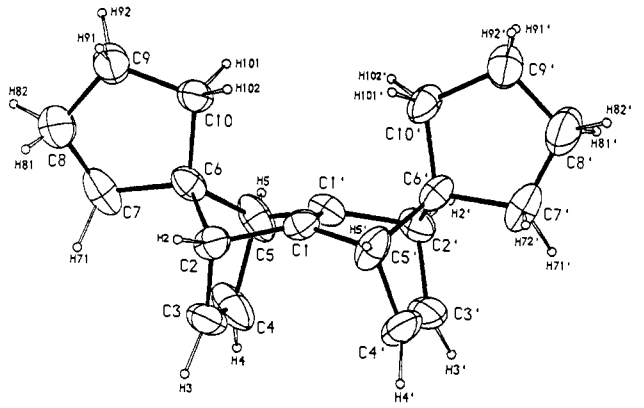

Figure 1. Computer-generated perspective drawing of the final X-ray model of **10**. The non-hydrogen atoms are represented by 30% probability thermal ellipsoids. The hydrogen atoms are drawn with an artificial radius.

7 was conducted in dichloromethane solution at ambient temperature in a high pressure reactor at 160000 psi for 6 days. These conditions furnished a chromatographically separable mixture of **8** (77%) and **9** (11%), the relative stereochemistries of which were distinguished by ^{1}H NMR spectroscopy.[12] Reductive desulfonylation[19] of syn adduct **8** gave rise to **10** (47%). Following recrystallization of this hydrocarbon from methanol in open vessels, large clear crystals were obtained that melted at 86 °C. The C_{2v} symmetry of this molecule is clearly apparent from its ^{1}H [$CDCl_3$ δ 6.29 (t, J = 1.7 Hz, 4 H), 3.19 (t, J = 1.7 Hz, 4 H), 1.84-1.44 (m, 16 H)] and ^{13}C NMR spectra [$CDCl_3$ 172.00, 141.31, 90.46, 59.94, 34.23 (2C), 26.10, 25.40 ppm]. Of particular note is the highly deshielded chemical shift of the central olefinic carbons (172.00 ppm), which falls within experimental error of the value recorded for the same atoms in **3** (172.14 ppm).[12] On this basis, the two molecules seemingly share a close conformational relationship.

Examination of the X-ray diffraction pattern for **10** obtained at −45 °C indicated it to be monoclinic [space group $C2/c$ (no. 15)] and to have a 2-fold crystallographic axis. The unit cell parameters are a = 21.004 (7) Å, b = 7.782 (2) Å, c = 9.970 (2) Å, and β = 114.28 (2)°. The structure was solved by MULTAN 11/82,[20] the final refinement cycle for 730 unique reflections with $I > 3\sigma(I)$ resulting in 91 variable parameters (the non-hydrogen atoms were refined anisotropically). A clear disorder of the atoms C3, C4, and C8 was apparent. The final X-ray model shown in Figure 1 is the result of agreement indices R_f 0.083 and Rw_f 0.116. The dihedral angle and nonbonded contacts were determined by CHEM-X.

These results show that **10** has a central flap angle of 157.3 (4)° (ψ = 22.7 (5)°), a record deformation level for these systems.[21] The relevant pyramidalization angle ϕ (see **1**) is 32.4°.[22] Adoption of this equilibrium geometry has the effect of positioning the key methylene protons on the exo surface (H101-H102′) at a closer distance (3.001 Å) than either the trigonal carbons (C3-C4′ and C3′-C4 = 3.442 Å) or the vinylic hydrogens (H3-H4′ and H4-H3′ = 3.790 Å) present on the endo surface. The relatively small size of the "hole" extant above the π system clearly contributes in a significant way to the greatly attenuated reactivity of this triene.

Noteworthily, **10** exhibits no sensitivity to atmospheric oxygen under normal circumstances. Nor is reaction seen between **10** and buffered ($NaHCO_3$) *m*-chloroperbenzoic acid in dichloromethane at room temperature during 24 h.[23] The unreactivity of the triene is further reflected in its total inertness to both phenyl azide (CH_2Cl_2, room temperature, 2 days) and diazomethane (Et_2O, 0 °C/4 h → room temperature/16 h).

At 32.4°, the ϕ value for **10** is seen to exceed that of 9,9′,10,10′-tetradehydrodianthracene (19.7°),[7] tricyclo[4.2.2.2^{2,5}]dodeca-1(2),5(6)-diene (**11**, 27.3°),[8] and the methiodide of 10-selenatricyclo[3.3.3.0^{3,7}]undec-3(7)-ene (20.3° and 12.3°).[9] Molecules such as **11** do indeed have larger ψ values (e.g., 35.6°) which are however counteracted by a markedly widened C-C-(sp^2)-C angle.

In light of the kinetic stability of **10**, prospects for the utilization of steric screening to gain access to chemically persistent alkenes having still greater levels of pyramidalization seem bright.

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Supplementary Material Available: Tables of crystallographic data, bond distances and angles, positional parameters, and anisotropic thermal parameters for **10** (6 pages); tables of observed and calculated structure factors for **10** (8 pages). Ordering information is given on any current masthead page.

(18) De Lucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. *J. Org. Chem.* **1984**, *49*, 596.
(19) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477.
(20) Structure determination package: Frenz, B. A. and associates, College Station, TX, 1982.
(21) The two atoms of the central double bond in *syn*-oxabenzosesquinorbornene deviate from planarity by 22.1 (2)° [Watson, W. K.; Galloy, G.; Grossie, D. A.; Bartlett, P. D.; Combs, G. L., Jr. *Acta Crystallogr.* **1984**, *C40*, 1050] and therefore most closely approach **10** in level of inherent distortion. However, the contributions of the bridging oxygen atom and benzene ring fusion to the overall geometry cannot yet be suitably gauged.
(22) As defined in ref 3: cos ϕ = −cos (R-C-C)/cos $^1/_2$(R-C-R).
(23) Heating of these reagents in chloroform for 15-22 h did, however, bring about gradual decomposition.

A New Synthesis of Rhenium-Carbene Complexes from the Reaction of $Cp(CO)_2ReH^-$ with $Cp_2Zr(\eta^2\text{-COR})Cl$

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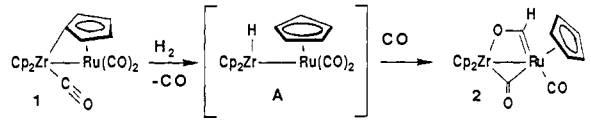
Previously we had discovered that the reaction of the zirconium-ruthenium compound **1** with H_2 led to the reduction of coordinated CO and formation of the zirconoxycarbene complex of ruthenium **2**.[1] The reaction was suggested to proceed by hydrogenolysis of the strained Zr-C_5H_4 bond of **1** to give a reactive zirconium hydride intermediate A. The product ruthenium-carbene complex **2** was inert to further reduction by H_2.



Since the rearrangement of metal-carbene-hydride complexes to metal-alkyl complexes is a facile and well-studied process,[2] it seemed likely that a zirconoxycarbene-metal complex might be further reduced if a hydride were present on the same metal as the carbene ligand. In an effort to prepare such a complex, we have studied the reaction of the η^2-acylzirconium compounds $Cp_2Zr(\eta^2\text{-COR})Cl$ (**3**, R = CH_3; **4**, R = $CH_2CH_2CMe_3$) with the rhenium hydride anion $K^+Cp(CO)_2ReH^-$ **5**. It appeared plausible that formation of a Re-Zr bond in intermediate B might occur and that acyl migration from zirconium to rhenium might

(1) Casey, C. P.; Palermo, R. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 549.
(2) (a) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. (b) Crocker, C.; Errington, R. J.; McDonald, W. S.; Odell, K. J.; Shaw, B. L.; Goodfellow, R. J. *J. Chem. Soc., Chem. Commun.* **1979**, 498. (c) LeBozec, H.; Fillaut, J.-L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1182. (d) Osborn, V. A.; Parker, C. A.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1185. (e) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121. (f) Canestrari, M.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1982**, 1789.

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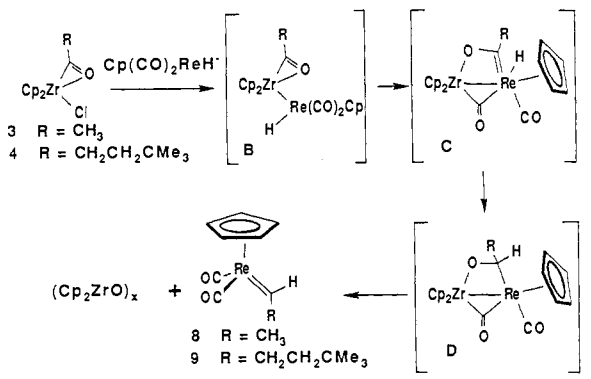
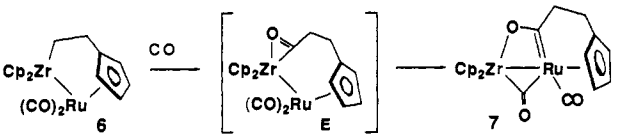
Scheme I



ensue to produce intermediate C which possesses the desired zirconoxycarbene and hydride ligands on rhenium (Scheme I). A similar migration of an η^2-acyl ligand from zirconium to ruthenium was proposed earlier to explain the carbonylation of the alkyl zirconium-ruthenium compound **6** to the zirconoxycarbeneruthenium compound **7** via intermediate E.[1] Here we report that reaction of η^2-acylzirconium compounds **3** and **4** with $K^+Cp(CO)_2ReH^-$ **5** leads not only to the reduction of the acyl ligand but also to formation of mononuclear rhenium-carbene complexes $Cp(CO)_2Re{=}CHR$ (**8**, R = CH_3; **9**, R = $CH_2CH_2CMe_3$).



The reaction of $Cp_2Zr(\eta^2\text{-}COCH_3)Cl$[3] and $K^+Cp(CO)_2ReH^-$[4] in THF-d_8 was followed by ^1H NMR at room temperature. New resonances were assigned to the mononuclear rhenium-carbene complex $Cp(CO)_2Re{=}CHCH_3$ (**8**) and to $(Cp_2ZrO)_x$[5] (major resonance at δ 6.31 and several minor resonances nearby). In a preparative reaction, a suspension of $K^+Cp(CO)_2ReH^-$ **5** (68 mg, 0.20 mmol) in 10 mL of THF was slowly added to a solution of $Cp_2Zr(\eta^2\text{-}COCH_3)Cl$ (**3**) (83 mg, 0.27 mmol) in 10 mL of THF at −40 °C. The resulting red solution was evaporated under vacuum at 10 °C, and the residue was dissolved in 4 mL of CH_2Cl_2 and chromatographed (silica gel, 10% CH_2Cl_2-hexane) to give an orange solid which was sublimed at 40 °C (0.05 mmHg) to give **8**[6] (35 mg, 52% yield), mp 68-69 °C. The key spectral features that establish the structure of **8** include characteristically far downfield chemical shifts of the carbene carbon at δ 292.3 (d, J_{CH} = 134 Hz) and of the proton on the carbene carbon at δ 16.11 (q, J = 7.3 Hz).

Similarly, the reaction of $Cp_2Zr(\eta^2\text{-}COCH_2CH_2CMe_3)Cl$[7] (92 mg, 0.25 mmol) with $K^+Cp(CO)_2ReH^-$ **5** (67 mg, 0.20 mmol) in THF followed by chromatography and sublimation at 50-60 °C under high vacuum led to the isolation of rhenium-carbene complex **9**[8] (47 mg, 58%) as an orange solid, mp 118-119 °C.

The formation of rhenium-carbene complexes **8** and **9** is necessarily a complex process since it must involve, at some stage, hydride addition to the acyl carbon, migration of carbon from zirconium to rhenium, and cleavage of the carbon-oxygen bond of the acyl unit. While we have no direct evidence favoring the mechanistic hypothesis shown in Scheme I, there are good analogies for the individual steps in the mechanism as pointed out earlier. The final step involving cleavage of the carbon-oxygen bond and breakup of the heterobimetallic complex is driven by formation of a zirconium oxo species which then oligomerizes.

The closest analogy to the formation of rhenium-carbene complexes **8** and **9** is the reaction of $Cp_2Zr(\eta^2\text{-}COC_6H_5)C_6H_5$ with Cp_2WH_2 which leads to the formation of $Cp_2W{=}CHC_6H_5$.[5]

The reactions reported here provide a very convenient, if nonobvious, synthesis of the previously unknown alkyl-substituted rhenium-carbene complexes. Earlier syntheses of $Cp(CO)_2Re$ carbene complexes include the reaction of $CpRe(CO)_3$ with RLi followed by O-alkylation which yields $Cp(CO)_2Re{=}C(OR')R$[9] and the reaction of cationic rhenium-carbyne complexes with nucleophiles which yields complexes such as $Cp(CO)_2Re{=}CHC_6H_5$.[10] These earlier routes are unsuitable for synthesis of **8** or **9** because cationic alkyl-carbyne complexes are unstable. In addition, any synthesis of **8** or **9** must avoid acidic workup since these rhenium-carbene complexes are rapidly decomposed by acid.

Acknowledgment. Support from the Department of Energy, Division of Basic Energy Sciences, is gratefully acknowledged.

(3) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* **1980**, *201*, 389.
(4) Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6500.
(5) Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596.
(6) For **8**: ^1H NMR (270 MHz, benzene-d_6) δ 16.11 (q, J = 7.3 Hz, Re=CH), 4.88 (s, C_5H_5), 2.00 (d, J = 7.3 Hz, CH_3); ^{13}C NMR (126 MHz, benzene-d_6) δ 292.3 (d, J = 134 Hz, Re=C), 204.5 (s, CO), 91.4 (d, J = 178 Hz, C_5H_5), 50.4 (q, J = 124 Hz, CH_3); IR (THF) 1980, 1900 cm^{-1}. HRMS calcd for $C_9H_9O_2{}^{187}Re$ 336.0158, found 336.0161. Anal. Calcd for $C_9H_9O_2Re$: C, 33.23; H, 2.71. Found: C, 33.25; H, 2.76.
(7) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521.
(8) For **9**: ^1H NMR (270 MHz, benzene-d_6) δ 16.07 (t, J = 7.6 Hz, Re=CH), 4.94 (s, C_5H_5), 2.49 (m, Re=CHCH_2), 1.43 (m, CH_2CMe$_3$), 0.91 (s, C(CH_3)$_3$); ^{13}C NMR (126 MHz, benzene-d_6, couplings from INEPT) δ 298.1 (d, J = 129 Hz, Re=CH), 204.2 (s, CO), 91.5 (d, J = 179 Hz, C_5H_5), 59.4 (t, J = 126 Hz, Re=CHCH_2), 40.5 (t, J = 126 Hz, CH_2CMe$_3$), 29.9 (s, CMe_3), 29.3 (q, J = 124 Hz, C(CH_3)$_3$); IR (THF) 1980, 1900 cm^{-1}; HRMS calcd for $C_{14}H_{19}O_2{}^{187}Re$, 406.0943, found 406.0965. Anal. Calcd for $C_{14}H_{19}O_2Re$: C, 41.47; H, 4.72. Found: C, 41.34; H, 4.91.
(9) Fischer, E. O.; Riedel, A. *Chem. Ber.* **1968**, *101*, 156.
(10) (a) Fischer, E. O.; Clough, R. L.; Stückler, P. *J. Organomet. Chem.* **1976**, *120*, C6. (b) Fischer, E. O.; Frank, A. *Chem. Ber.* **1978**, *111*, 3740.

The Stereoselective Synthesis of α-Amino Acids by Phase-Transfer Catalysis

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New syntheses of α-amino acids are important because of the widespread use of these compounds in the physical and life sciences.[1] During the past 20 years major advances have been realized in the asymmetric synthesis[2] of amino acids, especially those which use stoichiometric amounts of chiral auxiliaries.[3-5]

(1) (a) *α-Amino Acid Synthesis*; O'Donnell, M. J., Ed. Tetrahedron Symposium-in-Print, Pergamon: London, 1988; Vol. 44, Issue 17. (b) Barrett, G. C. *Chemistry and Biochemistry of the Amino Acids*; Chapman and Hall: London, 1985. (c) *Amino Acids, Peptides and Proteins*; Specialist Periodical Reports, The Royal Society of Chemistry: London, 1969-1985; Vol. 1-16. (d) *Amino Acids and Peptides*; Specialist Periodical Reports, The Royal Society of Chemistry: London, 1986-1987; Vol. 17-18.
(2) Evans, D. A. *Science* **1988**, *240*, 420-426, and cited references.
(3) Recent lead references involving stoichiometric auxiliaries in the asymmetric synthesis of α-amino acids by C_α-C_β bond formation with anionic or cationic amino acid precursors: (a) Owa, T.; Otsuka, M.; Ohno, M. *Chem. Lett.* **1988**, 83-86. (b) Belokon', Y. N.; Bakhmutov, V. I.; Chernoglazova, N. I.; Kochetkov, K. A.; Vitt, S. V.; Garbalinskaya, N. S.; Belikov V. M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 305-312. (c) McIntosh, J. M.; Leavitt, R. K.; Mishra, P.; Cassidy, K. C.; Drake, J. E.; Chadha, R. *J. Org. Chem.* **1988**, *53*, 1947-1952. (d) Harding, K. E.; Davis, C. S. *Tetrahedron Lett.* **1988**, *29*, 1891-1894. (e) Fitzi, R.; Seebach, D. *Tetrahedron* **1988**, *44*, 5277-5292. (f) Schöllkopf, U.; Tiller, T.; Bardenhagen, J. *Tetrahedron* **1988**, *44*, 5293-5305. (g) Ojima, I.; Chen, H.-J. C.; Qiu, X. *Tetrahedron* **1988**, *44*, 5307-5318. (h) El Achqar, A.; Boumzebra, M.; Roumestant, M.-L.; Viallefont, P. *Tetrahedron* **1988**, *44*, 5319-5332. (i) Ikegami, S.; Uchiyama, H.; Hayama, T.; Katsuki, T.; Yamaguchi, M. *Tetrahedron* **1988**, *44*, 5333-5342. (j) Bretschneider, T.; Miltz, W.; Münster, P.; Steglich, W. *Tetrahedron* **1988**, *44*, 5403-5414. (k) Yamamoto, Y.; Ito, W. *Tetrahedron* **1988**, *44*, 5415-5423. (l) Williams, R. M.; Zhai, W. *Tetrahedron* **1988**, *44*, 5425-5430, and cited references.

0002-7863/89/1511-2353$01.50/0