Isonitrile Insertion of a β-CH Agostic Alkenylzirconocene Complex

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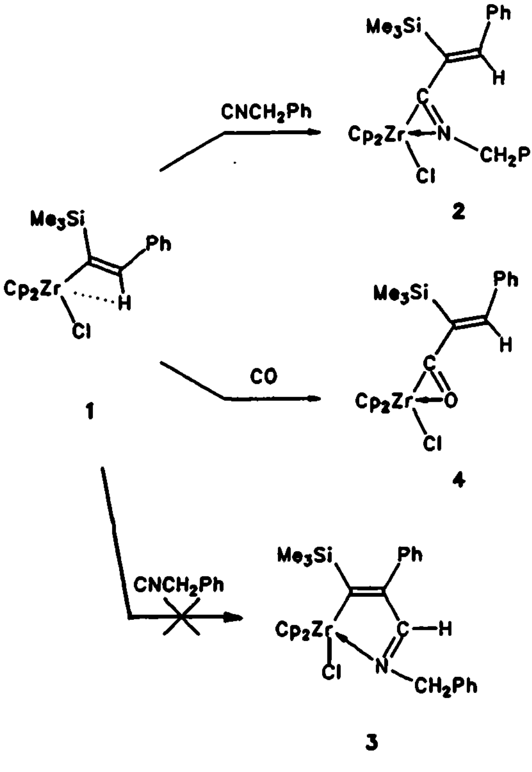
Received February 1, 1989

Key Words: Agostic interaction / Isonitrile insertion / Zirconocene complex

Reaction of the β-CH agostic alkenylzirconocene complex $Cp_2ZrCl[C(SiMe_3){=}CHPh]$ (1) with benzyl isonitrile yields the (η^2-iminoacyl)zirconocene complex $PhCH{=}C(SiMe_3)-C[\overline{ZrCp_2Cl]{=}N}CH_2Ph$ (2). Complex 2 crystallizes in space group $P2_1/a$ with cell parameters a = 8.928(2), b = 18.888(3), c = 16.163(1) Å, β = 93.45(1)°, Z = 4. Carbon monoxide analogously inserts only into the Zr – C bond of 1. No evidence has been found for insertion reactions involving the alkenyl β-carbon-to-hydrogen bond "activated" by the agostic Zr ··· H – C interaction in this system.

Metal complexes exhibiting a three-center two-electron M ··· H – C agostic interaction with carbon – hydrogen bonds of a variety of ligand types can no longer be regarded as structural curiosities. Such compounds are abundant. Numerous examples comprising almost every transition metal have been described[1]. Reports about specific reactions of metal-coordinated agostic C – H bonds are, however, extremely rare[2]. So it is not at all clear at present whether the formation of the agostic M ··· H – C situation can be regarded as a process of activating an otherwise non-activated carbon – hydrogen bond or not. Competition experiments using, e. g., isonitrile or carbon monoxide insertion reactions should be helpful to establish an order of relative reactivities of metal-to-carbon σ-bonds vs. adjacent M ··· H – C moieties.



We have carried out such an experiment using the β-CH agostic alkenylzirconocene complex 1 which is readily available by hydrozirconation of phenyl(trimethylsilyl)acetylene[2b]. Complex 1 reacts readily at ambient temperature with 1 molar equivalent of benzyl isonitrile to give the insertion product 2 in high yield. Structural identification by NMR [^1H: δ = 6.88 (alkenyl CH); ^{13}C: δ = 238.0 (iminoacyl C)] and IR spectra ($\tilde{\nu}_{C=N}$ = 1616 cm^{-1}) as well as X-ray diffraction revealed that only isonitrile insertion into the reactive zirconium-to-carbon σ-bond of 1 has taken place. We have not found any evidence for the formation of the alternative product 3 involving cleavage of the alkenyl β-C – H bond.

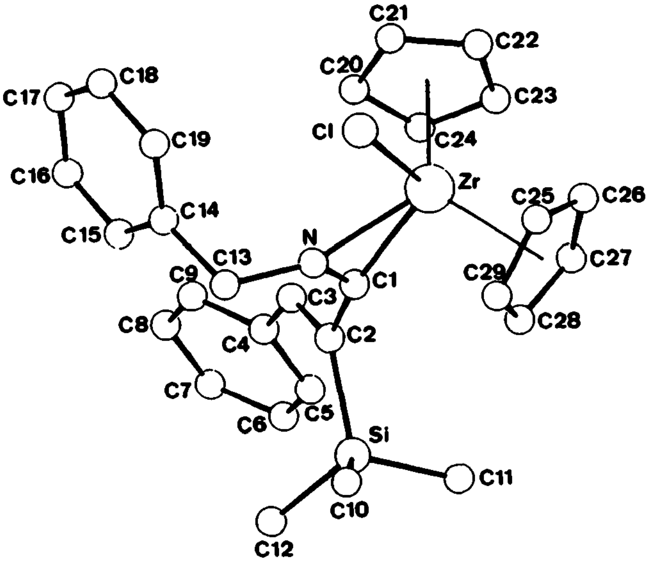


Figure 1. View of the molecular structure of the (η^2-iminoacyl)zirconocene complex 2

In the solid state complex 2 exhibits a three-membered metallacyclic $\overline{ZrCN}$ ring system with bond lengths Zr – C(1) 2.250(4), Zr – N 2.200(3), and C(1) – N 1.267(5) Å. These bonding parameters are clearly within the characteristic range of (η^2-iminoacyl)zirconium complexes [four typical examples reported in the literature[3] showing values of 2.20(1) – 2.249(3) Å for Zr – C(1), 2.194(8) – 2.257(3) Å for Zr – N, and 1.263(7) – 1.286(4) Å for C = N]. Within these limits the Zr – N distance of 2 is at the lower end while the Zr – C(iminoacyl) bond is rather long. The iminoacyl-CN bond is close to the average value of organic azomethin C = N double bonds

(d = 1.279 Å[4]), despite the internal coordination to the Lewis-acidic zirconium center. The π systems of the α,β-unsaturated heterocarbonyl ligand are almost bisected [dihedral angle N,C(1),C(2),C(3): 87.3°]. This probably helps to avoid unfavourable steric Me_3Si/Cp and/or alkenyl/*N*-benzyl interactions [angle C(1),N,C(13),C(14): −91.9°; C(2),C(1),N,C(13): 0.0°][5].

Table 1. X-ray crystal structure analysis of **2**: selected bond lengths and angles

Zr	- Cl	2.571(1)	C(1)	- Zr	- Cl	115.7(1)
Zr	- N	2.200(3)	N	- Zr	- Cl	82.6(1)
Zr	- C(1)	2.250(4)	C(1)	- Zr	- N	33.1(1)
Si	- C(2)	1.908(4)	C(13)	- N	- C(1)	128.0(3)
N	- C(1)	1.267(5)	C(13)	- N	- Zr	155.3(3)
N	- C(13)	1.476(6)	C(1)	- N	- Zr	75.7(2)
C(1)	- C(2)	1.468(5)	C(2)	- C(1)	- N	130.3(4)
C(2)	- C(3)	1.352(5)	C(2)	- C(1)	- Zr	157.4(3)
C(3)	- C(4)	1.463(6)	N	- C(1)	- Zr	71.3(2)
C(4)	- C(5)	1.397(6)	C(3)	- C(2)	- C(1)	115.9(3)
C(13)	- C(14)	1.504(6)	C(3)	- C(2)	- Si	128.1(3)
C(14)	- C(15)	1.393(7)	C(1)	- C(2)	- Si	116.0(3)
			C(4)	- C(3)	- C(2)	130.6(4)

Table 2. Positional parameters of **2**

Atom	x	y	z	U_{eq}
Zr	0.1407(1)	0.0991(1)	0.3209(1)	0.039(1)
CL	-0.1268(1)	0.1336(1)	0.3558(1)	0.066(1)
Si	0.3300(1)	-0.1433(1)	0.3273(1)	0.044(1)
N	0.0371(4)	-0.0056(2)	0.3012(2)	0.038(2)
C1	0.1727(5)	-0.0146(2)	0.2846(2)	0.036(2)
C2	0.2469(4)	-0.0761(2)	0.2494(2)	0.034(2)
C3	0.2431(5)	-0.0792(2)	0.1658(2)	0.041(2)
C4	0.3131(5)	-0.1292(2)	0.1107(2)	0.043(3)
C5	0.4553(5)	-0.1581(3)	0.1288(3)	0.055(3)
C6	0.5190(5)	-0.2045(3)	0.0748(3)	0.066(4)
C7	0.4428(6)	-0.2223(3)	0.0014(3)	0.063(3)
C8	0.3070(6)	-0.1939(3)	-0.0187(3)	0.064(4)
C9	0.2413(5)	-0.1467(2)	0.0350(3)	0.053(3)
C10	0.2147(6)	-0.1418(3)	0.4197(3)	0.069(4)
C11	0.5250(5)	-0.1192(3)	0.3578(3)	0.065(3)
C12	0.3166(6)	-0.2356(3)	0.2867(3)	0.069(4)
C13	-0.0889(5)	-0.0559(2)	0.2890(3)	0.050(3)
C14	-0.1710(5)	-0.0459(2)	0.2059(3)	0.045(3)
C15	-0.1422(5)	-0.0903(3)	0.1399(3)	0.057(3)
C16	-0.2086(7)	-0.0792(3)	0.0620(3)	0.074(4)
C17	-0.3053(7)	-0.0231(4)	0.0488(3)	0.077(4)
C18	-0.3366(6)	0.0200(3)	0.1127(4)	0.070(4)
C19	-0.2694(5)	0.0095(3)	0.1911(3)	0.057(3)
C20	0.0951(6)	0.1118(3)	0.1634(3)	0.057(3)
C21	0.0469(6)	0.1750(3)	0.1978(3)	0.067(4)
C22	0.1691(8)	0.2092(3)	0.2362(3)	0.070(4)
C23	0.2947(6)	0.1677(3)	0.2237(3)	0.068(4)
C24	0.2492(6)	0.1070(3)	0.1802(3)	0.062(3)
C25	0.1765(7)	0.1494(3)	0.4657(3)	0.077(4)
C26	0.3000(8)	0.1715(3)	0.4257(4)	0.079(4)
C27	0.3835(6)	0.1128(4)	0.4066(3)	0.073(4)
C28	0.3163(7)	0.0540(3)	0.4381(3)	0.072(4)
C29	0.1867(7)	0.0757(3)	0.4733(3)	0.072(4)

Carbonylation of the β-CH agostic alkenylzirconocene complex **1** (50 bar) proceeds analogously. Only carbonyl insertion into the Zr−C σ-bond to give **4** is observed. The formation of the (η^2-acyl)zirconocene product is evident from its very characteristic spectroscopic data[6] [^{13}C NMR: δ = 306.8 (s, acyl C). − IR: $\tilde{\nu}_{C=O}$ = 1494 cm^{-1}].

Our experiments show that the alkenyl C−H bond of **1** is not sufficiently activated by coordination to the electrophilic transition metal center to undergo a direct intermolecular isonitrile (or CO) insertion reaction with formation of a new CC bond. A common insertion reaction into the Zr−C σ-bond is observed instead. It is probably initiated by preceeding alkenylzirconocene/isonitrile adduct formation, which can only take place after termination of the agostic M···H−C interaction.

Financial support from the *Stiftung Volkswagenwerk*, the *Fonds der Chemischen Industrie*, and the *Alfried Krupp von Bohlen und Halbach-Stiftung* is gratefully acknowledged.

Experimental

[η^2-(Z)-1-(Benzylimino)-3-phenyl-2-(trimethylsilyl)-2-propenyl-N]chlorobis(cyclopentadienyl)zirconium (**2**): Benzyl isonitrile (0.19 g, 1.62 mmol) is added to 0.61 g (1.41 mmol) of **1** in 20 ml of toluene. After stirring for 3 h at 20°C the yellow solution is concentrated in vacuo to about 1 ml. Hexane (5 ml) is added. The resulting yellow precipitate is collected by filtration under argon using Schlenk-type glassware, washed twice with additional 2 ml of hexane, and dried in vacuo to give 0.62 g (80%) of **2**, mp 113−114°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1616 cm^{-1}. − ^1H NMR ([D_6]benzene): δ = 0.01 (s, 9H, $SiMe_3$), 4.78 (s, 2H, NCH_2Ph), 5.73 (s, 10H, Cp), 6.88 (s, 1H, =C*H*Ph), 7.01−7.30, 7.66−7.74 (m, 10H, Ph). − ^{13}C NMR ([D_6]benzene): δ = 1.0 [$^1J_{CH}$ = 122 Hz, $Si(CH_3)_3$], 54.1 ($^1J_{CH}$ = 139 Hz, NCH_2Ph), 109.5 ($^1J_{CH}$ = 172 Hz, Cp), 127.8, 128.2, 128.4, 128.7, 129.0, 130.9 (d each, phenyl CH), 136.8, 139.3, 148.2 (s each, phenyl and alkenyl quart. C), 139.0 ($^1J_{CH}$ = 152 Hz, alkenyl CH), 238.0 (s, iminoacyl-C).

$C_{29}H_{32}ClNSiZr$ (549.3)	Calcd.	C 63.41	H 5.87	N 2.55
	Found	C 62.73	H 5.90	N 2.67

Chlorobis(cyclopentadienyl){η^2-(Z)-[3-phenyl-2-(trimethylsilyl)-propenoyl-O]}zirconium (**4**): A solution of 0.78 g (1.80 mmol) of **1** in 20 ml of toluene is carbonylated for 17 h at 20°C with 50 bar CO (autoclave). The resulting red solution is concentrated in vacuo to ca. 2 ml. Hexane (10 ml) is added. The orange colored solid is collected by filtration, washed twice with 2 ml of hexane and dried in vacuo to give 0.70 g (85%) of **4**, mp 115−116°C. The product was not obtained completely analytically pure but showed no admixtures by ^1H-NMR spectroscopy. − IR (KBr): $\tilde{\nu}$ = 1494 cm^{-1} (C=O). − ^1H NMR ([D_6]benzene): δ = 0.10 (s, 9H, $SiMe_3$), 5.73 (s, 10H, Cp), 7.05−7.28 (s, 5H, Ph), 8.55 (s, 1H, =C*H*Ph). − ^{13}C NMR ([D_6]benzene): δ = 0.6 ($^1J_{CH}$ = 120 Hz, $SiMe_3$), 109.7 ($^1J_{CH}$ = 173 Hz, Cp), 128.5, 129.4, 130.3 (d each, phenyl CH), 137.9, 144.2 (s each, phenyl and alkenyl quart. C), 172.1 ($^1J_{CH}$ = 151 Hz, =CHPh), 306.8 (s, acyl C).

CAS Registry Numbers

1: 119747-83-0 / **2**: 119747-84-1 / **4**: 119747-85-2 / $CNCH_2Ph$: 28064-79-1

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[5] Crystal structure analysis of **2**: $C_{29}H_{32}ClNSiZr$, M = 549.3, $P2_1/a$, a = 8.928(2), b = 18.888(3), c = 16.163(1) Å, β = 93.45(1)°, V = 2720.8 Å^3, Z = 4, $D_{calcd.}$ = 1.34 gcm^{-3}, μ = 5.55 cm^{-1}, Enraf-Nonius diffractometer, 6542 measured reflexes, 3817 observed [$I \geq 2\sigma(I)$], heavy atom method, positions of hydrogen atoms calculated, not refined, R = 0.043, R_w = 0.045 for 298 parameters. Further details of the crystal structure analysis are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-53900, the names of the authors, and the journal citation.

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