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Developing potentially useful organometallic Lewis acid catalysts: (η-cyclopentadienyl)zirconium trichloride derivatives *

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Abstract

The organometallic Lewis acid (η-cyclopentadienyl)zirconium trichloride (**2**) was obtained from bis(cyclopentadienyl)zirconium dichloride (**1**) and chlorine by means of a radical induced metal–Cp bond cleavage. Reaction of **2** with tetrahydrofuran gave the $CpZrCl_3$-bis(tetrahydrofuran) adduct **3**; treatment of either **2** or **3** with excess dimethylformamide furnished $CpZrCl_3(dmf)_2$ (**4**). (η-Methylcyclopentadienyl)bis(tetrahydrofuran)zirconium trichloride (**7**) was prepared by treatment of $ZrCl_4(thf)_2$ (**6**) with one molar equivalent of the (methylcyclopentadienyl)thallium reagent **5**. Complexes **3**, **4** and **7** were characterized by X-ray diffraction studies and their dynamic NMR spectra were recorded. Complex **3** crystallizes in space group $P2_1/n$ with cell parameters a 8.155(1), b 13.342(2), c 15.775(1) Å, β 104.81(1)°, $Z = 4$, $R = 0.041$, $R_w = 0.056$. $CpZrCl_3(dmf)_2$ (**4**) crystallizes in space group $P2_1/c$ with cell parameters a 7.790(1), b 15.445(2), c 13.893(1) Å, β 93.94(1)°, $Z = 4$, $R = 0.032$, $R_w = 0.052$. Complex **7** crystallizes in space group $P2_1/n$ with cell parameters a 10.242(2), b 12.836(2). c 13.683(1) Å, β 106.37 (1)°, $Z = 4$, $R = 0.037$, $R_w = 0.039$. The (cyclopentadienyl)bis(tetrahydrofuran)zirconium trichloride adduct **3** selectively catalyzed the Diels–Alder addition of 2,3-dimethylbutadiene and methacrolein at ambient temperature to give 1,3,4-trimethyl-3-cyclohexenyl-1-carbaldehyde (**13**). However, the $CpZrCl_3$-Lewis acid catalyzed rearrangement of **13** to 1,3,4-trimethylbicyclo[2.2.1]heptan-2-one (**14**) does not take place at a significant rate until ca. 150 °C.

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* Dedicated to Professor Dr. Günther Wilke on the occasion of his 65. birthday.

Introduction

Many important carbon–carbon coupling reactions can be accelerated by Lewis acid catalysis, while others can only proceed with the aid of such a catalyst. There is a growing body of evidence that when the CC-coupling of a variety of organic substrates is catalyzed by selected Lewis acid systems, increasing reactivity is often compatible with a higher selectivity [1].

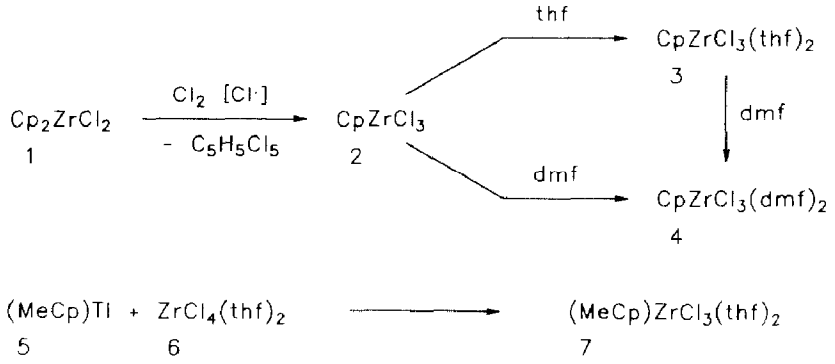
Simple inorganic Lewis acids such as BF_3, $TiCl_4$, $AlCl_3$, etc., are commonly used for catalyzing organic reactions. These systems allow only a limited number of structural variations, e.g. by introducing stereochemical information by attaching chiral alkoxide substituents [1b]. Organometallic Lewis acids should be much more versatile because they can incorporate a wider range of structural and stereochemical variations. A number of electron deficient organometallic systems having thermodynamically sufficiently strong metal–carbon bonds are known that are potential candidates for use as Lewis acid catalysts in organic synthesis [2]. We here report on the preparation and coordination chemistry of derivatives of d^0/12-electron mono(cyclopentadienyl)zirconium trihalide systems and the application of a $CpZrCl_3$ derived Lewis acid for catalyzing a Diels–Alder reaction.

Preparation and structures of $(RCp)ZrCl_3L_2$ complexes

We have previously shown that $CpZrCl_3$ can very conveniently be prepared from Cp_2ZrCl_2 by a radical induced CpZr cleavage reaction [3]. The controlled radical chain chlorination of zirconocene dichloride in CCl_4 in the temperature range between 18 and 23°C very cleanly leads to mono(cyclopentadienyl)zirconium trichloride (**2**) and a single 1,2,3,4,5-pentachlorocyclopentane isomer.

Reaction of **2** with excess tetrahydrofuran in toluene solution gave a single crystalline $CpZrCl_3(thf)_2$ isomer **3** in 67% yield. Treatment of **3** with slightly more than two molar equivalents of dimethylformamide (dmf) resulted in a clean displacement of both tetrahydrofuran units at zirconium by the stronger donor ligand dmf to give $CpZrCl_3(dmf)_2$ (**4**) in almost quantitative yield. Complex **4** was also prepared, albeit in much lower yield, directly from ligand free $CpZrCl_3$ (**2**) by treatment with excess dimethylformamide.

We have tried to prepare Cp-substituted analogues $(RCp)ZrCl_3$ of **2** by the radical chain chlorination method mentioned above, but without success. Thus, the chlorination of e.g. $(MeCp)_2ZrCl_2$ under various reaction conditions in our hands produced only intractable mixtures of as yet unidentified organic and organome-



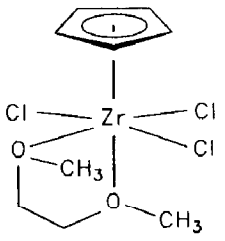
tallic products (in addition to some $ZrCl_4$). We were not able to confirm whether the desired compound $(MeCp)ZrCl_3$ was among the reaction products.

The synthesis of a mono(methylcyclopentadienyl)zirconium trihalide system was achieved by a substitution reaction using a methylcyclopentadienyl anion equivalent. The selective replacement of only one chloride ligand was observed when strictly equimolar equivalents of $ZrCl_4(thf)_2$ and methylcyclopentadienylthallium were allowed to react at 0 °C in toluene. (η-Methylcyclopentadienyl)bis(tetrahydrofuran)zirconium trichloride (**7**) was obtained by this method in ca. 50% yield. We assume that other Cp-substituted $(RCp)ZrX_3$ complexes can be prepared analogously using suitably substituted (RCp)Tl reagents [4].

The solid state structures of the complexes $CpZrCl_3(thf)_2$ (**3**), $(MeCp)ZrCl_3(thf)_2$(**7**), and $CpZrCl_3(dmf)_2$ (**4**) were determined by X-ray diffraction studies. All three complexes exhibit independent monomeric $(RCp)ZrCl_3L_2$ units in the crystal. The coordination geometries around zirconium are distorted octahedral, one coordination site being occupied by the Cp-ligand. In each case the crystals of **3**, **7** and **4** contain only one isomer, which can be described as *mer*-$(RCp)ZrCl_3L_2$.

Two *trans*-effects can be discerned which are different in magnitude and probably different in origin. In complex **3**, the zirconium–chlorine bond oriented *trans* to the tetrahydrofuran ligand is shorter (Zr–Cl(3) 2.468(1) Å) than the two adjacent *cis*-Cl–Zr linkages (Zr–Cl(1) 2.492(1) Å; Zr–Cl(2) 2.511(1) Å). This effect is also present in **7** (*trans*: Zr–Cl(3) 2.473(1) Å; *cis*: Zr–Cl(1) 2.490(1), Zr–Cl(2) 2.493(1) Å). A similar *trans*-influence has been observed with $CpZrCl_3(dme)$ (**8**) [5] (Zr–Cl (*trans*): 2.438(3) Å, (*cis*): 2.468(3), 2.487(3) Å); it is just noticeable in the analogously structured actinide complex $(MeCp)UCl_3(thf)_2$ (**9**) [6] (U–Cl (*trans*): 2.614(4) Å, (*cis*): 2.625(3), 2.631(3) Å) and the pseudooctahedral titanium complex $CpTiCl_3(dmpe)$ (**10**) [7] (Ti–Cl (*trans*): 2.375(12) Å, (*cis*): 2.400(10), 2.385(9) Å).

In the complexes **3** and **7** the metal atom is clearly above the plane defined by the three adjacent halogen atoms. The Zr–Cl bonds are noticeably bent away from the Cp-ligand. In **3** the Zr atom lies 0.53 Å above the Cl(1), Cl(2), Cl(3) plane; in **7** it is 0.57 Å above it. This bending of the ligands *cis* to the Cp-group causes a difference in the Zr–O bond distances of the coordinated tetrahydrofuran donor ligands. The thf-ligand oriented *trans* to the Cp-ring features a Zr–O(1) distance of 2.393(3) whereas the oxygen–zirconium bond length of the *cis*-thf ligand is notably shorter (Zr–O(2) 2.314(3) Å). The same is true for the methylcyclopentadienyl complex **7** (Zr–O(1) 2.377(2), Zr–O(2) 2.310(2) Å). A similar difference in metal–oxygen bond distances has been observed for the zirconium complex **8** (Zr–O(*trans*) 2.37(1), Zr–O(*cis*) 2.26(1) Å) whereas complexes **9** and **10** feature equidistant metal–O and metal–P linkages, respectively (**9**: U–O(*trans*) 2.451(7), U–O(*cis*) 2.449(8) Å; **10**: Ti–P(*trans*) 2.609(11), Ti–P(*cis*) 2.602(12) Å). The Zr–O bond in cationic $Cp_2ZrCl(thf)^+$ is much shorter (2.122(14) Å) than in **3** or **7** [8].



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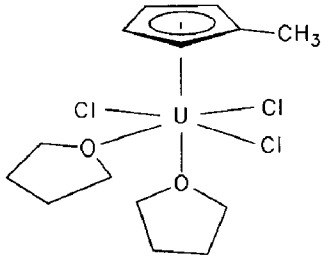

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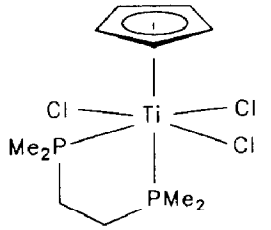

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Table 1

X-ray crystal structure analyses of the mono(η-cyclopentadienyl)zirconium complexes **3**, **4** and **7**: data collection and structure solution [a]

	3	**7**	**4**
formula	$C_{13}H_{21}Cl_3O_2Zr$	$C_{14}H_{23}Cl_3O_2Zr$	$C_{11}H_{19}Cl_3O_2N_2Zr$
M_r	406.9	420.9	408.9
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	8.155(1)	10.242(2)	7.790(1)
b, Å	13.342(2)	12.836(2)	15.445(2)
c, Å	15.775(1)	13.683(1)	13.893(1)
α, deg	90	90	90
β, deg	104.81(1)	106.37(1)	93.94(1)
γ, deg	90	90	90
V, Å^3	1659.4	1726.1	1667.5
Z	4	4	4
d_{calc}, g cm^{-3}	1.63	1.62	1.63
λ, Å	0.71069	0.71069	0.71069
μ, cm^{-1}	11.35	10.93	11.32
$F(000)$	824	856	824
T, °C	20	20	20
crystal dimens, mm	$0.29\times0.58\times0.58$	$0.25\times0.43\times0.36$	$0.36\times0.36\times0.43$
scan-mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
$\sin\theta/\lambda_{max}$	0.65	0.65	0.66
refl. measured	4058	4242	4299
R_{av}	0.02	0.01	0.01
refl. unique	3759	3909	3993
refl. obs ($I > 2\sigma(I)$)	3175	2896	3535
parameter refined	172	181	172
max shift/esd	0.11	0.001	0.01
R	0.041	0.037	0.032
Rw	0.056	0.039	0.052
ρ (max), eÅ^{-3}	0.82	0.54	0.54

[a] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7414 Eggenstein-Leopoldshafen 2 (F.R.G.), on quoting the depository number CSD53983, the name of the authors, and the journal citation.

The coordination geometries of the thf ligands in **3** and **7** and the relative orientation of the heterocyclic donor ligands at the $(RCp)MCl_3$ moiety are similar to those reported for the actinide complex $(MeCp)UCl_3(thf)_2$ (**9**). Like in **9**, the mean plane of the *cis*-thf ligand in **7** is oriented parallel to the MeCp plane. The mean plane of the *trans*-thf ligand bisects the Cl(2), Zr, Cl(3) angle: this five-membered donor ligand is found in an orientation eclipsed with the C(9)–C(14) vector.

The overall coordination geometry of $CpZrCl_3(dmf)_2$ (**4**) is similar to that of **3** and **7**. Three Cl-ligands are bonded at zirconium in *cis*-positions to the η-cyclopentadienyl ligand. The dimethylformamide ligands are η^1-coordinated through the carbonyl oxygen atoms. One dmf-ligand is oriented *cis* to the Cp-ligand, the other is found in the *trans*-position. The order of relative bond distances closely follows the scheme that has already become apparent with complexes **3** and **7**. The zirconium to chlorine bond *trans* to the coordinated oxygen donor ligand is slightly shorter (Zr–Cl(3) 2.501(1) Å) than the adjacent *cis* Zr–Cl bonds (Zr–Cl(1) 2.542(1),

Table 2

Bond lengths (Å) and angles (°) of $CpZrCl_3(thf)_2$ (3) and $(MeCp)ZrCl_3(thf)_2$ (7)

	3	7
Zr–Cl(1)	2.492(1)	2.490(1)
Zr–Cl(2)	2.511(1)	2.493(1)
Zr–Cl(3)	2.468(1)	2.473(1)
Zr–O(1)	2.393(3)	2.377(2)
Zr–O(2)	2.314(3)	2.310(2)
Zr–C(9)	2.489(8)	2.551(5)
Zr–C(10)	2.500(6)	2.528(5)
Zr–C(11)	2.51(2)	2.527(5)
Zr–C(12)	2.516(8)	2.527(4)
Zr–C(13)	2.50(1)	2.527(4)
C(9)–C(10)	1.37(1)	1.393(7)
C(9)–C(13)	1.34(1)	1.404(7)
C(9)–C(14)		1.485(7)
C(10)–C(11)	1.32(2)	1.383(7)
C(11)–C(12)	1.29(2)	1.372(8)
C(12)–C(13)	1.24(1)	1.386(8)
O(2)–Zr–O(1)	74.6(1)	76.1(1)
O(2)–Zr–Cl(3)	154.7(1)	156.6(1)
O(2)–Zr–Cl(2)	84.4(1)	85.5(1)
O(2)–Zr–Cl(1)	83.7(1)	83.5(1)
O(1)–Zr–Cl(3)	80.1(1)	80.5(1)
O(1)–Zr–Cl(2)	77.4(1)	76.6(1)
O(1)–Zr–Cl(1)	77.9(1)	76.8(1)
Cl(3)–Zr–Cl(2)	89.9(1)	91.1(1)
Cl(3)–Zr–Cl(1)	91.3(1)	89.2(1)
Cl(2)–Zr–Cl(1)	154.7(1)	152.9(1)
C(4)–O(1)–C(1)	107.7(3)	107.1(3)
C(4)–O(1)–Zr	124.6(2)	124.6(2)
C(1)–O(1)–Zr	127.0(3)	127.2(2)
C(8)–O(2)–C(5)	106.8(3)	107.8(3)
C(8)–O(2)–Zr	125.9(2)	124.3(2)
C(5)–O(2)–Zr	126.9(3)	126.1(2)
C(14)–C(9)–C(13)		126.5(5)
C(14)–C(9)–C(10)		127.0(5)
C(13)–C(9)–C(10)	105.4(8)	106.4(4)
C(11)–C(10)–C(9)	105.5(8)	108.3(4)
C(12)–C(11)–C(10)	108.7(8)	109.0(5)
C(13)–C(12)–C(11)	110.9(9)	107.6(5)
C(12)–C(13)–C(9)	109.4(8)	108.7(5)

Zr–Cl(2) 2.515(1) Å). The zirconium–oxygen bond to the dmf ligand in *cis*-orientation to the Cp-ligand is shorter (Zr–O(2) 2.198(2) Å) than the *trans* Zr–oxygen linkage (Zr–O(1) 2.253(2) Å).

Both dimethylformamide ligands exhibit planar frameworks. The angle between the planes of the dmf ligand oriented *trans* to Cp (O(1), C(1), N(1), C(2), C(3)) and the *cis*-dmf donor (O(2), C(4), N(2), C(5), C(6)) is 87.1°. Relative to the Cp-plane (Cp(1)–Cp(5)) the planes of the *cis*- and *trans*-dimethylformamide ligands are rotated by 49.5° and 72°, respectively. The Cl(1), Cl(2), Cl(3), O(2) plane is located almost perfectly parallel to the Cp(1)–Cp(5) plane (1.4°). The zirconium atom lies

Table 3

Positional parameters of **3**

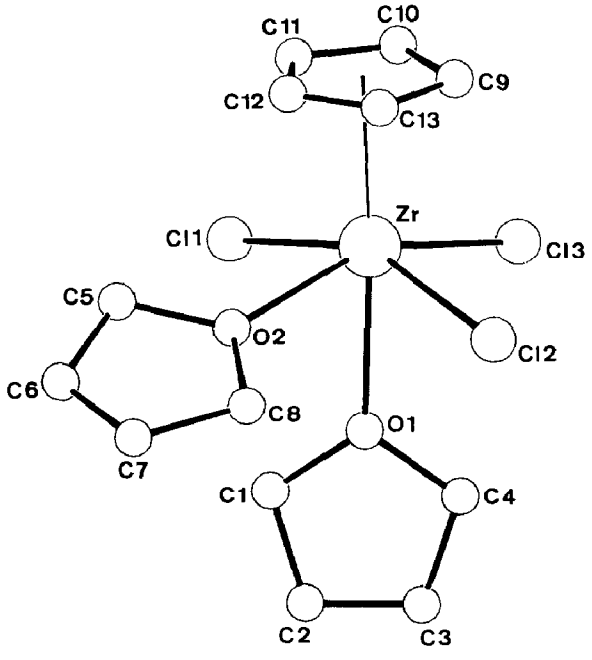
Atom	*x*	*y*	*z*
Zr	0.0831(1)	0.0144(1)	0.2812(1)
Cl(1)	−0.1736(1)	−0.0188(1)	0.3351(1)
Cl(2)	0.2373(1)	0.0658(1)	0.1693(1)
Cl(3)	0.1005(2)	0.1880(1)	0.3367(1)
O(1)	−0.1364(3)	0.0903(2)	0.1695(2)
O(2)	−0.0244(3)	−0.1129(2)	0.1832(2)
C(1)	−0.3094(6)	0.0554(4)	0.1371(4)
C(2)	−0.3837(8)	0.1170(5)	0.0605(4)
C(3)	−0.2858(7)	0.2073(4)	0.0660(3)
C(4)	−0.1252(6)	0.1886(4)	0.1325(3)
C(5)	−0.1109(8)	−0.2027(4)	0.2004(3)
C(6)	−0.180(1)	−0.2501(5)	0.1205(5)
C(7)	−0.0966(7)	−0.2163(4)	0.0561(3)
C(8)	0.0022(6)	−0.1242(4)	0.0958(3)
C(9)	0.3751(8)	−0.0043(7)	0.3775(8)
C(10)	0.270(2)	−0.0115(8)	0.4321(4)
C(11)	0.1876(9)	−0.097(1)	0.4117(9)
C(12)	0.240(2)	−0.1396(5)	0.3502(9)
C(13)	0.348(1)	−0.088(1)	0.3285(5)

0.51 Å above the plane going through the three Cl ligands and the oxygen atom O(2). Relative to the latter the *cis*-dmf ligand plane is rotated by 48.9°, the *trans*-dmf ligand plane by 106.7°.

Table 4

Positional parameters of **7**

Atom	*x*	*y*	*z*
Zr	0.0982(1)	0.2151(1)	0.3502(1)
Cl(1)	0.1419(1)	0.2806(1)	0.1910(1)
Cl(2)	0.1542(1)	0.1067(1)	0.5076(1)
Cl(3)	0.2315(1)	0.3626(1)	0.4440(1)
O(1)	0.3213(2)	0.1538(2)	0.3632(2)
O(2)	0.0626(2)	0.0584(2)	0.2637(2)
C(1)	0.3642(4)	0.0919(4)	0.2896(3)
C(2)	0.5138(5)	0.0824(4)	0.3258(3)
C(3)	0.5592(4)	0.1390(4)	0.4254(3)
C(4)	0.4333(4)	0.1537(4)	0.4567(3)
C(5)	0.0152(4)	0.0450(3)	0.1521(3)
C(6)	−0.0699(5)	−0.0513(4)	0.1355(3)
C(7)	−0.0087(5)	−0.1162(4)	0.2256(4)
C(8)	0.0485(5)	−0.0429(3)	0.3109(3)
C(9)	−0.0858(4)	0.2881(4)	0.4236(3)
C(10)	−0.0838(4)	0.3507(4)	0.3409(4)
C(11)	−0.1283(4)	0.2919(5)	0.2531(3)
C(12)	−0.1560(4)	0.1928(4)	0.2788(4)
C(13)	−0.1300(4)	0.1894(4)	0.3837(4)
C(14)	−0.0583(6)	0.3211(6)	0.5315(4)



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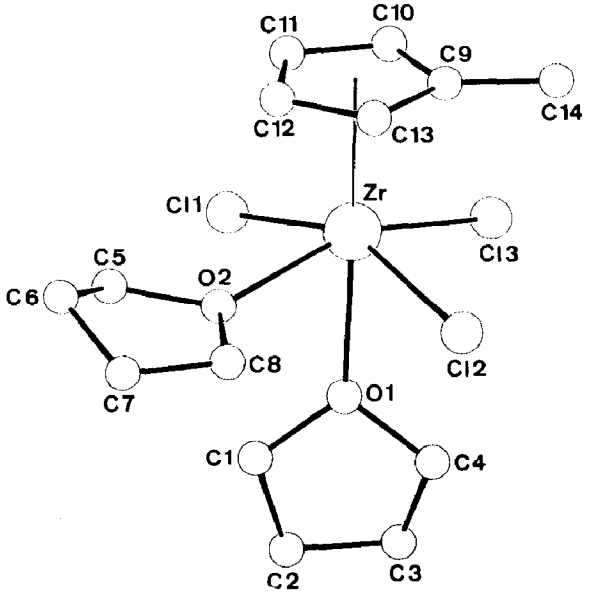
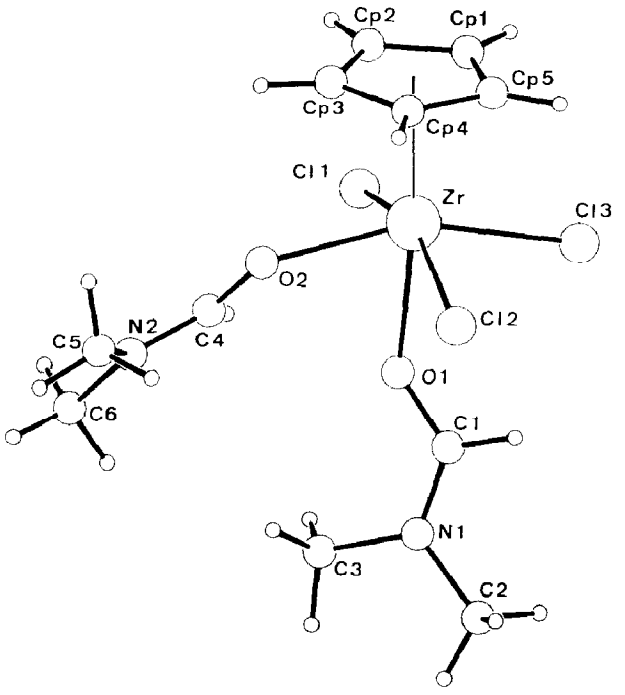


(7)

Fig. 1. Views of the molecular geometry of complexes 3 and 7.

The C(4), O(2), Zr angle is 128.4(2)°, the C(1), O(1), Zr angle is 130.6(2)°. In both cases the transition metal center is oriented towards the side of the dimethylformamide O=CH-hydrogen atom, away from the bulky Me_2N-groups (similar to the orientation reported for the benzaldehyde BF_3-adduct [9]). However, the Zr-atom



(**4**)

Fig. 2. Molecular geometry and atom numbering scheme of **4**.

Table 5

Bond lengths (Å) and angles (°) of $CpZrCl_3(dmf)_2$ (**4**)

Zr–Cl(1)	2.542(1)	O(2)–Zr–O(1)	74.2(1)
Zr–Cl(2)	2.515(1)	O(2)–Zr–Cl(3)	155.0(1)
Zr–Cl(3)	2.501(1)	O(2)–Zr–Cl(2)	89.0(1)
Zr–O(1)	2.253(2)	O(2)–Zr–Cl(1)	83.2(1)
Zr–O(2)	2.198(2)	O(1)–Zr–Cl(3)	81.2(1)
Zr–Cp(1)	2.503(4)	O(1)–Zr–Cl(2)	78.0(1)
Zr–Cp(2)	2.558(3)	O(1)–Zr–Cl(1)	78.2(1)
Zr–Cp(3)	2.567(4)	Cl(3)–Zr–Cl(2)	90.0(1)
Zr–Cp(4)	2.522(4)	Cl(3)–Zr–Cl(1)	87.7(1)
Zr–Cp(5)	2.482(4)	Cl(2)–Zr–Cl(1)	156.2(1)
O(1)–C(1)	1.261(4)	C(1)–O(1)–Zr	130.6(2)
O(2)–C(4)	1.257(4)	C(4)–O(2)–Zr	128.4(2)
N(1)–C(1)	1.296(4)	C(3)–N(1)–C(2)	117.7(3)
N(1)–C(2)	1.469(4)	C(3)–N(1)–C(1)	121.4(3)
N(1)–C(3)	1.468(5)	C(2)–N(1)–C(1)	120.7(3)
N(2)–C(4)	1.306(4)	C(6)–N(2)–C(5)	116.5(3)
N(2)–C(5)	1.471(4)	C(6)–N(2)–C(4)	121.9(3)
N(2)–C(6)	1.460(5)	C(5)–N(2)–C(4)	121.5(3)
Cp(1)–Cp(2)	1.393(6)	N(1)–C(1)–O(1)	123.3(3)
Cp(1)–Cp(5)	1.395(6)	N(2)–C(4)–O(2)	123.5(3)
Cp(2)–Cp(3)	1.385(5)	Cp(5)–Cp(1)–Cp(2)	107.9(4)
Cp(3)–Cp(4)	1.396(6)	Cp(3)–Cp(2)–Cp(1)	108.4(3)
Cp(4)–Cp(5)	1.393(7)	Cp(4)–Cp(3)–Cp(2)	107.9(3)
		Cp(5)–Cp(4)–Cp(3)	108.0(3)
		Cp(4)–Cp(5)–Cp(1)	107.8(4)

Table 6

Positional parameters of **4**

Atom	*x*	*y*	*z*
Zr	0.3598(1)	0.3546(1)	0.2343(1)
Cl(1)	0.0773(1)	0.3839(1)	0.3097(1)
Cl(2)	0.5552(1)	0.3349(1)	0.0993(1)
Cl(3)	0.4007(1)	0.5150(1)	0.2259(1)
O(1)	0.1814(3)	0.3824(1)	0.1035(1)
O(2)	0.2362(3)	0.2306(1)	0.1944(2)
N(1)	0.1086(3)	0.4153(2)	−0.0517(2)
N(2)	0.0356(3)	0.1477(2)	0.1138(2)
C(1)	0.2067(4)	0.4229(2)	0.0270(2)
C(2)	0.1483(5)	0.4619(3)	−0.1396(2)
C(3)	−0.0376(5)	0.3551(2)	−0.0584(3)
C(4)	0.0840(4)	0.2172(2)	0.1619(2)
C(5)	0.1582(5)	0.0785(2)	0.0944(3)
C(6)	−0.1431(5)	0.1336(3)	0.0786(3)
Cp(1)	0.5003(6)	0.3805(3)	0.3993(3)
Cp(2)	0.4101(4)	0.3035(3)	0.4091(2)
Cp(3)	0.4836(5)	0.2405(2)	0.3541(3)
Cp(4)	0.6211(5)	0.2781(3)	0.3102(3)
Cp(5)	0.6314(5)	0.3647(3)	0.3381(3)

in complex **4** does not lie exactly in either the *cis*- or the *trans*-dmf ligand plane (torsion angles Zr, O(2), C(4), N(2) 158.6°, Zr, O(1), C(1), N(1) 161.6°).

Coordination of dimethylformamide to the $CpZrCl_3$ Lewis acid results in slightly increased O=C bond lengths (O(2)–C(4) 1.257(4) Å, O(1)–C(1) 1.261(4) Å) and somewhat decreased (sp^2)C–N bond lengths (C(4)–N(2) 1.306(4) Å, C(1)–N(1) 1.296(4) Å) as compared to uncomplexed dimethylformamide [10] (O=C 1.24(1) Å, (sp^2)C–N 1.35(2) Å). A similar trend has been observed with a dmf-mercury complex ($C_6H_4(HgCl)_2 \cdot$ dmf: O=C 1.26(2), (sp^2)C–N 1.31(2) Å) [11].

Spectroscopic characterization

Coordination of dimethylformamide to the $CpZrCl_3$ Lewis acid leads to a reduced C=O stretching frequency in the infrared spectrum. For $CpZrCl_3(dmf)_2$ two ν(CO) bands were observed at 1655 and 1640 cm^{-1} (cf. ν(CO) = 1670 cm^{-1} for uncoordinated dmf (neat liquid); $C_6H_4(HgCl)_2 \cdot$ dmf: ν(CO) 1655 cm^{-1}) [11]. ^{13}C NMR spectra (75 MHz) of $CpZrCl_3(dmf)_2$ (**4**) were measured in CD_2Cl_2 at two temperatures (253 and 311 K) using solutions containing approximately 0.5 molar equivalents excess dimethylformamide. At the lower temperature signals of **4** were observed due to the Cp ligand (δ 118.7, ^1J(CH) 176 Hz) and two different coordinated dmf moieties (*trans*-dmf: δ 167.0 (204 Hz), 38.6, 33.1; *cis*-dmf: δ, 166.0 (204 Hz), 38.7, 33.8). Signals of uncoordinated dmf present in the solution appear at δ 162.6 (191 Hz), 36.4, and 30.9. In the presence of excess dimethylformamide, complex **4** exhibits dynamic ^{13}C NMR spectra at higher temperatures, indicating rapid exchange between free and coordinated dmf entities. At 311 K the signals of uncoordinated dmf and the set of resonances attributed to one of the coordinated amide ligands (δ(CO) 167.0) are already above their coalescence temperatures,

giving rise to only one equilibrated set of three ^{13}C NMR signals, whereas the NMR resonances of the other dmf ligand remain unaffected by the exchange process at this temperature. ^1H NMR experiments identify the rapidly exchanging dmf ligand as oriented *trans* to the cyclopentadienyl ligand at zirconium (vide infra).

The ^1H NMR spectrum (400 MHz) of **4** at 223 K shows a Cp singlet at δ 6.53, resonances of one dmf-ligand at δ 8.32 (C*H*O), 3.04 and 2.87 (NMe_2) and a second coordinated dimethylformamide at δ 8.00, 3.08 and 2.99 (free dmf: δ 7.91, 2.87, 2.77). The relative assignment follows from the observed homonuclear coupling as well as NOE-experiments [12]. The stereochemical assignment of the dmf-ligands is deduced from an NOE-experiment carried out on complex **4** in CD_2Cl_2 solution at 213 K. Nuclear Overhauser enhancement was observed between the Cp protons and the methyl group signal at δ 2.99, assigning this $N-CH_3$ resonance to the *cis*-dmf ligand. Magnetization transfer difference spectroscopy revealed that the other dmf ligand (coordinated *trans* to Cp) is rapidly exchanged on the NMR time scale with free dimethylformamide in solution at 233 K. Variable temperature ^1H NMR spectroscopy (200 MHz) of **4** in CD_2Cl_2 containing ca. 0.35 molar equivalents of additional dmf confirmed the rapid exchange taking place between free dmf and coordinated dmf *trans*-oriented to Cp in the temperature range between 243 K and 289 K. Under these conditions the *cis*-dmf signals remain unchanged. Eventually, the exchange reaction between the *cis*-dmf ligand and free dimethylformamide can be observed at higher temperatures in the presence of increased amounts of dmf. We conclude that there is experimental evidence for exchange of both dmf-ligands coordinated the $CpZrCl_3$ Lewis acid, but that the dmf-ligand oriented in a *trans*-position relative to Cp is exchanged faster than the *cis*-dmf moiety.

The complexes $CpZrCl_3(thf)_2$ (**3**) and $(MeCp)ZrCl_3(thf)_2$ (**7**) show similar dynamic behaviour in solution compared to that of **4**. At 233 K the (cyclopentadienyl)bis(tetrahydrofuran)zirconium trichloride adduct **3** exhibits a ^{13}C NMR Cp-signal (CD_2Cl_2, 50 MHz) at δ 118.7 (^1J(CH) 176 Hz) and resonances due to two different coordinated tetrahydrofuran ligands (*cis* and *trans* to Cp) at δ 76.0 (153 Hz), 72.5 (151 Hz) (thf, methylene groups α to oxygen), 25.2 (134 Hz), and 24.5 (133 Hz) (CH_2 β to oxygen). An averaged set of ^{13}C NMR thf signals is observed at 273 K (δ 74.0, 25.3). The ^1H NMR spectrum of **3** at 233 K (CD_2Cl_2, 200 MHz) similarly shows signals at δ 6.54 (s, 5H, Cp), 4.20, 4.04, 1.95, and 1.83 (m, each 4H, two thf ligands). At ambient temperature only one averaged set of thf-signals is observed. The temperature dependent dynamic ^1H NMR spectra of **3** in the presence of various concentrations of additional thf have shown that uncoordinated tetrahydrofuran present in the solution is involved in the observed ligand exchange process at the $CpZrCl_3$ Lewis acid. $(MeCp)ZrCl_3(thf)_2$ shows an equivalent behaviour as judged from its variable temperature ^1H NMR spectra [CD_2Cl_2, 400 MHz, 203 K: δ 6.41, 6.28 (m, 2H each, $C_5H_4CH_3$), 2.27 (s, 3H, $C_5H_4CH_3$), 4.16, 4.05, 1.95, 1.83 (m, 4H each, two thf ligands)].

Catalysis

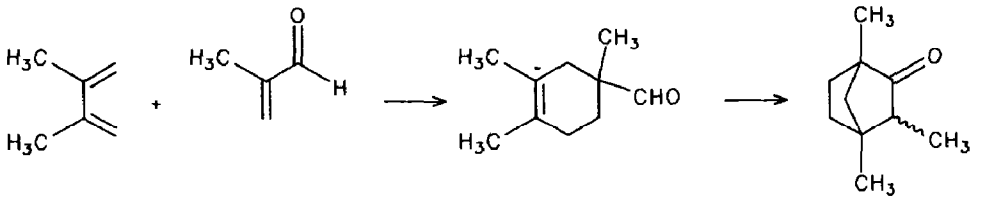
2,3-Dimethylbutadiene (**11**) reacts with methacrolein (**12**) at 150 °C (5 h) in a thermally induced Diels–Alder reaction to give 1,3,4-trimethyl-3-cyclohexenyl-1-carbaldehyde (**13**) (65%). Baldwin and Lusch had shown that the [4 + 2] cycloaddition of **11** and **12** can be accelerated by Lewis acid catalysis using $SnCl_4$ [13]. In the

presence of catalytic amounts of tin tetrachloride, the addition reaction proceeds rapidly at ambient temperature. However, it does not stop at the desired product **13** because this undergoes a rapid subsequent acid catalyzed rearrangement to 1,3,4-trimethylbicyclo[2.2.1]hepten-2-one (**14**). Using $TiCl_4$ instead of the $SnCl_4$ catalyst in our hands gave similar results.

$CpZrCl_3(thf)_2$ rapidly exchanges thf ligands in solution (vide supra). The octahedral d^0/16-electron complex **3** can therefore be used as a precursor for the in situ generation for $CpZrCl_3L$ or $CpZrCl_3$ Lewis acid catalysts of 14- or 12-electron configuration, respectively.

We have found that $CpZrCl_3(thf)_2$ at room temperature very selectively catalyzes the [4 + 2] cycloaddition of 2,3-dimethylbutadiene and methacrolein to give **13**. However, the rearrangement **13** → **14** induced by $CpZrCl_3(thf)_2$ required a temperature of 150 °C (2.5 h of a near to quantitative conversion of **13**).

We assured ourselves that when a solution of 0.6 mmol of **12** and 0.7 mmol of **11** in 0.6 ml $CDCl_3$ was kept at room temperature over a period of 8 days in the absence of a Lewis acid catalyst, no formation of product **13** was detectable by ^1H NMR spectroscopy. Addition of ca. 0.05 molar equivalents of $CpZrCl_3(thf)_2$ to such a solution gave rise to a quantitative formation of the addition product **13** over the same period of time. Product formation was followed continuously by ^1H NMR spectroscopy at 44 °C using a solution containing 0.71 mmol of methacrolein, 0.71 mmol of 2,3-dimethylbutadiene and 0.057 mmol of $CpZrCl_3(thf)_2$ (**3**) in 0.6 ml $CDCl_3$. Compound **13** was formed selectively. A 95% transformation of the starting materials was achieved during the first 110 min, corresponding to a turnover number of ca. 75 h^{-1} at the Lewis acid catalyst under the conditions present at the beginning of the reaction. Product **13** was prepared on a preparative scale from **11** and **12** using a catalytic amount of **3**, and isolated in 62% yield (2.7 g).



11 12 13 14

Conclusions

Titanium tetrachloride is a frequently used Lewis acid catalyst which forms numerous rather stable adducts with various donor ligands [14]. In contrast, $CpTiCl_3$ does not appear to favour similar coordination of O-donor ligands [5]. Therefore, in a direct comparison, $CpZrCl_3$ seems to be a stronger Lewis acid than $CpTiCl_3$. Moreover, (η-cyclopentadienyl)zirconium trichloride bis-donor adducts exhibit a well defined coordination chemistry and dynamic behaviour. We have presented evidence that rapid exchange of a donor ligand *trans* to Cp is possible at octahedral $CpZrCl_3L_2$ complexes. Exchange with Diels–Alder active α,β-unsaturated carbonyl compounds may be the important step in activating such reagents for the Lewis acid catalyzed [4 + 2] cycloaddition process with conjugated

dienes. Our observation that donor ligands at zirconium oriented *cis* to Cp can undergo an exchange process with donors in solution as well, albeit sometimes proceeding at a lower rate, may open ways to influence the selectivity of the catalyzed process by attaching suitable auxiliaries to the active Lewis acid catalyst. We are currently investigating if such systems can be used for asymetric catalysis.

Experimental section

Reactions were carried out in an inert atmosphere (argon) using Schlenk type glassware. Solvents were dried and freshly distilled from potassium/benzophenone, $LiAlH_4$, or P_4O_{10} (chloroform, methylene chloride) prior to use. Deuterated solvents were treated with sodium/potassium alloy (arom. solvents) or P_4O_{10} ($CDCl_3$, CD_2Cl_2), distilled, and stored under argon. The following spectrometers were used: NMR, Bruker, WP 80-FT, WP 200 SY, WM 300 FT, WH 400-FT; IR, Nicolet 7199 and DX 5 FT IR spectrometer. Elemental analyses were carried out by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, FRG and the Institut für Anorganische Chemie der Universität Würzburg. Melting points are uncorrected. $CpZrCl_3$ was prepared according to a published procedure [3a].

*(η-Cyclopentadienyl)bis(tetrahydrofuran)zirconium trichloride (**3**).* A sample of 12.0 g (45.7 mmol) of $CpZrCl_3$ is suspended in 150 ml of toluene. Tetrahydrofuran (18 g, 250 mmol) is added with stirring at ambient temperature over ca. 5 min. The mixture is refluxed for several min and filtered while still hot. Large colourless crystals form overnight at room temperature, which are collected by filtration (12.4 g, 67% yield), m.p. 128°C (decomp.). Anal. Found: C, 38.19; H, 4.86. $C_{13}H_{21}O_2Cl_3Zr$ (406.9) calcd.: C, 38.37; H, 5.20%. ^1H NMR (200 MHz, CD_2Cl_2, 27°C): δ 6.66 (s, 5H, Cp) 4.03, 1.92 (m, each 8H, thf); (200 MHz, CD_2Cl_2, −100°C): δ 6.54 (s, 5H, Cp), 4.20, 4.04, 1.95, 1.83 (m, each 4H, thf). ^{13}C NMR (50 MHz), CD_2Cl_2, 40°C): δ 120.3 (Cp), 72.4, 25.9 (thf); (CD_2Cl_2, −40°C): δ 118.7 (Cp), 76.0, 72.5, 25.7, 24.5 (CH_2, thf).

*(Methylcyclopentadienyl)thallium (**5**).* Potassium hydroxide (10.1 g, 180 mmol) and thallium(I)sulfate (24.0 g, 47.5 mmol) are dissolved in 200 ml of water (degassed and saturated with argon). Freshly distilled methylcyclopentadiene (8.0 g, 100 mmol) was added dropwise with rapid stirring to this solution at ambient temperature. The mixture is stirred for additional 20 min and then filtered. The recovered slightly yellowish solid is washed with 50 ml of H_2O and then with 50 ml of cold methanol. After drying in vacuo 17.5 g (65%) of **5** are recovered. ^1H NMR ($CDCl_3$): δ 5.99 (m, 2H), 5.85 (m, 2H), 2.20 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 122.8 (*ipso*-C), 108.7 (CH), 106.2 (CH), 14.3 (CH_3).

*(η-Methylcyclopentadienyl)bis(tetrahydrofuran)zirconium trichloride (**7**).* Tetrahydrofuran (200 ml) is added dropwise at −78°C to a suspension of 13.9 g (60.0 mmol) zirconium tetrachloride in 100 ml of toluene. The mixture is warmed up to 0°C. At 0°C a suspension of 17.0 g (60.0 mmol) (η-methylcyclopentadienyl)thallium in 100 ml of tetrahydrofuran is added slowly. The reaction mixture is stirred for 6 h at room temperature. Solvent is then removed in vacuo. The solid residue is extracted with 200 ml of methylene chloride and filtered. The filtrate is concentrated in vacuo to about 100 ml. Crystallization at −30°C gave **7** (13.2 g, 52%), m.p. 96–100°C. Anal. Found: C, 39.46; H, 5.70. $C_{14}H_{23}O_2Cl_3Zr$ (420.9) calcd.: C, 39.95; H, 5.51%. ^1H NMR (400 MHz, CD_2Cl_2, 20°C): δ 6.47, 6.30 (m, 2H each,

$C_5H_4CH_3$), 4.11, 1.92 (m, 8H each, thf), 2.37 (s, 3H, $C_5H_4CH_3$); (400 MHz, CD_2Cl_2, −70 °C): δ 6.41, 6.28 (m, 2H each, $C_5H_4CH_3$), 4.16, 4.05, 1.95, 1.83 (m, 4H each, thf), 2.27 (s, 3H, $C_5H_4CH_3$).

(η-Cyclopentadienyl)bis(dimethylformamide)zirconium trichloride (4). (a) *Synthesis from $CpZrCl_3$ (2)*: A sample of 2.54 g (9.67 mmol) $CpZrCl_3$ is suspended in 120 ml of toluene. Dimethylformamide (4.7 g, 65 mmol) is added slowly with stirring. The dark coloured mixture is heated to reflux temperature. The resulting solution is filtered while still hot. Upon cooling to room temperature a small amount of a brown oil separates from the solution. The solution is decanted from this oily precipitate. From the resulting clear, yellow coloured solution $CpZrCl_3(dmf)_2$ (**4**) slowly crystallizes over several days (large colourless crystals, 0.83 g, 21%). (b) *Synthesis from $CpZrCl_3(thf)_2$ (3)*: (η-Cyclopentadienyl)bis(tetrahydrofuran)zirconium trichloride (**3**) (10.1 g, 24.7 mmol) is partially dissolved in 150 ml of toluene. To the rapidly stirred suspension one slowly adds 4.7 g (65 mmol) of dimethylformamide at ambient temperature. The $CpZrCl_3(dmf)_2$ adduct (**4**) precipitates from the solution. The mixture is stirred for additional 30 min at room temperature and then filtered. The recovered solid is dried in vacuo (10^{-3} bar) to remove any excess dmf. Yield of **4**: 9.8 g (98%), m.p. 165 °C. Anal. Found: C, 32.26; H, 4.33. $C_{11}H_{19}N_2O_2Cl_3Zr$ (408.8) calcd.: C, 32.31; H, 4.68%. IR (KBr): ν(C=O) 1655, 1640 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, −50 °C): δ 6.53 (s, 5H, Cp), *trans*-dmf ligand: 8.32 (1H, CHO), 3.04 (^4J 0.7 Hz), 2.87 (^4J 0.9 Hz, 3H each, NMe_2), *cis*-dmf ligand: 8.00 (1H, CHO), 3.08 (^4J 0.87 Hz), 2.99 (^4J 0.9 Hz, 3H each, NMe_2). ^{13}C NMR (75 MHz, CD_2Cl_2, −20 °C): δ 118.7 (^1J(CH) 176 Hz, Cp), two dmf-ligands at δ 167.0 [^1J(CH) 204 Hz, CHO], 38.6, 33.1 (NMe_2) and δ 166.0 (^1J(CH) 204 Hz, CHO), 38.7, 33.8 (NMe_2).

Catalytic formation of 1,3,4-trimethyl-3-cyclohexenyl-1-carbaldehyde (13). A mixture of 2.36 ml (28.5 mmol) methacrolein and 3.22 ml (28.5 mmol) 2,3-dimethylbutadiene in 10 ml of chloroform at room temperature is charged with 660 mg (1.6 mmol) of $CpZrCl_3(thf)_2$ (**3**). The mixture is stirred for 20 h at ambient temperature and then filtered. Solvent is removed from the filtrate in vacuo. Distillation gives 2.7 g (62%) of **13**, b.p. (15 mbar) 72 °C. Identification by comparison with an authentic sample [13]. IR(film): ν(C=C) 1725 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.03 (s, 3H, CH_3), 1.59, 1.65 [m, 3H each, $=C(CH_3)$], 1.46, 1.82 (m, 2H, CH_2), 1.97 (m, 2H, CH_2), 1.75, 2.25 (m, 2H, CH_2), 9.47 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ 18.7, 19.2, 20.7 (each CH_3), 29.3, 28.4, 37.9 (each CH_2), 45.2 (quart. C), 123.0, 125.1 (olef. C), 206.0 (CHO).

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References

1 For examples see: (a) B.B. Snider, Acc. Chem. Res. 13 (1980) 426; W. Oppolzer, Angew. Chem. 96 (1984) 840. Angew. Chem. Int. Ed. Engl. 23 (1984) 876; M.T. Reetz, Angew. Chem. 96 (1984) 542, Angew. Chem. Int. Ed. Engl. 23 (1984) 556. (b) S.J. Danishefsky, E. Larson, D. Askin, N. Kato, J.

Am. Chem. Soc. 107 (1985) 1246; S.J. Danishefsky, W.H. Pearson, D.F. Harvey, C.J. Maring, J.P. Springer, ibid., 107 (1985) 1256; T. Poll, J.O. Metter, G. Helmchen, Angew. Chem. 97 (1985) 116, Angew. Chem. Int. Ed. Engl. 24 (1985) 112; S.F. Pedersen, J.C. Dewan, R.R. Eckman, K.B. Sharpless, J. Am. Chem. Soc. 109 (1987) 1279, loc. cit. C. Chapuis, J. Juczak, Helv. Chim. Acta 70 (1987) 436; K. Narasaka, M. Inouye, N. Okada, Chem. Lett. (1986) 1109; D.A. Evans, K.T. Chapman, J. Bisaha, J. Am. Chem. Soc. 110 (1988) 1238, and refs. cited therein.

2 Review: W. Beck, K. Sünkel, Chem. Rev. 88 (1988) 1405.

3 (a) G. Erker, K. Berg, L. Treschanke, K. Engel, Inorg. Chem. 21 (1982) 1277; L.M. Engelhardt, R.I. Papasergio, C.L. Raston, A.H. White, Organometallics 3 (1984) 18; A. Terpstra, J.N. Louwen, A. Oskam, J.H. Teuben, J. Organomet. Chem. 260 (1984) 207. (b) See for a comparison: K. Berg, G. Erker, J. Organomet. Chem. 263 (1984) 37; G. Erker, K. Berg, C. Krüger, G. Müller, K. Angermund, R. Benn, G. Schroth, Angew. Chem. 96 (1984) 445, Angew. Chem. Int. Ed. Engl. 23 (1984) 455; G. Erker, K. Berg, R. Benn, G. Schroth, Angew. Chem. 96 (1984) 621, Angew. Chem. Int. Ed. Engl. 23 (1984) 625; K. Berg, G. Erker, J. Organomet. Chem. 270 (1984) C53; G. Erker, K. Berg, R. Benn, G. Schroth, Chem. Ber. 118 (1985) 1383; G. Erker, K. Berg, K. Angermund, C. Krüger, Organometallics 6 (1987) 2620. (c) C.P. Casey, F. Nief, Organometallics 4 (1985) 1218, ref. 17.

4 (a) L.T. Reynolds, G. Wilkinson, J. Inorg. Nucl. Chem. 9 (1959) 86; M. Arthurs, H.K. Al-Daffaee, J. Haslop, G. Kubal, M.D. Pearson, P. Thatcher, E. Curzon, J. Chem. Soc. Dalton Trans. (1987) 2615. (b) E. Frasson, F. Menegus, C. Panattoni, Nature 199 (1963) 1087; H.P. Fritz, F.H. Köhler, J. Organomet. Chem. 30 (1971) 177; A.A. Koridze, N.A. Ogorodnikova, P.V. Petrovsky, J. Organomet. Chem. 157 (1978) 145; H. Werner, H. Otto, H.J. Kraus, J. Organomet. Chem. 315 (1986) C57; R. Blom, H. Werner, J. Wolf, J. Organomet. Chem. 354 (1988) 293.

5 N.J. Wells, J.C. Huffman, K.G. Caulton, J. Organomet. Chem. 213 (1981) C17.

6 R.D. Ernst, W.J. Kennelly, C.S. Day, V.W. Day, T.J. Marks, J. Am. Chem. Soc. 101 (1979) 2656; J.F. Le Marechal, M. Ephritikhine, G. Folcher, J. Organomet. Chem. 299 (1986) 85.

7 D.L. Hughes, G.J. Leigh, D.G. Walker, J. Organomet. Chem. 355 (1988) 113.

8 R.F. Jordan, C.S. Bajgur, R. Willett, B. Scott, J. Am. Chem. Soc. 108 (1986) 7410.

9 M.T. Reetz, M. Hüllmann, W. Massa, S. Berger, P. Rademacher, P. Heymanns, J. Am. Chem. Soc. 108 (1986) 2405.

10 H. Ohtaki, S. Itoh, T. Yamaguchi, S. Ishiguro, B.M. Rode, Bull. Chem. Soc. Jpn. 56 (1983) 3406; F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans., II (1987) S1.

11 (a) A.L. Beauchamp, M.J. Olivier, J.D. Wuest, B. Zacharie, Organometallics 6 (1987) 153. (b) It is consistent with the observed structural trend that the activation energy for $R_2N-C(R)=O$ bond rotation increases with the solvent polarity. L.H. Jackman in L.M. Jackman, F.A. Cotton (Eds.) Dynamic Nuclear Magnetic Spectroscopy, Academic Press, New York, 1975, Chapter 7; L. Brun, C.J. Bränden, Acta Crystallogr. 20 (1966) 749; D. Fenske, K. Jansen, K. Dehnicke, Z. Naturforsch., B, 41 (1986) 523; see also T.J. LePage, K.B. Wiberg, J. Am. Chem. Soc. 110 (1988) 6642, (loc. cit.). (c) G. Valle, S. Calogero, U. Russo, J. Organomet. Chem. 228 (1982) C79; A. Bittner, D. Männig, H. Nöth, Z. Naturforsch., B. 41 (1986) 587.

12 R. Benn, A. Rufińska, G. Schroth, J. Organomet. Chem. 217 (1981) 91.

13 J.E. Baldwin, M.J. Lusch, J. Org. Chem. 44 (1979) 1923.

14 I. Lindquist, Inorganic Adduct Molecules of Oxocompounds, Springer Verlag, Heidelberg, 1963; L. Brun, Acta Crystallogr. 20 (1966) 739; I.W. Bassi, M. Calcaterra, R. Intrito, J. Organomet. Chem. 127 (1977) 305; J. Utko, P. Sobota, T. Lis, J. Organomet. Chem. 334 (1987) 341.