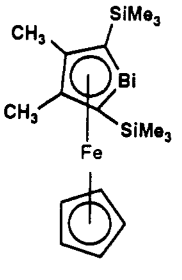

6

indicate that the bismolyl groups of 3 are π-complexed heteroaromatic rings. As had previously been found for other group 15 heteroferrocenes,[3,8-11] the heteroatoms are displaced out of the ring planes away from iron. Since the average displacement (0.28 Å) is smaller than the 0.39 Å found for the monobismaferrocene 6, the Bi atoms are closer than anticipated. In fact, the 3.69-Å interannular separation of the Bi atoms is nearly 1 Å below the van der Waals distance of 4.6 Å. Therefore, the structural data give evidence of a direct inter-ring Bi···Bi bond. If the primary π-bonding of the Bi atoms of 3 involves the Bi(6p_z) orbitals, these orbitals are aligned so that the inter-ring Bi···Bi bond is likely due to p–p σ-overlap.

For comparison we have also obtained a structure of the green thermochromic bibismole 4.[6] The molecular structure of 4, as shown in Figure 2, has a staggered trans conformation as is the case for all reported distibines[2,4,12] and dibismuthines.[13,14] The Bi–Bi bond distance of 2.990 Å is identical with that found for the nonthermochromic tetraphenyldibismuthine[13] but somewhat shorter than the 3.04 Å reported for the thermochromic tetrakis(trimethylsilyl)dibismuthine (7).[14] The crystal packing of bibismole 4 shows the Bi atoms are aligned in zigzag chains[15] with alternating intramolecular Bi–Bi bonds (2.99 Å) and slightly longer intermolecular Bi···Bi contacts (3.66 Å). All structures of thermochromic distibines and dibismuthines contain similar metal atom chains which are associated with their intense solid-phase colors.[2,5] However, the intermolecular contacts of 4 are distinctly shorter than the 3.80 Å found for the sterically congested 7. Unfortunately, there are no other reported structures for thermochromic dibismuthines.[16]

$$(SiMe_3)_2Bi\text{-}Bi(SiMe_3)_2$$

7

The comparison of the juxtaposition of Bi atoms in 3 and 4 suggests a similar origin for the secondary bonding. For structure 4 the CBiC and CBiBi bond angles are significantly smaller than tetrahedral angles, implying that the Bi atoms are p^3-hybridized. Since the Bi(6p_z) orbitals are approximately aligned with the metal chain, the intermolecular bonding is likely due to p–p overlap. Indeed, the intermolecular Bi(6p_z)–Bi(6p_z) overlap integral (0.252) is 60% as large as the intramolecular overlap integral (0.417).[17] Pseudopotential calculations which may provide an estimate of the strength of this bonding are now in progress and will be communicated elsewhere in detail.

Acknowledgment. We are grateful to the Research Corp., to NATO Scientific Affairs, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We also wish to thank Professor S. L. Buchwald for informing us of his results prior to publication and Professor L. L. Lohr for stimulating discussions.

Supplementary Material Available: Tables of crystal data and data collection and solution and refinement details, bond lengths and angles, and positional and thermal parameters and packing diagrams for 3 and 4 and a table of least-squares planes for 3 (13 pages). Ordering information is given on any current masthead page. Tables of calculated and observed structure factors are available from A.J.A. on request.

OM9202938

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Homogeneous Catalysis. $[Ti(Cp)_2(CF_3SO_3)_2]$ and $[Zr(Cp)_2(CF_3SO_3)_2THF]$, Efficient Catalysts for the Diels–Alder Reaction

T. Keith Hollis, N. P. Robinson, and B. Bosnich*

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

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Summary: The readily prepared species $[Ti(Cp)_2(CF_3SO_3)_2]$ and $[Zr(Cp)_2(CF_3SO_3)_2THF]$ are efficient catalysts for the Diels–Alder reaction at very low catalyst loadings, giving accelerations of between 10^3 and $>10^5$ over the corresponding thermal reactions.

The classical Diels–Alder reaction is promoted by a variety of Lewis acids, most commonly by the halides of tervalent boron and aluminum and tetravalent titanium and tin. These traditional Lewis acids present a number of difficulties when they are modified for enantioselection by incorporation of chiral ligands. The problems that arise are dependent on the Lewis acidic element and on the ligand chosen, but in general, the difficulties are associated with the tendency of these chelated species to oligomerize, to exchange their ligands rapidly, and to produce a variety of species. As a consequence there can exist a complex equilibrium, making identification of the catalytic species difficult. Although very high enantioselectivities have been reported,[1] most Lewis acid chiral catalysts have been prepared in situ, which can lead to an additional complication. Since the parent halide is nearly always more catalytically active than the ligand-incorporated Lewis acid, the presence of any remaining Lewis acid halide could lead to a major part of the catalysis proceeding via an achiral path. Finally, traditional Lewis acids, modified or otherwise, in many cases tend to have low turnover numbers and frequencies so that the practice of using 10–100 mol % catalyst loading has been generally followed.

These inherent problems associated with traditional Lewis acids have prompted us to search for transition-metal-based Lewis acids which would have stable, defined geometries, which have high turnover numbers and frequencies, and which could be readily modified into enantioselective catalysts. A number of low-valent molybdenum and tungsten nitrosyl complexes[2,3] have been found to be effective Diels–Alder catalysts, but these species suffer from being powerful polymerization catalysts of 1,3-dienes. It appears that, with transition-metal Lewis acid catalysts, the ability to catalyze the classical Diels–Alder reaction is associated with a proclivity to polymerization. One of the challenges, therefore, is to find the window of reactivity where the rate of the Diels–Alder reaction is much faster than polymerization. We report on Diels–Alder catalysis using the two related, readily prepared catalysts $[Ti(Cp)_2(CF_3SO_3)_2]$[4] and $[Zr(Cp)_2(CF_3SO_3)_2THF]$[5] (Cp is the cyclopentadienyl ligand), which bear some resemblance to the slow Diels–Alder catalyst $[Zr(Cp)_2(t\text{-}BuO)THF]BPh_4$ that was reported on briefly.[6]

These catalysts are prepared from commercially available $[Ti(Cp)_2Cl_2]$ and $[Zr(Cp)_2Cl_2]$ by reaction with $AgCF_3SO_3$.[4,5] The catalysts are stable in air for short periods but are best stored in a drybox. They are soluble in moderately polar solvents such as CH_2Cl_2 and CH_3NO_2 but are insoluble in nonpolar solvents such as benzene.

Catalysis of the Diels–Alder reaction was carried out in CD_2Cl_2 solution at 25 °C using 1 mol % of the $[Zr(Cp)_2(CF_3SO_3)_2THF]$ and 0.5 mol % of the $[Ti(Cp)_2(CF_3SO_3)_2]$ catalysts.[7] The initial concentration of each substrate was 1 M. Some of the results are collected in Table I. Included in this table is the time taken for 90% completion of the catalytic reaction and for 90% completion of the corresponding thermal reaction. The thermal times were estimated by extrapolating a second-order plot obtained under the same concentration, solvent, and temperature conditions as for the corresponding catalytic reaction. Where no thermal reaction was detected after 24 h at 25 °C the time for 90% thermal reaction was estimated to be $>10^5$ h.

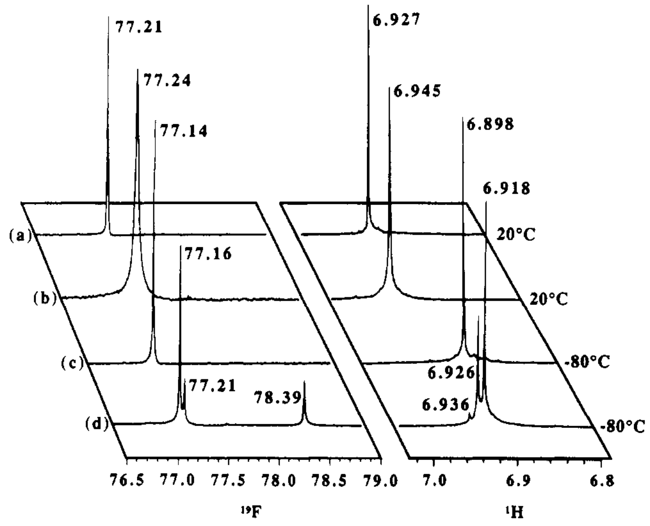

Figure 1. ^{19}F NMR and ^1H NMR spectra of $[Ti(Cp)_2(CF_3SO_3)_2]$ in CD_2Cl_2 under a variety of conditions at 400 MHz: (a) $[Ti(Cp)_2(CF_3SO_3)_2]$ (0.005 M) at 20 °C; (b) $[Ti(Cp)_2(CF_3SO_3)_2]$ (0.005 M) + 100 equiv of MVK (0.5 M) at 20 °C; (c) $[Ti(Cp)_2(CF_3SO_3)_2]$ (0.005 M) at -80 °C; (d) $[Ti(Cp)_2(CF_3SO_3)_2]$ (0.005 M) + 100 equiv of MVK (0.5 M) at -80 °C.

It will be noted that even at these low catalyst loadings rate accelerations of between 10^3 to $>10^5$ are observed. As is generally observed, the isomer ratio is improved in the catalytic reaction. No special precautions were taken to dry the solvents or the substrates,[8,9] except for the cases of acrolein and methacrolein, which were distilled under reduced pressure from molecular sieves and CaH_2, respectively. This convenience is in contrast to the case for traditional Lewis acids, which require either predried solvents or high catalyst loadings to circumvent catalyst deactivation by adventitious water. Similarly, unlike traditional Lewis acids the present catalysts have high turnover frequencies at very low catalyst loadings and we have determined that catalysis will continue indefinitely, although at a progressively slower rate.

These two catalysts, however, do not work well for all Diels–Alder partners because they are slow polymerization catalysts of 1,3-dienes. Thus, with the zirconium catalyst the reaction of either 1-cyclopentenone or methylacrylate with isoprene leads only to polymerization of the diene and with cinnamaldehyde the Diels–Alder reaction occurs to about 10% before all of the diene is consumed in the

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[1] (a) Rebiere, F.; Riant, O.; Kagan, H. B. *Tetrahedron: Asymmetry* **1990**, *1*, 199. (b) Kaufmann, D.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 545. (c) Corey, E. J.; Imwinkelried, R.; Pikul, S.; Xiang, Y. B. *J. Am. Chem. Soc.* **1989**, *111*, 5493. (d) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340. (e) Furuta, K.; Shimizu, S.; Miwa, Y.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 1481. (f) Corey, E. J.; Matsumura, Y. *Tetrahedron Lett.* **1991**, *32*, 6289.

[2] Faller, J. W.; Ma, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1579.

[3] Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070.

[4] Thewalt, U.; Klein, H.-P. *Z. Kristallogr.* **1980**, *153*, 307. The literature procedure was followed except that $[Ti(Cp)_2(CF_3SO_3)_2]$ was recrystallized from dry THF by the slow addition of hexane to give red flakes, which were dried under high vacuum. Anal. Calcd for $C_{12}H_{10}F_6O_6S_2Ti$: C, 30.27; H, 2.12. Found: C, 30.28; H, 2.07.

[5] Thewalt, U.; Lasser, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 1501. The literature procedure was followed except that exactly 1 equiv of $AgCF_3SO_3$ was employed, the white needles were recrystallized from dry THF by the addition of hexane, and the product was dried under high vacuum. Anal. Calcd for $C_{16}H_{18}F_6O_7S_2Zr$: C, 32.48; H, 3.07. Found: C, 32.42; H, 3.06.

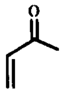
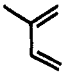
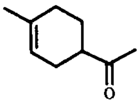
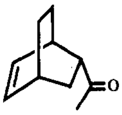
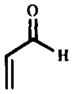
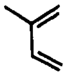
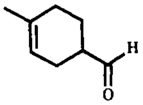
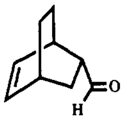
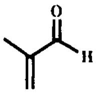
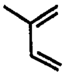
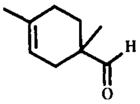
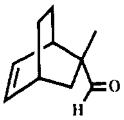
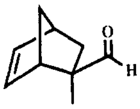
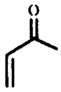
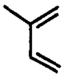
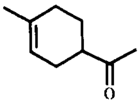
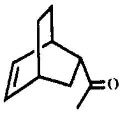
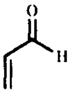
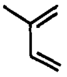
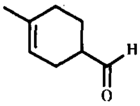
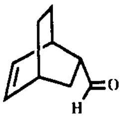
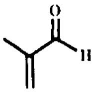
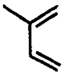
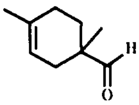
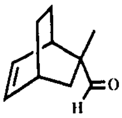
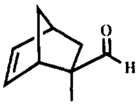
[6] Collins, S.; Koene, B. E.; Ramachandran, R.; Taylor, N. J. *Organometallics* **1991**, *10*, 2092.

[7] A typical catalysis was performed as follows. $[Zr(Cp)_2(CF_3SO_3)_2THF]$ (0.0030 g, 0.0051 mmol) was weighed under an inert atmosphere into an NMR tube which was sealed with a septum. CD_2Cl_2, a volume such that the final concentration of substrate would be 1 M, was injected, followed by the dienophile (0.51 mmol) and then by the diene (0.51 mmol). The reaction was followed by the ^1H NMR signals of the substrate and product. The isomer ratios were determined by comparison with literature data or by comparison with analogous compounds.

[8] It is conceivable that protons in the solvent or substrates, or protons arising from the presence of water forming acidic aquo complexes (Döppert, K. *J. Organomet. Chem.* **1979**, *178*, C3), could be responsible for at least some of the catalysis. This is not the case because the Diels–Alder reaction between MVK and isoprene does not occur in 24 h in the presence of 1 mol % of either CH_3CO_2H or CF_3CO_2H in CD_2Cl_2 solutions.

[9] In order to check the effect of the purity of the materials on the Diels–Alder catalysis, we have distilled commercial MVK and isoprene over CaH_2 and dried the CD_2Cl_2 solvent (3-Å sieves) and distilled it from K_2CO_3. Using these materials, we find that the rate of the Diels–Alder catalysis was the same as that found using commercial (Aldrich) materials.

Table I. Diels–Alder Catalysis by [Zr(Cp)$_2$(CF$_3$SO$_3$)$_2$THF] (1 mol %) and by [Ti(Cp)$_2$(CF$_3$SO$_3$)$_2$] (0.5 mol %) in CD$_2$Cl$_2$ Solutions at 25 °C

			catalytic reacn			thermal reacn	
reacn no.	dienophile[a]	diene[a]	time for 90% reacn, h	isomer ratio	major product	time for 90% reacn, h	isomer ratio
			[Zr(Cp)$_2$(CF$_3$SO$_3$)$_2$THF]				
1			13	94:6		6×10^3	70:30
2			3.7	95:5		$>10^5$	93:7
3			18	87:13		5×10^3	70:30
4			0.4	97:3		$>10^5$	89:11
5			5.7	92:8		$>10^5$	70:30
6			66	80:20		$>10^5$	ND[b]
7			<0.05	85:15		7×10^2	82:18
			[Ti(Cp)$_2$(CF$_3$SO$_3$)$_2$]				
8			3.8	92:8		6×10^3	70:30
9			4.9	93:7		$>10^5$	93:7
10			22	90:10		5×10^3	70:30
11			3.0	91:9		$>10^5$	89:11
12			8.9	88:12		$>10^5$	70:30
13			160	82:18		$>10^5$	ND
14			0.2	85:15		7×10^2	82:18

[a] Catalysis was carried out at 1 M concentration in each substrate. [b] ND = not determined.

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polymerization side reaction. These are inherently sluggish Diels–Alder reactions and, as a consequence, the polymerization pathway dominates. Even so, the catalysts are very effective for many Diels–Alder partners.

We have investigated adduct formation of methyl vinyl ketone (MVK) with $[Ti(Cp)_2(CF_3SO_3)_2]$ in CD_2Cl_2 under catalytic concentrations by ^{19}F and ^1H NMR spectroscopy. The ^{19}F NMR spectra and ^1H NMR Cp signals of a 0.005 M solution of $[Ti(Cp)_2(CF_3SO_3)_2]$ by itself and in the presence of 100 equiv of MVK at 20 and −80 °C are shown in Figure 1. At 20 °C the ^{19}F NMR signal broadens upon addition of MVK, but at −80 °C the spectrum shows three signals at 77.16, 77.21, and 78.39 ppm relative to internal $CFCl_3$. The signal at 78.39 ppm corresponds to free triflate anion,[10] which we have confirmed by finding that the ^{19}F NMR signal of $Bu_4N^+CF_3SO_3^-$ in CD_2Cl_2 under the same conditions occurs at 78.37 ppm. The corresponding ^1H NMR spectrum also displays a single resonance at 20 °C when 100 equiv of MVK is added, and when the temperature is lowered to −80 °C, three signals are observed at 6.918, 6.926, and 6.936 ppm. In the presence of MVK, the species $[Ti(Cp)_2(CF_3SO_3)_2]$, $[Ti(Cp)_2(CF_3SO_3)_2MVK]$, $[Ti(Cp)_2(CF_3SO_3)MVK]^+$, $[Ti(Cp)_2(CF_3SO_3)(MVK)_2]^+$, $[Ti(Cp)_2(MVK)_2]^{2+}$, and $[Ti(Cp)_2(MVK)_3]^{2+}$ could possibly exist in solution.[11] Even so, the NMR results can be interpreted with a reasonable degree of confidence.

If we assume that the ^{19}F NMR signal at 77.16 ppm observed in the presence of MVK at −80 °C corresponds to either $[Ti(Cp)_2(CF_3SO_3)_2]$ or $[Ti(Cp)_2(CF_3SO_3)_2MVK]$ or an average signal of the two and that the 77.21 ppm signal corresponds to $[Ti(Cp)_2(CF_3SO_3)MVK]^+$ or $[Ti(Cp)_2(CF_3SO_3)(MVK)_2]^+$ or the average, we may correlate the ^{19}F NMR signals with those observed for the Cp proton signals at −80 °C by assigning the ^1H NMR signals at 6.918 ppm to either $[Ti(Cp)_2(CF_3SO_3)_2]$ or $[Ti(Cp)_2(CF_3SO_3)_2MVK]$, the 6.926 ppm signal to $[Ti(Cp)_2(CF_3SO_3)MVK]^+$ or $[Ti(Cp)_2(CF_3SO_3)(MVK)_2]^+$, and the 6.936 ppm signal to $[Ti(Cp)_2(MVK)_2]^{2+}$ or $[Ti(Cp)_2(MVK)_3]^{2+}$ or the corresponding averages. These assignments are self-consistent with the integrated intensities of the proton and fluorine signals. Thus, the relative intensity ratios of the ^1H NMR signals 6.918:6.926:6.936 are 1.55:1.0:0.1, respectively. With the assignments just given, these ratios predict relative intensities of 3.1, 1.0, and 1.2 for the ^{19}F NMR signals δ 77.16, 77.21, and 78.39, respectively. The intensities found are 3.4, 1.0, and 1.2, which is well within the experimental error.[12]

From these data we may draw the following conclusions. First, the dienophile is capable of displacing the triflate ligand to form substantial concentrations of mono- and dicationic species under catalytic conditions. Second, adduct formation is rapid and reversible under catalytic conditions. If, as we believe, the present Diels–Alder catalyses proceed via cationic adducts where the dienophile binds to the metal by its carbonyl oxygen atom, the catalyst possesses ideal characteristics. The substantial concentrations of the cationic adducts and their high lability will lead to high turnover frequencies and high turnover numbers as observed.

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[11] It is probable that the Cp_2Ti^{2+} unit is unlikely to form strong 18-electron complexes of the type $[Ti(Cp)_2(CF_3SO_3)_2MVK]$, $[Ti(Cp)_2(CF_3SO_3)(MVK)_2]^+$ and $[Ti(Cp_2)(MVK)_3]^{2+}$. We cannot exclude the possibility, however, since the complex $[Ti(Cp)_2(CH_3CN)_3](AsF_6)_2$, with admittedly sterically undemanding CH_3CN ligands, has been isolated and characterized. Klapötke, T. *Polyhedron* **1989**, *8*, 311.

[12] The ^1H and ^{19}F NMR spectra shown in Figure 1 were the same whether or not the MVK and CD_2Cl_2 were purified.

A Stable Compound with a Formal Tin–Carbon Double Bond: The Bis(2,4,6-triisopropylphenyl)(fluorenylidene)stannene

G. Anselme, H. Ranaivonjatovo, J. Escudié,* C. Couret, and J. Satgé
Laboratoire de Chimie des Organominéraux, URA 477, Université Paul Sabatier,
118 route de Narbonne, 31062 Toulouse Cedex, France

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Summary: Bis(2,4,6-triisopropylphenyl)(fluorenylidene)stannene–diethyl ether (**1a**), a new stable compound with a formal tin–carbon double bond, has been synthesized by dehydrofluorination of the corresponding fluorostannane with *tert*-butyllithium; it has been characterized by NMR ($\delta(^{119}Sn)$ + 288 ppm, $\delta(^{13}C)$ +133.85 ppm) and UV spectroscopy (λ_{max} 542 nm) and by electrophilic addition reactions to the tin–carbon unsaturation.

Low-coordinated species of group 14 elements have been studied intensively in recent years.[1] In the field of "metallaalkenes" (>M=C<; M = Si, Ge, Sn), the chemical behavior of silenes (>Si=C<)[1a,b] and germenes (>Ge=C<)[1e,f] is now well-known. The reactivity of the double bond appears to be very high, and such derivatives are good synthons in organometallic chemistry. In contrast, the chemistry of stannenes (>Sn=C<) is as yet relatively undeveloped, except for some limited reactions.[2-4] Only the two stable stannenes **2a** and **2b** have been synthesized up to now, by Berndt et al.[2] In order to more effectively study the chemical behavior of the tin–carbon double bond, we have synthesized the new stable stannene **1a**. We report here its synthesis and our initial studies of its reactivity.

Preliminary attempts to stabilize a stannene by having

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