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Notes

Structural Characterization of the Product of Intramolecular Oxygen Transfer from a Ketone to CO within the Coordination Sphere of a Zr−Fe Heterodimetallic Complex

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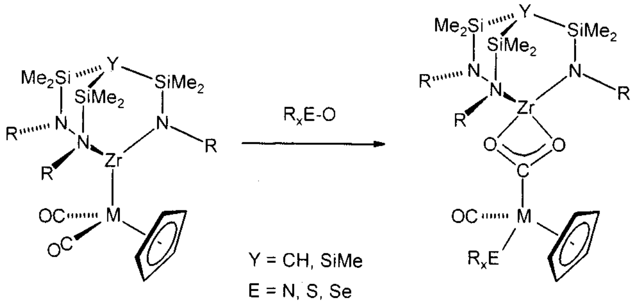
Summary: The Zr−Fe complex $[HC\{SiMe_2N(2,3,4\text{-}F_3C_6H_2)\}_3Zr{-}FeCp(CO)_2]$ *(**1**) reacts with 1,2-diphenylcyclopropenone to give* $[HC\{SiMe_2N(2,3,4\text{-}F_3C_6H_2)\}_3Zr(\mu\text{-}CO_2)FeCp(CO)(C_3Ph_2)]$ *(**2**). A single-crystal X-ray structure analysis has now established the molecular structure of the product of oxygen transfer of the cyclopropenone to a carbonyl ligand. The chiral Fe center in complex **2** bears a carbonyl, a cyclopropenylidene ligand, and the C atom of a* μ_2-η^3*-bridging* CO_2 *ligand.*

Introduction

The potential cooperative reactivity of early−late heterodinuclear complexes with organic substrates has been much debated since the early 1980s.[1−3] Examples of this type of reactive behavior have been fairly rare until recently.[4−6] In the course of several systematic studies of the reactivity of early−late heterodimetallic complexes containing highly polar metal−metal bonds toward polar organic substrates we discovered an oxygen transfer reaction, in which an oxygen atom is transferred from an element oxide to a CO ligand.[7,8] The CO_2 thus formed inserts into the metal−metal bond to give a metallacarboxylato complex of the early transition metal (Scheme 1). Not only sulfoxides and amine oxides were found to react according to this pattern but also highly polarized ketones such as 1,2-diphenylcyclopropenone.[8] We found that the Zr−Fe complex $[HC\{SiMe_2N(2,3,4\text{-}F_3C_6H_2)\}_3Zr{-}FeCp(CO)_2]$ (**1**) reacts with 1,2-diphenylcyclopropenone to give [HC{SiMe2N(2,3,4-

Scheme 1



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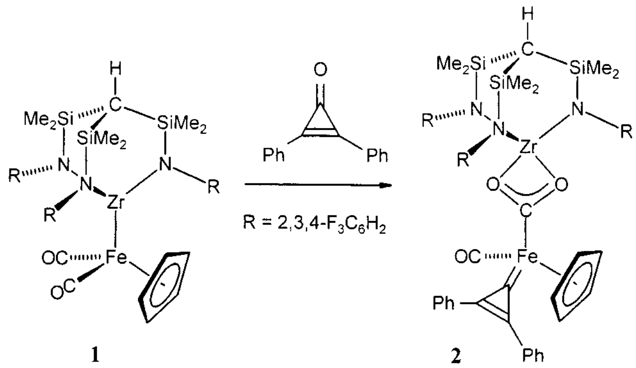
Scheme 2



1 **2**

$F_3C_6H_2)\}_3Zr(\mu\text{-}CO_2)FeCp(CO)(C_3Ph_2)]$ (**2**) (Scheme 2). On the basis of the analytical as well as the NMR and infrared spectroscopic data, the structure represented in Scheme 2 was proposed for the reaction product **2**, while difficulties in obtaining suitable crystals for an X-ray diffraction study of the compound precluded its complete structural characterization. Here we report the results of the X-ray crystallographic study of the unusual structure of this compound.

Results and Discussion

Reaction of the Zr–Fe complex **1** with 1 molar equiv of 1,2-diphenylcyclopropenone at ambient temperature in toluene instantaneously gave complex **2** (Scheme 2). Its single infrared ν(CO) band at 1953 cm^{-1} established the presence of only one Fe-bonded carbonyl ligand, while the ^{13}C NMR resonances at δ 219.3, 224.1, and 259.0 are consistent with the presence of, respectively, the CO, CO_2, and carbene C_3Ph_2 ligands. The structural assignment was further supported by the disappearance of the signal attributed to the carbonyl function in 1,2-diphenylcyclopropenone (δ 156.4), the shift of the resonances of the C=C olefin unit in the cyclopropene ring from δ 146.7 to 179.5, and the diastereotopic splitting of the $SiMe_2$ groups in the ^1H and ^{13}C NMR (^1H, δ 0.29 and 0.35; ^{13}C, δ 4.0 and 4.5) indicating the formation of a chiral iron center. The transfer of the oxygen atom from the ketone to the CO was demonstrated by us by ^{17}O labeling.[8] Slow cooling of the benzene solution of the compound now gave single crystals of the complex which were suitable for an X-ray diffraction study. The molecular structure of complex **2** is depicted in Figure 1, and the principal bond lengths and angles are listed in Table 1.

The bridging CO_2 ligand adopts a μ_2-η^3 coordination mode found previously in several dinuclear complexes.[9–11] Its arrangement between the two metal centers is highly symmetrical, the two Zr–O bond lengths (Zr(1)–O(1) = 2.148(3) Å, Zr(1)–O(2) = 2.152(3) Å) and C–O bond lengths (C(51)–O(1) = 1.302(5) Å, C(51)–O(2) = 1.308(5) Å) being identical within experimental error.

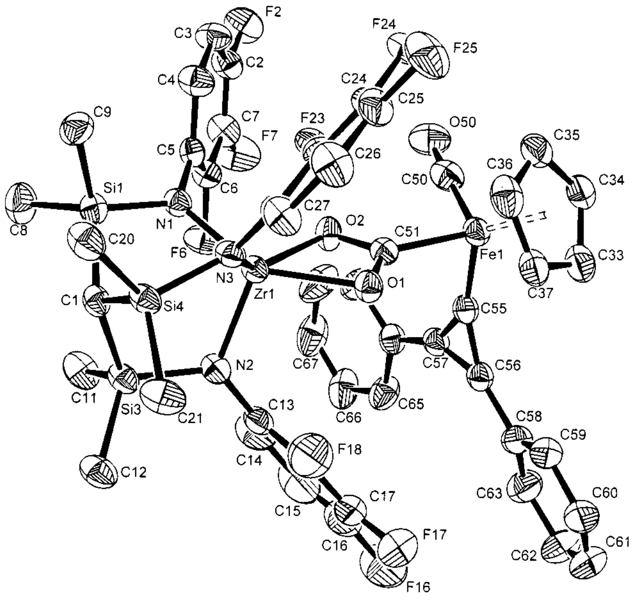
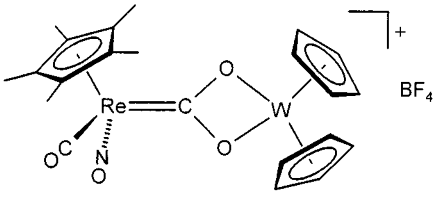


Figure 1. ORTEP plot of compound **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogens have been omitted for clarity. The principal bond lengths and angles are given in Table 1.

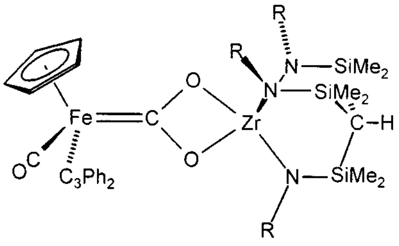
Table 1. Principal Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) of Compound 2

Zr(1)–O(1)	2.148(3)	Fe(1)–C(55)	1.860(5)
Zr(1)–O(2)	2.152(3)	C(55)–C(56)	1.406(6)
O(1)–C(51)	1.308(5)	C(55)–C(57)	1.414(6)
O(2)–C(51)	1.302(5)	C(56)–C(57)	1.340(6)
Fe(1)–C(51)	1.893(4)	C(56)–C(58)	1.457(6)
Fe(1)–C(50)	1.741(5)	C(57)–C(64)	1.447(7)
O(1)–Zr(1)–O(2)	60.43(11)	C(50)–Fe(1)–C(51)	92.5(2)
C(51)–O(1)–Zr(1)	93.6(2)	C(55)–Fe(1)–C(51)	85.26(18)
O(2)–C(51)–O(1)	112.0(3)	C(56)–C(55)–C(57)	56.8(3)
O(1)–C(51)–Fe(1)	123.1(3)	C(57)–C(56)–C(55)	61.9(3)
O(2)–C(51)–Fe(1)	125.0(3)	C(56)–C(57)–C(55)	61.4(3)
C(50)–Fe(1)–C(55)	94.7(2)		
C(55)–C(56)–C(58)–C(63)	–161.3(7)		
C(55)–C(56)–C(58)–C(59)	18.2(10)		
C(55)–C(57)–C(64)–C(69)	–0.5(10)		
C(55)–C(57)–C(64)–C(65)	–178.4(7)		

The geometry of this subunit thus is similar to that of most dinuclear metallacarboxylate complexes in which two transition elements are bridged.[9] The first example



A



B

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Table 2. Comparison of the Metric Parameters of the M(μ-CO_2)M′ Unit[12] in [HC{$SiMe_2N$(2,3,4-$F_3C_6H_2$)}$_3$Zr(μ-CO_2)FeCp(CO)(C_3Ph_2)] (2), [Cp*Ru$(CO)_2$(μ-CO_2)Zr(Cl)Cp_2] (3), and [MeSi{$SiMe_2N$(*p*-Tol)}$_3$(O═SMe_2)-Zr(μ-CO_2)RuCp(CO)(SMe_2)] (4)[7]

	d[C−O(1)], *d*[C−O(1)], Å	*d*[Zr−O(1)], *d*[Zr−O(1)], Å	∠[O(1)−C−O(2)], deg	*d*(M−C), Å
2	1.302(5), 1.308(5)	2.148(3), 2.152(3)	112.0(3)	1.893(4)
3	1.271(7), 1.296(8)	2.201(3), 2.245(4)	113.9(4)	2.050(4)
4	1.276(11), 1.295(11)	2.222(6), 2.255(7)	115.9(8)	2.083(9)

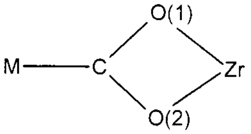
Table 3. Crystal Data and Structure Refinement Details for [HC{$SiMe_2N$(2,3,4-$F_3C_6H_2$)}$_3$-Zr(μ-CO_2)FeCp(CO)(C_3Ph_2)] (2)

empirical formula	$C_{47}H_{40}F_9FeN_3O_3Si_3Zr$
fw	1097.16
T (K)	120
wavelength (Å)	0.710 73
cryst size (mm)	0.20 × 0.10 × 0.10
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell dimens	
a (Å)	10.6981(3)
b (Å)	12.5334(3)
c (Å)	19.8791(7)
α (deg)	84.4941(9)
β (deg)	75.4340(11)
γ (deg)	65.242(2)
V (Å^3)	2342.53(12)
Z	2
D_{calcd} (g cm^{-3})	1.555
abs coeff (mm^{-1})	0.689
F(000)	1112
θ range for data collecn (deg)	2.61−25.06
limiting *hkl* indices	$-12 \le h \le 12$
	$-14 \le k \le 14$
	$-23 \le l \le 23$
no. of rflns collected	28 421
no. of indep rflns	8080
R_{int}	0.0616
max and min transmission	0.308 91/0.259 85
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	8080/0/610
goodness of fit on F^2	1.108
final *R* indices[a]	
$I > 2\sigma(I)$	R1 = 0.0501, wR2 = 0.1165
all data	R1 = 0.0733, wR2 = 0.1292
largest diff peak/hole (e Å^{-3})	0.743/−0.713

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$.

to be reported was the rhenium/tungsten complex [Cp*(CO)(NO)Re(μ-CO_2)WCp_2][BF_4], for which the dimetalated dioxocarbene formulation **A** was discussed.[10] The relatively short Re−C distance in **A** (2.04 Å) appears to support the relative weight of this resonance form, as does the Fe(1)−C(51) distance of 1.893(4) Å in the dioxocarbene formulation **B** of compound **2**.

It is interesting to compare the structural details of the metallacarboxylato unit with those of two previously reported Zr/Ru complexes, the compound [Cp*Ru$(CO)_2$-(μ-CO_2)Zr(Cl)Cp_2] (**3**) characterized by Gibson et al.[12] and the complex [MeSi{$SiMe_2N$(p-Tol)}$_3$(O═SMe_2)Zr(μ-CO_2)RuCp(CO)(SMe_2)] (**4**).[7] The principal metric parameters of these three complexes are summarized in Table 2.



We note that the C−O bond lengths in the Ru/Zr complexes are somewhat shorter than those in **2**, while the Zr−O distances are significantly longer than in the Zr/Fe complex presented in this paper. This may be due to a higher degree of electronic unsaturation of the Zr center in **2** in comparison to the Zr/Ru species, which induces a contraction of the Zr−O bonds. The O(1)−C(51)−O(2) angle lies in the range of values found previously for symmetrically coordinated metallacarboxylates.[9]

The 1,2-diphenylcyclopropenylidene ligand, first introduced to organometallic chemistry by Öfele in 1968,[13] is coordinated to the chiral iron center and is the result of the oxygen transfer from the cyclopropenone. The Fe(1)−C(55) bond of this carbene ligand of 1.860(5) Å is shorter than the corresponding value in the only previously structurally characterized iron complex bearing this molecular fragment (1.901(7) Å in a trinuclear iron cluster).[14] The intracyclic C−C bond lengths in the cyclopropenylidene unit are similar to those found in related complexes,[15] the C(56)−C(57) bond being shorter (1.340(6) Å) than the other two C−C distances (1.414(6) and 1.406(6) Å), indicating a partial double-bond character.

In complexes having a carbene ligand coordinated to a $CpML_2$ fragment the conformation is electronically favored in which the plane of the substituents bonded to the carbene C atom coincides with the mirror plane of the complex fragment.[16] This is clearly not the case in the structure of **2**, which we attributed primarily to the steric interaction of the phenyl substituents with the ligand periphery of the amido tripod. A conformational study of the C_3Ph_2 fragment using least-squares planes revealed that the phenyl substituent adjacent to the CO ligand is coplanar with the cyclopropenylidene unit (angle between planes 1.97(0.53)°), whereas the phenyl substituent adjacent to the Cp ligand is significantly distorted (angle between planes 20.39(0.37)°), displaying the greater steric repulsion in the environment of the Cp ligand.

Conclusion

The X-ray diffraction study of compound **2** has established unambiguously its molecular structure, which we previously postulated on the basis of the spectroscopic data of the compound. This along with the isotope labeling studies[8] confirms the oxygen transfer from a cyclopropenone derivative to CO in the coordination sphere of an early−late heterodimetallic complex. The

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thermodynamic driving force is most probably the formation of two Zr−O bonds and the stable CO_2 unit linking the two metal centers.

Experimental Section

The synthesis of compound **2** was carried out according to the published procedure.[8] Single crystals suitable for an X-ray diffraction study were obtained by slow cooling of a yellow solution of the compound in benzene.

X-ray Crystallographic Study of 2. The X-ray diffraction data set was collected with a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Denzo and Scalepack[17] programs were used for cell refinements and data reduction, while the structure was solved by direct methods using the SIR97[18] program with the WinGX[19] graphical user interface. The structure refinements were carried out with SHELXL97,[20] and a multiscan absorption correction, based on equivalent reflections (XPERP in SHELXTL v5.1),[21] was applied to the data. All hydrogen atoms were constrained to ride on their parent atom. Crystallographic data are summarized in Table 3.

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Supporting Information Available: Text detailing the structure determination and tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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