Merck 60, petroleum ether → CH₂Cl₂/petroleum ether 5/1). Yield 163 mg (90%). By a similar procedure, triethylamine (0.21 mL, 1.5 mmol), **2** (0.19 g, 0.59 mmol), and ethyl chlorooximidoacetate (0.18 g, 1.2 mmol) afforded **3**. Yield 172 mg (95%); orange crystals (petroleum ether/CH₂Cl₂); m.p. 191–193 °C (decomp). MS (EI, 70 eV): m = (%): 307 (75) [M^+], 292 (25) [$M^+ - CH_3$], 279 (62) [$M^+ - CO$], 251 (32) [$M^- - 2CO$], 219 (39) [$M^+ - 2CO - S$], 191 (27) [$M^+ - C_5 2_0$]. 175 (59) [$M^+ - C_5 S_1$], 159 (48) [$M^+ - C_5 S_3$ (0, 126 (45) [$M^+ - C_5 S_4 - C_2 H_3$], 114 (80) [$M^+ - C_5 S_4 - NC_2 H_3$]; HRMS: calcd 306.8926, found 306.8924; IR (CCl₄): $\tilde{v} = 2945$, 1676, 1626, 1553, 1145, 1024 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): $\delta = 1.32$ (t, J = 7.2 Hz, 3H, CH₃), 3.80 (q, J = 7.2 Hz, 2H, CH₂); ¹³C NMR (100 MHz, CDCl₃): $\delta = 14.57$ (CH₃, DEPT). 42.42 (CH₂, DEPT), 136.83 and 146.57 (quaternary C), 182.16 (C=O): Elemental analysis calcd for C₈H₃NO₂S₅: C 31.27, H 1.63, N 4.56; found: C 31.07, H 1.59, N 4.51.

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- J. M. Williams, A. J. Schultz, U. Geiser, K. D. Carlson, A. M. Kini, H. H. Wang, W.-K. Kwok, M.-H. Whangbo, J. E. Schirber, *Science* **1991**, 252, 1501–1508;
 M. R. Bryce, *Chem. Soc. Rev.* **1991**, 20, 355–390; J. Garín, *Adv. Heterocycl. Chem.* **1995**, 62, 249–304; Y. Misaki, N. Higuchi, H. Fujiwara, T. Yamabe, T. Mori, H. Mori, S. Tanaka, *Angew. Chem.* **1995**, 107, 1340–1343; *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 1222–1225.
- [2] T. Jørgensen, T. K. Hansen, J. Becher, Chem. Soc. Rev. 1994, 23, 41-51; W. F. Jager, J. C. de Jong, B. de Lange, N. P. M. Huck, A. Meetsma, B. L. Feringa, Angew. Chem. 1995, 107, 346-348; Angew. Chem. Int. Ed. Engl. 1995, 34, 348-350; G. M. Tsivgoulis, J.-M. Lehn, *ibid.* 1995, 107, 1188-1191 bzw. 1995, 34, 1119-1122; S. L. Gilat, S. H. Kawai, J.-M. Lehn, *Chem. Eur. J.* 1995, 1, 275-284; S. H. Kawai, S. L. Gilat, R. Ponsinet, J.-M. Lehn, *ibid.* 1995, 1, 285-293.
- [3] M. J. Plater, C. W. Rees, D. G. Roe, T. Torroba, J. Chem. Soc. Chem. Commun. 1993, 293-294; J. Chem. Soc. Perkin Trans. 1 1993, 769-774.
- [4] O. A. Rakitin, C. W. Rees, T. Torroba, Chem. Commun. 1996, 427-428.
- [5] O. A. Rakitin, C. W. Rees, D. J. Williams, T. Torroba, J. Org. Chem., in press.
- [6] D. J. Williams, Imperial College, London, personal communication.
- [7] F. Boberg, J. Knoop, Justus Liebigs Ann. Chem. 1967, 708, 148-154; R. Huisgen, W. Mack, E. Anneser, Angew. Chem. 1961, 73, 656-657. For a recent application and leading references see: J. N. Kim, E. K. Ryu, Tetrahedron Lett. 1993, 34, 8283 - 8284.
- [8] H. W. Pinnick in Comprehensive Organic Synthesis, Vol. 7 (Eds.: B. M. Trost, I. Fleming, S. V. Ley), Pergamon, Oxford, 1991, p. 221.
- [9] D. M. McKinnon in Comprehensive Heterocyclic Chemistry, Vol. 6 (Eds.: A. R. Katritzky, C. W. Rees), Pergamon, Oxford, 1984, Chapter 4.31; Comprehensive Heterocyclic Chemistry II, Vol. 3 (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Elsevier, Oxford, 1996, Chapter 3.11.

New Surprises with Fischer Carbene Complexes: Formal [3 + 2] Cycloadditions with and without Preceding Carbene–Ligand Metathesis**

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Dedicated to Professor Roland Mayer on the occasion of his 70th birthday

Fischer carbene complexes have proved to be versatile and interesting building blocks in organic synthesis.^[1] Widely applicable procedures have been developed based on their initially surprising reactions with unsaturated substrates such as alkenes, alkynes, nitriles, isonitriles, and imines. Thermal reactions of carbene chromium complexes 1 with dienes provide the expected cyclopropane derivatives with high regio- and periselectivity.^[2] When α,β -unsaturated carbene complexes such as 1c and 1d are employed, the initially formed cyclopropane products rearrange to give cycloheptadienes.^[3] We have now found a new unexpected reaction sequence with dienes 2 and 4: a carbene metathesis is followed by a formal [3+2]cycloaddition of the newly generated carbene ligands to dienes 2 and 4 to furnish highly functionalized alkenyl siloxycyclopentene derivatives 3 and 5, respectively.



 $TBS = tBuMe_2Si$

By heating complex 1a with three equivalents of methyl 4-(*tert*-butyldimethylsiloxy)-2,4-pentadienecarboxylate (2)^[4] in 1,2-dichloroethane or cyclohexane, cyclopentene derivative 3 (diastereomeric ratio >95:5) was obtained in nearly quantitative yield after chromatographic workup. The product was also formed when 2 was treated with the less reactive methyl-substituted carbene complex 1b (17% yield, one diastereomer (>90%)). Based on its ¹H NMR spectrum, a byproduct from the reaction of 1a with 2 was identifed as 1-methoxy-1phenylethene (8).

Similar results were obtained from the reactions of siloxybutadiene 4 with complexes 1a and 1b. Both carbene complexes furnished the corresponding siloxycyclopentene 5 as a diastereomerically pure product. As in the previous case, the more reactive complex 1a gave higher yields than 1b. The constitution and relative configuration of the unexpected products 3 and 5,



which do not incorporate the carbene ligand of the starting material, were determined by 1D- and 2D-INADEQUATE NMR spectra, which established the connectivity, and by 2D-NOESY NMR spectra.^[5]

These results can be explained by postulating the formation of new α , β -unsaturated carbene complexes from complexes 1a and 1b by an initial carbene ligand metathesis.^[6] Accordingly, the highly reactive donor-acceptor-substituted carbene complex 7 and enol ether 8 (which was indeed found) should be formed

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COMMUNICATIONS



from 1a and 2 via chromacyclobutane 6. The further reaction of 7 with 2 to give product 3 will be discussed below.

The postulated formation of the α,β -unsaturated carbene complex 7 led us to conduct experiments with isolable complexes of this type. Indeed, the corresponding alkenyl-substituted methoxycyclopentene derivatives 9 and 10 were obtained



from thermal reaction of 1c and 1d,^[7] respectively, with siloxydiene 2, in these cases without preceding carbene metathesis. In contrast, the same reactions carried out with diene 4 furnished only cycloheptadienes.^[8] Similarly, the reaction with the electron-rich 1-methoxy-3-siloxy-1,3-butadiene (Danishefsky diene) gave the "normal" seven-membered ring products.^[8]

The simplest way to explain the surprising formation of cyclopentenes **3**, **5**, **9**, and **10** from α,β -unsaturated carbene complexes is the [3+2]cycloaddition of the carbene ligand to the electronrich terminal double bond of siloxydienes **2** and **4**. Formal [3+2]cycloadditions of α,β -unsaturated carbene complexes to *electron-poor* olefins have been reported recently.^[9] In these reactions with only low diastereoselectivities, a competition of the cyclopropane-forming [2+1]cycloaddition and the [3+2]cycloaddition was observed, strongly depending on substituents and the donor ability of the solvent. A mechanism^[10] similar to that discussed there should provide regioisomeric products **12** for the new reaction, and therefore a different mechanism has to be considered.

In our opinion, the [4+2] cycloaddition of the electron-poor chromadiene system^[11] as the 4π component and the terminal double bond of the siloxydienes as the dienophile is the most probable explanation.^[12] The regio- and *endo*-selectively formed chromacyclohexene intermediate 13 would then lead to cyclopentene 14 by reductive elimination of the metal fragment with retention of configuration; 14 exhibits the connectivity of atoms and configuration found experimentally. Examples for this postulated Diels-Alder reaction with a metalladiene component are rare but not unknown.^[13]

Although we do not yet understand the effects of substituents in the reactions of unsaturated carbene complexes with dienes in detail, the formal [3 + 2] cycloaddition described here may be of preparative interest due to the high functionality of the formed



cyclopentenes.^[14] When combined with an initial carbene ligand metathesis, this transformation is the first example of a previously unknown dimerization of dienes with fragmentation of methylene.



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- Review: K. H. Dötz, Angew. Chem. 1984, 96, 573-594; Angew. Chem. Int. Ed. Eng. 1984, 23, 587; H.-U. Reissig in Organic Synthesis Highlights (Eds.: J. Mulzer, H.-J. Altenbach, M. Braun, K. Krohn, H.-U. Reissig), VCH, Weinheim 1991, pp. 186-191; W. D. Wulff in Comprehensive Organic Synthesis Vol. 5 (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford 1991, pp. 1065-1127; R. Aumann, Angew. Chem. 1988, 100, 1512-1524; Angew. Chem. Int. Ed. Eng. 1988, 27, 1456; C. Betschart, L. S. Hegedus, J. Am. Chem. Soc. 1992, 114, 5010-5017, and earlier publications by this group.
- [2] For the regioselective cyclopropanation of electron-poor 1,3-dienes with Fischer carbene complexes see: M. Buchert, M. Hoffmann, H.-U. Reissig, *Chem. Ber.* 1995, 128, 605-614. In this paper, further publications concerning the reaction of Fischer carbene complexes with different 1,3-dienes are compiled.
- [3] First examples: W. D. Wulff, D. C. Yang, C. K. Murray, J. Am. Chem. Soc. 1988, 110, 2653-2655. More recently, the investigations of Barluenga and co-workers are of importance: J. Barluenga, F. Aznar, A. Martin, J. T. Vázquez, J. Am. Chem. Soc. 1995, 117, 9419-9426, and references therein.
- [4] For syntheses and Diels-Alder reactions of the corresponding trimethylsiloxysubstituted diene see: J. Oren, M. Demuth, B. Fuchs, Synthesis 1987, 850-853.
- [5] NMR data of product 3: ¹H NMR (300 MHz, CDCl₃): $\delta = 6.89$, 6.07 (2 d, J = 15.6 Hz, 1 H each; HC=CH), 4.79 (d, J = 2.4 Hz, 1 H; 2-H), 3.72, 3.69 (2 s, 3H each; CO_2Me), 3.57 (ddd, J = 8.2, 5.0, 2.4 Hz, 1H; 1-H), 2.41 (dd, J = 14.3, 5.0 Hz, 1 H; 5-H), 2.22 (dd, J = 14.3, 8.2 Hz, 1 H; 5-H), 0.88, 0.16, 0.13 (3 s, 9H, 3H, 3H; OSiMe₂/Bu); ¹³C NMR (75.5 MHz, CDCl₃): $\delta = 174.9, 167.1 \ (2 \text{ s}; \text{CO}_2\text{Me}), 156.8 \ (\text{s}; \text{C}-3), 151.8, 119.6 \ (2 \text{ d}; \text{HC}=\text{CH}),$ 103.6 (d; C-2), 83.8 (s; C-4), 52.0, 51.4 (2 q; CO₂Me), 43.4 (d; C-1), 40.2 (t; C-5), 25.8, 18.3, -3.8 (q, s, q; OSiMe2tBu). The configuration was confirmed by 2D-NOESY experiments. NMR data of product 5: ¹H NMR (300 MHz, CDCl₃): $\delta = 7.40 - 7.22$ (m, 10 H; Ph), 6.64, 6.34 (2 d, J = 16.0 Hz, 1 H each; HC = CH, 4.91 (d, J = 2.0 Hz, 1H; 2-H), 4.05 (ddd, J = 8.0, 6.0, 2.0 Hz, 1H; 1-H), 2.61, 2.11 (2 dd, J = 14.0, 8.0 Hz, J = 14.0, 6.0 Hz, 1 H each; 5-H), 1.01, 1.00 (2 s, 9H each; tBu), 0.28, 0.26, 0.20, 0.19 (4 s, 3H each; Me); ¹³C NMR $(75.5 \text{ MHz, CDCl}_3)$: $\delta = 157.3$ (s; C-3), 146.3, 137.2 (2 s; *ipso*-C-Ph), 134.0, 128.8 (2 d; HC=CH), 128.7, 127.2, 126.7 (3 d; Ph), 108.3 (d; C-2), 84.7 (s; C-4), 48.5 (t; C-5), 44.0 (d; C-1), 25.6 (2 q; tBu), 18.4, 18.1 (2 s; tBu), -3.0, -4.3, -4.6 (3 q; Me). The assignments were confirmed by 2Dand 1D-INADEQUATE experiments.

- [6] For competition between cyclopropanation and olefin metathesis see: C. P. Casey, N. L. Hornung, W. P. Kosar, J. Am. Chem. Soc. 1987, 109, 4908-4916 and references therein. More recent examples for the formation of isolable amino carbene complexes are given in: J. Barluenga, F. Aznar, A. Martin, Organometallics 1995, 14, 1429-1433.
- [7] R. Aumann, H. Heinen, Chem. Ber. 1987, 120, 537-540.
- [8] M. Hoffmann, H.-U. Reissig, unpublished results; see also ref. [3] (Wulff et al.).
- [9] M. Hoffmann, H.-U. Reissig, Synlett 1995, 625-627. See ref. [14] therein for [3 + 2]cycloadditions of Fischer carbene complexes to alkynes; more recent work: B. L. Flynn, F. J. Funke, C. C. Silveira, A. de Meijere, Synlett 1995, 1007-1010. For [3 + 2]cycloadditions of alkyne carbene complexes to enamines, see: A. G. Meyer, R. Aumann, Synlett 1995, 1011-1013. For rhodium complex catalyzed [3 + 2]cycloadditions of vinyldiazo compounds to enol ethers see: H. M. L. Davies, B. Hu, E. Saikali, P. R. Bruzinski, J. Org. Chem. 1994, 59, 4535-4541.
- [10] The formation of a chromacyclobutane followed by rearrangement to a η³complex and reductive elimination was postulated.
- [11] For considerations of α,β-unsaturated carbene complexes as chromabutadiene derivatives see: R. Aumann, P. Hinterding, *Chem. Ber.* 1990, 123, 2047-2051; R. Aumann, H. Heinen, P. Hinterding, N. Sträter, B. Krebs, *ibid.* 1991, 124, 1229-1236.
- [12] As for all Diels-Alder reactions of two 1,3-dienes, an exchange of diene and dienophile in our example also leads to identical products if the [4 + 2]cycloaddition is followed by a [3,3]sigmatropic rearrangement. We see no reason to discuss this more complicated alternative for our case.
- [13] Postulated Diels-Alder reactions of metalladienes: with palladium: B. M. Trost, A. S. K. Hashmi, J. Am. Chem. Soc. 1994, 116, 2183-2184; with thodium: J. Schnaubelt, E. Marks, H.-U. Reissig, Chem. Ber. 1996, 129, 73-75.
- [14] L. A. Paquette, *Top. Curr. Chem.* 1984, 119, 1-158; T. Hudlicky, J. D. Price, *Chem. Rev.* 1989, 89, 1467-1486; for synthesis of cyclopentenes by formal [3 + 2]cycloaddition see: S. Ejiri, S. Yamago, E. Nakamura, *J. Am. Chem. Soc.* 1992, 114, 8707-8708, and references therein.

The Catalyst Precursor, Catalyst, and Intermediate in the Ru^{II}-Promoted Asymmetric Hydrogen Transfer between Alcohols and Ketones^{**}

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Well-designed chiral Ru^{II}-arene complexes catalyze the asymmetric transfer hydrogenation of ketones or imines with stable organic hydrogen donors such as 2-propanol^[1, 2] and formic acid.^[3] In these reactions certain derivatives of 1,2-diamines and β -amino alcohols can serve as excellent chiral modifiers and lead to high reactivity and enantioselectivity. For example, when a 0.1 M solution of acetophenone in 2-propanol containing [{RuCl₂(η^6 -arene)}₂], (1*S*,2*S*)-*N*-*p*-toluenesulfonyl-1,2-diphenylethylenediamine ((*S*,*S*)-TsDPEN), and KOH (ketone:Ru:diamine:KOH = 200:1:1:2 molar ratio) was allowed to stand at 28 °C for 10 h, (*S*)-1-phenylethanol was obtained in up to 97% *ee* and in 98% yield [Eq. (a)].^[1a] We here disclose the

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molecular structures of a preformed catalyst precursor 1, the true catalyst 2, and the reactive intermediate 3 for this asymmetric transfer hydrogenation using 2-propanol. The functions of the added KOH and the NH moiety in the TsDPEN auxiliary



have also been clarified. Here we describe a very rare catalytic system in asymmetric transformations for which both the true catalyst and the reactive species have been isolated in a pure state.^[4] The success can be attributed to the reversible reactions with different but comparable energy profiles.

First, the catalyst precursor 1 was prepared as orange crystals in >90% yield by reacting [{RuCl₂(η^6 -*p*-cymene)}₂], (*S*,*S*)-TsDPEN, and KOH (Ru:diamine:KOH = 1:1:1 molar ratio in CH₂Cl₂ at room temperature) or, more effectively, triethylamine (Ru:diamine:NEt₃ = 1:1:2 in 2-propanol at 80 °C). The single-crystal X-ray analysis illustrated in Figure 1 indicates



Figure 1. Molecular structure of 1 in the crystal. All hydrogen atoms except for the proton of the amine ligand and those at the carbon atoms in the chelate backbone and one crystal water molecule have been omitted for the sake of clarity. Selected distances [Å] and angles [°]: Ru-Cl 2.435(4), Ru-N1 2.117(9), Ru-N2 2.144(8), RuCl … HN 2.57; N1-Ru-N2 79.4(3), Ru-N1-Cl 112.8(7), Ru-N2-C2 111.6(6).

that this 18-electron Ru^{II} complex has a distorted octahedral coordination environment with η^6 -arene, amino, sulfonamido, and chloro ligands.^[5] The chirality of (S,S)-TsDPEN forming a δ -configurated five-membered ring determines the (R) configuration at the Ru center.^[6] Noteworthy is the very short Cl···HN distance of 2.57 Å (expected van der Waals separation, 3.0 Å), which is ascribed to an intramolecular hydrogen bond.^[7] The ¹H NMR spectrum confirmed that **1** exists as a single diastereomer in CDCl₃ solution.

The Ru complex 1, which catalyzes the asymmetric transfer hydrogenation of acetophenone in 2-propanol containing

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