 (Cp); 47.4, 45.6 [$CH(CH_3)_2$]; 22 (CH_3, partial overlap with solvent signals). MS: m/z: 1297 $[M+H]^+$, 588 $[ZrCp(O_2CN\textit{i}Pr_2)_3+H]^+$.

In a gas-volumetric experiment, a known amount of the ketenylidene complex (0.61 g, 0.45 mmol) in a thin-walled ampoule was brought into contact with toluene presaturated with CO_2; after 12 h of stirring at room temperature, 0.39 mmol of CO_2 was found to have reacted, corresponding to a CO_2/**1b** molar ratio of 0.86.

Reaction of 1b with acetone: Solid **1b** (0.36 g, 0.27 mmol) was treated with acetone (5 mL) at room temperature. A yellow solution was obtained after ca. 10 min. An IR spectrum of the solution did not show any absorption in the 2500−1800 cm^{-1} region. After 2 h of stirring at room temperature, the solvent was removed in vacuo at room temperature. A GC-MS analysis of the distillate showed $Me_2C{=}CHC(O)Me$ to be present in a much higher quantity than in the acetone used for the reaction. The residue was treated with heptane and the solvent removed in vacuo at ca. 70 °C collecting 0.180 g (51% yield) of **3** (IR and elemental analysis). The GC-MS of the distillate showed $Me_2C{=}CHC(O)N\textit{i}Pr_2$, $\textit{i}Pr_2NC(O)CH_3$ and $\textit{i}Pr_2NC(O)CH_2C(OH)Me$ to be present.

When the reaction was repeated with $[Zr_3Cp_2(\mu_2\text{-}{}^{13}C^{13}CO)(\mu_3\text{-}O)(O_2CN\textit{i}Pr_2)_6]$ under the same experimental conditions, the GC-MS of the heptane solution revealed the presence of $Me_2C{=}{}^{13}CH^{13}C(O)N\textit{i}Pr_2$, $\textit{i}Pr_2N^{13}C(O)^{13}CH_3$ and $\textit{i}Pr_2N\text{-}{}^{13}C(O)^{13}CH_2C(OH)Me$.

Thermal decomposition of 1b: A suspension of **1b** (0.46 g, 0.35 mmol) in toluene (25 mL) was refluxed for 3 h. After cooling to room temperature, the solution was evaporated to dryness under reduced pressure at room temperature. Heptane (20 mL) was added, and the resulting suspension filtered. The colourless solid was dried in vacuo (0.242 g, 53% yield). The compound was identified as **3** (IR, ^{1}H NMR, MS spectrum, elemental analysis).

Synthesis of $[Hf_3Cp_2(\mu_2\text{-}O)(\mu_3\text{-}O)(O_2CN\textit{i}Pr_2)_6]$ (4): A suspension of **2** (0.849 g, 0.53 mmol) in toluene (5 mL) was treated with an excess of CO_2. The pale brown suspension immediately turned into a red solution, and the absorption at 2024 cm^{-1} disappeared. A colourless solid then precipitated out from the solution. The suspension was filtered and the solid washed twice with heptane (2 mL) and dried, affording 0.242 g of the title compound as a colourless microcrystalline solid. The filtrate was evaporated under reduced pressure at room temperature giving additional 0.206 g of the product. The compound was identified as **4** (total yield 54%). Anal. found: Hf 35.0, CO_2 15.9. Calcd for $C_{52}H_{94}Hf_3N_6O_{14}$: Hf 34.3, CO_2 16.9%. IR (nujol and polychlorotrifluoroethylene): $\tilde{\nu}$ = 3105 (w), 1586 (s), 1533 (s), 1510 (s), 1505 (vs), 1212 (m−s), 1163 (s), 1137 (m−w), 1070 (s), 1020 (m−w), 973 (m), 903 (w), 874 (w), 636 (w), 608 (m−s), 557m cm^{-1}. ^{1}H NMR (200 MHz, [D$_6$]benzene, 25 °C): δ = 6.7 (m, 10H; Cp), 3.8 (m, 6H; CH), 1.5 (m, 72H; CH$_3$). MS: m/z: 1563 $[M+H]^+$, 1498 $[M+H-C_5H_5]^+$, 1721 $[Hf_3(O_2CN\textit{i}Pr_2)_8(O)_2+H]^+$, 678 $[HfCp(O_2CN\textit{i}Pr_2)_3+H]^+$, 757 $[Hf(O_2CN\textit{i}Pr_2)_4+H]^+$.

In a gas-volumetric experiment similar to that described for the analogous zirconium complex, the amount of CO_2 absorbed in the reaction corresponded to a CO_2/**2** molar ratio of 0.8.

X-ray structures and data collection: The structures **1b** and **3** were determined on an ENRAF Nonius CAD4 diffractometer with $Mo_{K\alpha}$ radiation (λ = 0.7107 Å, graphite monochromator). Crystal data, data collection parameters and convergence results are compiled in Table 5. Both structures were solved by direct methods [37] and refined with the local version of the SDP program system [38].

1b crystallized from toluene in the triclinic space group $P\bar{1}$ with two trinuclear molecules and one toluene molecule in the unit cell. After completion of the isotropic structural model, an empirical absorption correction with the program DIFABS [39] was applied before averaging over symmetrically equivalent reflections. The precision of the structure is reduced due to the disorder affecting one of the carbamato ligands (N4, C41−47) and the clathrated toluene molecule (close to a crystallographic inversion centre). The disordered carbamato moiety was assigned on the basis of the isotropic displacement parameters in the final refinement stages. Hydrogen atoms were not refined but included in the structure factor calculations; for the disordered part of the structural model, no hydrogen atom was taken into account. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-58071.

3: Single crystals were obtained by layering heptane over toluene solution of the compound at room temperature. The compound crystallized in the same space group and with similar lattice constants as **1b**, but without inclusion of solvent in the crystal. An empirical absorption correction on the basis of azimuthal scans [40] was applied to the intensity data. No disorder problems were encountered. In the

Table 5. Crystal data and structure refinement of **1b**·$0.5\,C_7H_8$ and **3**.

	1b·$0.5\,C_7H_8$	**3**
formula	$C_{54}H_{94}N_6O_{14}Zr_3 \cdot 0.5\,C_7H_8$	$C_{52}H_{94}N_6O_{14}Zr_3$
M_r	1371.1	1301.0
crystal dimensions (mm)	0.2 × 0.2 × 0.2	0.25 × 0.2 × 0.2
T (K)	263	253
space group	$P\bar{1}$ (no 2)	$P\bar{1}$ (no 2)
a (Å)	13.636(5)	13.154(3)
b (Å)	13.634(5)	13.632(3)
c (Å)	20.882(5)	24.444(4)
α (°)	92.55(2)	98.34(2)
β (°)	97.61(2)	116.29(2)
γ (°)	114.56(3)	115.52(2)
volume (Å^3)	3478(5)	3226(2)
Z	2	2
D_{calcd} (g cm^{-3})	1.309	1.339
μ (cm^{-1})	4.90	5.25
$F(000)$	1434	1360
θ (°)	3–25	3–25
scan type	ω	ω
measured reflections	10380	11818
absorption correction	DIFABS	PSI-SCAN
indep. refls	5340 [$I > 3\sigma(I)$]	7385 [$I \geq 3\sigma(I)$]
refined parameters	739	676
resd electron density (e Å^{-3})	1.27 [a]	0.55 [b]
R [c]	0.064	0.038
R_w [d]	0.076	0.043
GOF	1.897	1.161

[a] Close to the disordered ligand. [b] Close to Zr3. [c] $\sum|\Delta F|/\sum|F_o|$. [d] $[\sum w(\Delta F)2/\sum w|F_o|2]^{1/2}$; $w = 1/\sigma^2|F_o|$.

final refinement procedure, all non-hydrogen atoms were included in the structure factor calculations. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-59099.

Acknowledgements: This work was supported by the Consiglio Nazionale delle Ricerche (CNR, Roma), Progetto Finalizzato Chimica Fine II, and by the Erasmus Programme (grant no. ICP-95-UK-2044/13 to G.T.).

Received: July 24, 1995 [F174]

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