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Reduction of Conformational Space by 1,2-Diketone·Lewis Acid Chelates

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Key Words: Single crystal X-ray structure; 1,2-diketones attached to various central metal atoms

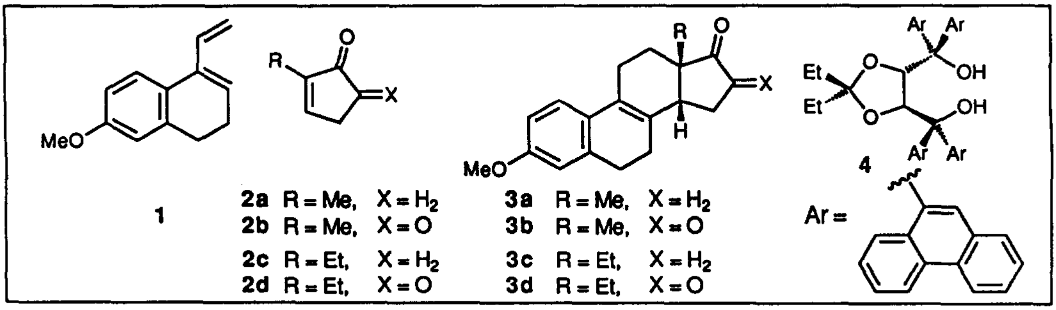
Abstract: *Various 1,2-diketones function as chelating ligands with Ti and Sn, but not with Al*

The *Diels-Alder* reaction of the *Dane* diene **1** and dienophiles of type **2** is a reliable test system for the control *Lewis* acids may exert on adduct formation [1]. The reaction with dienophiles **2b** and **2d** affords steroids *rac*-**3b** or *rac*-**3d** [2] as the major components only in the presence of a *Lewis* acid, while **2a** and **2c**, in the absence of a *Lewis* acid do not furnish steroids *rac*-**3a** or *rac*-**3c** at al..

In order to execute the chirogenic [3] adduct formation in an enantioselective manner, an *in situ* production of a chiral-nonracemic *Lewis* acid is required. The coordination number of the metal atom and the number of coordination sites of the ligands are of prime significance. A bidentate diketone, if forming a chelate ring, would be the dienophile of choice, reduction of conformational space being one of the most effective means of promoting stereoselection.

In order to ascertain whether a chelate ring actually had been formed, the four structures depicted in *Fig. 1* were examined using X-ray crystallography [4]. Structural details specified according to *Scheme 1* are presented in *Table 1*.

Among a series of combinations considered, the best results are given by a complex in which a 1,2-diketone and a 1,4-dihydroxy compound (preferably a TADDOL [11]) are both believed to be attached to the central Ti atom [12,13].



1

2a R = Me, X = H_2
2b R = Me, X = O
2c R = Et, X = H_2
2d R = Et, X = O

3a R = Me, X = H_2
3b R = Me, X = O
3c R = Et, X = H_2
3d R = Et, X = O

4

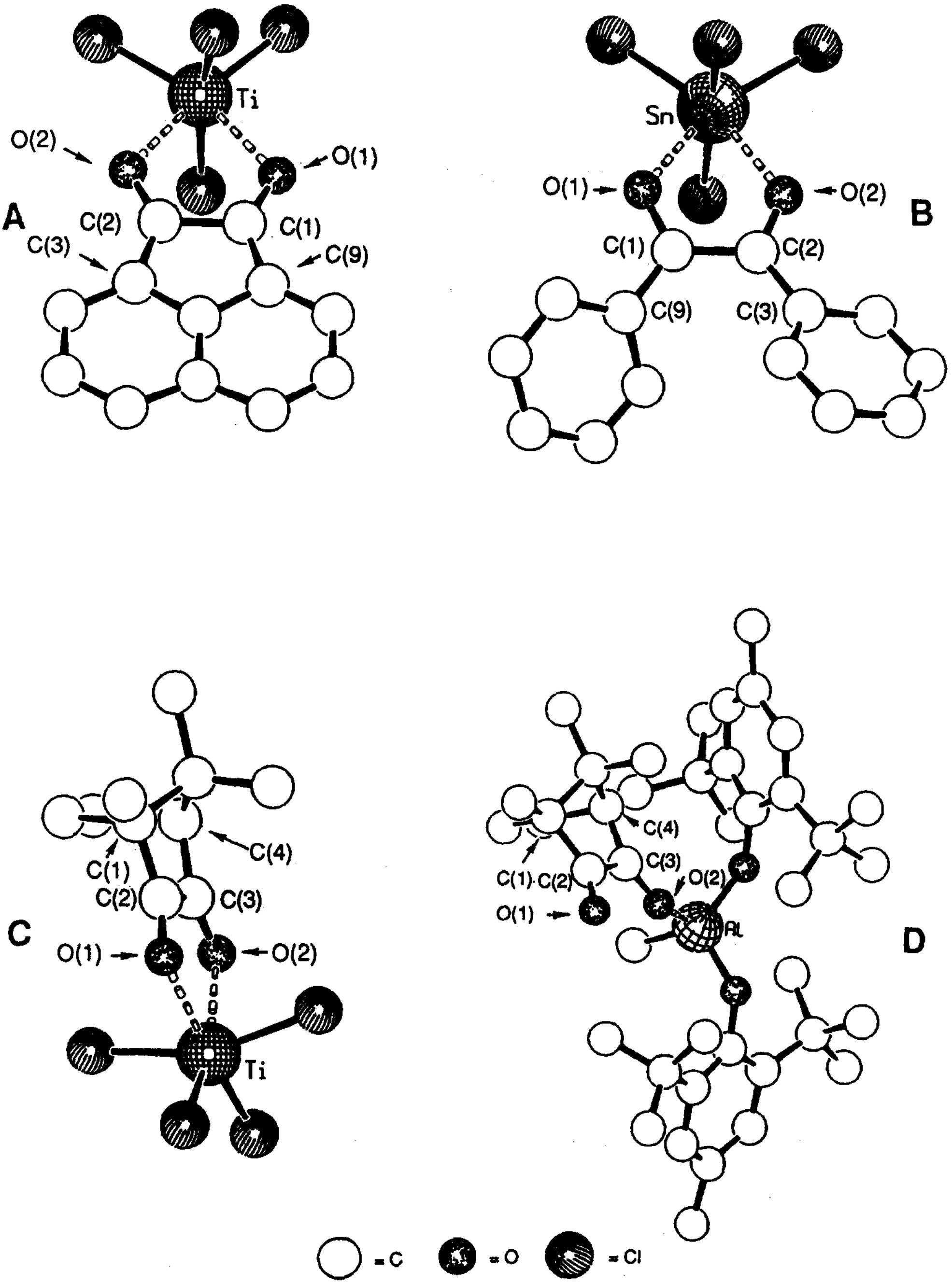
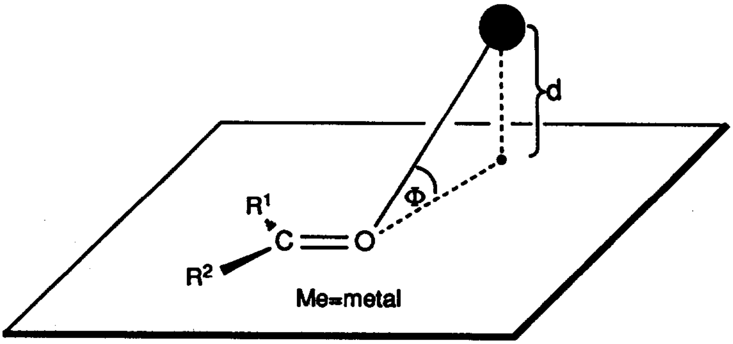


Fig.1. SCHAKAL [5] representation of the single crystal X-ray structures of compounds A–D. The hydrogen atoms are omited for the sake of clarity.



Scheme 1: Characteristic parameters of metal-carbonyl coordination in Lewis acid-base adducts [6].

Table 1: Selected bond lengths, bond angles, torsion angles in the complexes A–D. The coordination parameters **d** and Φ according to *Scheme 1* are given relative to the indicated plane.

A 7)

bond lengths [Å]	bond angles [°]	torsion angles[°]	plane	**d** [Å]	Φ [°]
C(1)=O(1) 1.225	C(1)=O(1)···Ti 113.7	C(9)–C(1)=O(1)···Ti 179.3	C(9), C(1), O(1)	-0.027	-0.7
C(2)=O(2) 1.227	C(2)=O(2)···Ti 116.0	C(2)–C(1)=O(1)···Ti -1.0	C(2), C(1), O(1)	-0.036	-0.9
O(1)···Ti 2.272		C(3)–C(2)=O(2)···Ti -175.8	C(3), C(2), O(2)	-0.144	-3.8
O(2)···Ti 2.194		C(1)–C(2)=O(2)···Ti 5.4	C(1), C(2), O(2)	-0.186	-4.9

B 8)

bond lengths [Å]	bond angles [°]	torsion angles[°]	plane	**d** [Å]	Φ [°]
C(1)=O(1) 1.245	C(1)=O(1)···Sn 115.8	C(9)–C(1)=O(1)···Sn -162.0	C(9), C(1), O(1)	-0.630	-16.2
C(2)=O(2) 1.226	C(2)=O(2)···Sn 121.9	C(2)–C(1)=O(1)···Sn 18.1	C(2), C(1), O(1)	-0.631	-16.2
O(1)···Sn 2.259		C(3)–C(2)=O(2)···Sn 175.8	C(3), C(2), O(2)	-0.138	-3.6
O(2)···Sn 2.204		C(1)–C(2)=O(2)···Sn -5.3	C(1), C(2), O(2)	-0.172	-4.5

C 9)

bond lengths [Å]	bond angles [°]	torsion angles[°]	plane	**d** [Å]	Φ [°]
C(2)=O(1) 1.209	C(2)=O(1)···Ti 115.1	C(1)–C(2)=O(1)···Ti 177.4	C(1), C(2), O(1)	0.092	2.3
C(3)=O(2) 1.203	C(3)=O(2)···Ti 113.5	C(3)–C(2)=O(1)···Ti -3.4	C(3), C(2), O(1)	0.120	3.0
O(1)···Ti 2.266		C(4)–C(3)=O(2)···Ti -175.3	C(4), C(3), O(2)	0.169	4.3
O(2)···Ti 2.258		C(2)–C(3)=O(2)···Ti 1.6	C(2), C(3), O(2)	0.058	1.5

D 10)

bond lengths [Å]	bond angles [°]	torsion angles[°]	plane	**d** [Å]	Φ [°]
C(2)=O(1) 1.194	C(3)=O(2)···Al 139.6	C(4)–C(3)=O(2)···Al -11.3	C(4), C(3), O(2)	0.380	11.4
C(3)=O(2) 1.233		C(2)–C(3)=O(2)···Al 163.2	C(2), C(3), O(2)	0.211	6.3
O(2)···Al 1.923					

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2. Compounds **3b** and **3d** are found to exist as enols.
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4. The structures of the complexes **A**–**D** were determined by X-ray structure analysis, direct methods, SDP program system. A temperature of about 115K was maintained during the measurement using an *Enraf-Nonius* CAD4 diffractometer, Cu-K_α radiation. Further details of the crystal structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the deposit number CSD 57702, the names of the authors, and the journal citation.
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6. S. Shambayati, W.E. Crowe, S.L. Scheiber, *Angew. Chem.* **1990**, *102*, 273.
7. The crystals of Adduct **A** were protected from moisture using "PFPE-oil RS 3000" (Hoechst AG). Adduct **A** ($C_{12}H_6O_2TiCl_4$): The crystals of the complex are monoclinic; $P2_1/c$ (No. 14); a = 11.863(6), b = 10.058(3), c = 12.876(5) Å; β = 117.16(4)°; V = 1367(2)Å^3; Z = 4; ρ_{calc} = 1.807 g/cm^3; hemi-sphere through 2Θ = 120°; 3668 reflections measured, 1919 independent with I > O; R(F) = 0.068; R_w(F) = 0.071.
8. Measurement was done in a sealed tube. Adduct **B** ($C_{14}H_{10}O_2SnCl_4$): The crystals of the complex are monoclinic; $P2_1/n$ (No. 14): a = 11.614(5), b = 10.745(3), c = 13.886(5)Å; β = 109.09(4)°; V = 1637(2)Å^3; Z = 4; ρ_{calc} = 1.909 g/cm^3; hemi-sphere through 2Θ = 100°; 3576 reflections measured, 1671 independent with I>O; R(F) = 0.063; R_w(F) = 0.072.
9. The crystals of adduct **C** were handled analogously to **A**[7]. Adduct **C** ($C_{10}H_{14}O_2TiCl_4 \cdot CHCl_3$): The crystals of the complex are monoclinic: $P2_1$ (No. 4): a = 8.937(5), b = 11.503(3), c = 9.827(5)Å; β = 113.75(4)°; V = 925(2)Å^3; Z = 2; ρ_{calc} = 1.707 g/cm^3; hemi-sphere through 2Θ = 120°; 2905 reflections measured, 2893 independent with I>O; R(F) = 0.077; R_w(F) = 0.098.
10. For crystals of Adduct **D**, no further protection from moisture was needed. Adduct **D** ($C_{41}H_{63}O_4Al$): The crystals of the complex are monoclinic; $P2_1$ (No. 4); a = 10.541(2), b = 15.808(4), c = 11.885(1) Å; β = 103.49(1)°; V = 1926(1)Å^3; Z = 2; ρ_{calc} = 1.116 g/cm^3; hemi-sphere through 2Θ = 130°; 5269 reflections measured, 3282 independent with I>O; R(F) = 0.030; R_w(F) = 0.035.
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12. The *Diels/Alder* reaction of diene **1** with dienophile **2b** in the presence of 2.2 eq of ligand **4** and 2.0 eq of $Ti(OiPr)_2Cl_2$ (CH_2Cl_2, 2d, -80°C) leads to adduct **3b** in 65% yield and 93% e.e. The reaction of diene **1** with **2d** (0.22 eq **4**, 0.20 eq $Ti(OiPr)_2Cl_2$, CH_2,Cl_2, 7 d, -80°C) affords **3d** with 77% yield and 88% e.e. [14].
13. The work reported here was generously supported by Deutsche Forschungsgemeinschaft (Project Qu 15/26), Fonds der Chemischen Industrie, Bundesminister für Forschung und Technologie (Project No. 0318801B), and Hoechst AG.
14. Satisfactory spectroscopic and elemental analysis data were obtained using chromatographically purified and homogeneous samples.

Dedicated to Professor Sir Derek Barton on the occasion of his seventyfifth birthday.

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