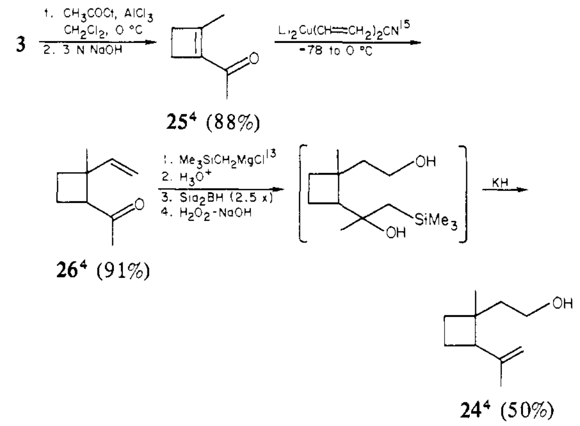
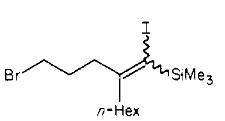
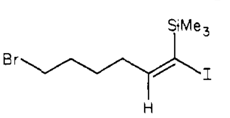
Scheme I



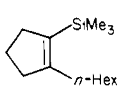
zation, the alkenyllithium **20** must have cyclized. We have indeed found that the treatment of **19** with 2 equiv of *t*-BuLi in Et_2O (-78 to 25 °C) cleanly produces **5** in 81% yield. This reaction, presumably a σ-process, has indeed turned out to be more general with respect to ring size than that described above. Thus, **21**[10] and **22**[4] were converted into **23**[4] (84%) and **18**[4] (64%), respectively, upon treatment with *t*-BuLi (2 equiv). We then found that **23** could also be obtained cleanly in ca. 80% GLC yield by treating **21** with 1 equiv of *n*-BuLi. Although the applicability of this simplified procedure is yet to be fully explored, the above results indicate that intramolecular displacemenet of a bromide anion is much faster than intermolecular displacement of an iodide anion from *n*-BuI. It should be emphasized that (*E*)-1-iodo-6-bromo-1-hexene does not produce cyclohexene upon treatment with 2 equiv of *t*-BuLi. Nor does it produce any other monomeric product either in Et_2O or in Et_2O–THF. We conclude that polymerization must be the course of the reaction. Clearly, Si plays a critical role in promoting this cyclization as well. The precise nature of the promotion by Si is not clear. However, an increasing number of 1,1-dimetalloalkenes[11] have been shown to exhibit configurational instability presumably through interaction of the C=C bond with low-lying empty metal orbitals.



21

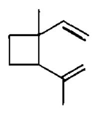


22

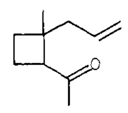


23

To demonstrate the synthetic utility of the above-described cyclization reactions, we synthesized grandisol[12] (**24**) from **3**, as shown in Scheme I. Although the formation of a ca. 2:1 mixture of the *Z* and *E* isomers of **26**[4] leaves room for improvement, no other significant byproduct is formed in this four-step conversion of **1** to **24** in overall 37% yield. The use of Me_3SiCH_2MgCl[13] in place of a Wittig-type reagent avoids the intermediacy of **27**, which was used as a key intermediate in one of the reported syntheses but is known to readily undergo the Cope rearrangement.[12b] The reaction of **25** with allyltrimethylsilane in the presence of $TiCl_4$[14] (-30 °C) also gives a ca. 2:1 *Z* and *E* mixture of **28**[4] in essentially quantitative yield.



27



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Acknowledgments. We thank the National Science Foundation, the National Institutes of Health, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support. We also thank Professor B. H. Lipshutz for helpful suggestions. Trimethylalane was kindly supplied by Ethyl Corp.

Registry No. 1a, 58435-00-0; **1b**, 69361-41-7; **1c**, 41423-29-4; **1d**, 86994-11-8; **3**, 86994-12-9; **5**, 83094-06-8; **6**, 86994-13-0; (*E*)-**8**, 86994-10-7; (*Z*)-**8**, 87038-35-5; **10**, 86994-14-1; **11**, 86994-15-2; **12**, 86994-16-3; **13**, 38002-45-8; **14a**, 86994-17-4; **14b**, 86994-18-5; **18**, 17874-17-8; **19**, 86994-20-9; **21**, 86994-22-1; **22**, 86994-23-2; **23**, 86994-24-3; **24**, 26532-22-9; **25**, 67223-99-8; (*Z*)-**26**, 30346-11-3; (*E*)-**26**, 30346-12-4; (*Z*)-**28**, 86994-21-0; (*E*)-**28**, 86994-25-4; (*E*)-1-iodo-6-bromo-1-hexene, 86994-19-6.

Supplementary Material Available: Listing of experimental data (2 pages). Ordering information is given on any current masthead page.

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(10) The procedure for preparing **21** is due to Dr. J. A. Miller of our laboratory. Its details will shortly be published elsewhere.

(11) See, for example: Yoshida, T.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 1276.

(12) (a) Tumlinson, J. H.; Hardee, D. D.; Gueldner, R. C.; Thompson, A. C.; Hedin, P. A.; Minyard, J. P. *Science* (*Washington, D.C.*) **1969**, *166*, 1010. (b) Billups, W. E.; Cross, J. H.; Smith, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 3438. (c) Stork, G.; Cohen, J. F. *Ibid.* **1974**, *96*, 5270.

(13) Chan, T. H.; Chang, E. *J. Org. Chem.* **1974**, *39*, 3264.

(14) Hosomi, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 1673.

(15) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. *Tetrahedron Lett.* **1982**, *23*, 3755.

Tungsten Carbene Complexes in Olefin Metathesis: A Cationic and Chiral Active Species

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Received March 21, 1983

We have briefly reported[1] the synthesis of the tungsten carbene complexes $W(CHR)(OCH_2R)_2X_2$ (R = *t*-Bu; X = Cl, Br) (**1**) and the conversion to extremely active catalysts for olefin metathesis on addition of 1 mol equiv of AlX_3. Although we formulated the predominant complex in solution under these conditions as the adduct **2a** (Scheme I, A = Al), we could not exclude the possibility that cationic species **2b**, in rapid equilibration with **2a**, was more directly involved in (i.e., within) the catalytic cycle, and we present evidence here that clarifies this important point.

Progressive addition of Ga_2Br_6 to **1** (X = Br) in halobenzene solution was followed by NMR (^1H and ^{13}C) at -35 °C and by conductivity measurements. Two regimes of behavior are observed: (a) As *n* (the Ga/W ratio) increases from 0 to 1, all resonances[2] (^1H and ^{13}C) are displaced in a *linear* fashion. The formation of a strong 1:1 adduct (K_1 >100 mol^{-1} at -35 °C) is indicated with a structure analogous to that previously proposed involving $AlBr_3$.[1]. Further the conductivity increase is small and at *n* = 1 a maximum of ca. 15% dissociation into **2b** is possible (K_2 ~0.1 at 20 °C). Hence the *major* species present under these conditions is indeed **2a** (Scheme I).

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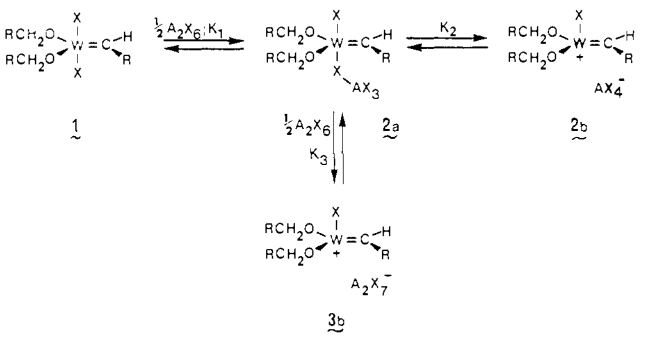
(1) Kress, J.; Wesolek, M.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 514. Note that a square-pyramidal geometry (C_s symmetry) is also consistent with these results but this does not alter the conclusions reached below.

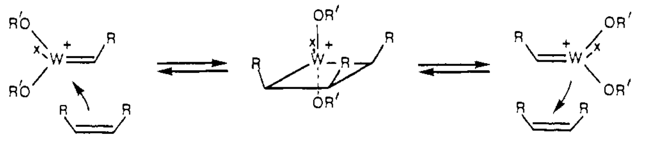
(2) ^1H NMR (C_6D_5Br, -35 °C) for $n = 0$: δ 11.22 (s, 1 H, $CHCMe_3$, $J_{W\text{-}H} = 11$ Hz), 4.44 (s, 4 H, OCH_2CMe_3), 1.18 (s, 9 H, $CHCMe_3$), 0.91 (s, 18 H, OCH_2CMe_3). The 4.44 and 0.91 peaks are each resolved into two singlets at room temperature. For $n = 1$: δ 12.12 (s, 1 H, $J_{W\text{-}H} = 12$ Hz, $CHCMe_3$), 4.52, 4.49 (s, 2 H, OCH_2CMe_3), 1.12 (s, 9 H, $CHCMe_3$), 0.95, 0.90 (s, 9H, OCH_2CMe_3). ^{13}C NMR (ppm, C_6D_5Br, -35 °C) for $n = 0$: 297.2 (d, $J_{C\text{-}H} = 135$, $J_{C\text{-}W} = 159$ Hz, $CHCMe_3$), 92.2, 90.9 (t, OCH_2CMe_3), 45.3 (s, $CHCMe_3$), 34.2, 34.0 (s, OCH_2CMe_3), 31.9 (q, $CHCMe_3$), 26.4 (q, OCH_2CMe_3). For $n = 1$: 315.2 (d, $J_{C\text{-}H} = 133$, $J_{C\text{-}W} = 158$ Hz, $CHCMe_3$), 91.5, 91.3 (t, OCH_2CMe_3), 48.2 (s, $CHCMe_3$), 35.1, 35.0 (s, OCH_2CMe_3), 31.8 (q, $CHCMe_3$), 26.8, 26.4 (q, OCH_2CMe_3).

0002-7863/83/1505-6346$01.50/0

Scheme I



Scheme II



(b) For $n > 1$, further NMR displacements are observed, and many of the plots of chemical shift displacement against n show cusps at $n = 1$, indicating the formation of a second species between **2a** (A = Ga; X = Br) and gallium bromide. The nonlinear behavior of these displacements, where limiting values are only achieved at $n > 6$, shows that the corresponding formation constant K_3 is small and is calculated as 5 ± 1 mol^{-1} at −35 °C.

We propose (Scheme I) that the new complex formed is **3b**, $W(=CRH)(OCH_2R)_2Br^+Ga_2Br_7^-$, on the following observations:[3] (a) whereas the resonances of W=C*H*-*t*-Bu (in ^{1}H) and W=*C*H-*t*-Bu (in ^{13}C) shift in lower field, the $J_{C\alpha-H}$ coupling constant remains essentially unchanged for all values of n. (b) The two OCH$_2$-*t*-Bu ligand resonances (^{1}H, ^{13}C) suffer only slight displacements. (c) The conductivity of solutions increases dramatically after $n = 1$, approaching an asymptotic limit (allowing for excess Ga_2Br_6) only at higher values of n, corresponding to a 1:1 electrolyte.

The catalytic activity of this system in the metathesis of *cis*-pent-2-ene (ca. 10^{-2} M carbene, 10^4 mol equiv of olefin, C_6H_5Cl, 20 °C) follows a similar profile, the initial rates increasing linearly until $n = 1$ (650 mol of olefin (mol W)$^{-1}$ min^{-1}) and then rapidly and nonlinearly with $n > 1$ reaching a limiting value at high values of n (5000 mol of olefin (mol W)$^{-1}$ min^{-1}). This parallel relationship between catalytic activity and the concentration of **3b** implies strongly that this cationic species is the active species for $n > 1$. Further, the initial rate of metathesis for $n = 1$ as well as the conductivity are both ca. 15% of the limiting values found for large n. Thus we propose that the *same cationic complex* (**2b** = **3b**) is the active species[4] for all values of n, even for $n < 1$ where **2a** is the major complex in solution. Also the initial ratio (t = 0) of *cis*-/trans-but-2-ene produced in the metathesis of *cis*-pent-2-ene is the same (1.0 ± 0.1) for all values of n.

The NMR data of **3b** show[3] that the two OCH$_2$-*t*-Bu groups are diastereotopic indicating that irrespective of the precise stereochemistry about W, no rotation about the metal–carbene bond takes place on the NMR time scale and **3b** is *chiral*.[5]

We thus propose that (a) the olefin interacts with **3b** via the site vacated by the halide ion (Scheme II), this approach allowing a suprafacial interaction of the olefin and metal carbene π-orbitals leading to metallacycle formation, and (b) the metallacycle so formed whether as an intermediate or transition state must possess a plane of symmetry imposed by the principle of microscopic reversibility.[6] Hence ligand rearrangement must accompany metallacycle formation, the most feasible mechanism of which is shown in Scheme II. Hence a cis olefin reacting to give a cis olefin product should occur with inversion of chirality of the carbene and hence the catalyst; a cis olefin giving trans olefin as product occurs with retention of configuration. Indeed classical catalysts have been shown to exhibit enantiomeric selectivity in the polymerization[7] of (±)-1-methylbicyclo[2.2.1]hept-2-ene.

Acknowledgment. We thank the C.N.R.S. and Rhône-Poulenc for financial aid.

Registry No. 1, 82958-93-8; **2a**, 86993-74-0; **3b**, 86993-76-2; Ga_2Br_6, 18897-68-2; *cis*-pent-2-ene, 627-20-3; *cis*-but-2-ene, 590-18-1; *trans*-but-2-ene, 624-64-6.

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(3) By extrapolation to high n we obtain for **3b** (C_6D_5Br, −35 °C): ^{1}H NMR δ 13.15 (s, 1 H, C*H*CMe$_3$, J_{W-H} = 12 Hz), 4.72, 4.55 (s, 2 H, OC*H*$_2$CMe$_3$), 1.18 (s, 9 H, CHC*Me*$_3$), 0.94, 0.85 (s, 9 H, OCH$_2$C*Me*$_3$); ^{13}C NMR (ppm) 333 (d, J_{C-H} = 134 Hz, *C*HCMe$_3$), 93.0, 92.5 (t, O*C*H$_2$CMe$_3$), 51.5 (s, CH*C*Me$_3$), 35.2, 34.9 (s, OCH$_2$*C*Me$_3$), 32.5 (q, CHC*Me*$_3$), 26.7 (q, OCH$_2$C*Me*$_3$).

(4) Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148 (ref 21).

(5) Note: (a) The active species described here are chiral even if all ligands are identical (if R ≠ H). (b) Chiral forms are interchanged, however, if halide exchange occurs between cation and anion (**3** ↔ **1**). The equivalence of the diastereotopic protons in **2** and **3b** is consistent with such an exchange process occuring at −35 °C. The implications in catalysis will be discussed fully elsewhere.

(6) This argument strictly applies only to degenerate metathesis.

(7) Hamilton, G. J.; Ivin, K. J.; Rooney, J. J.; Waring, L. C. *J. Chem. Soc., Chem. Commun.* **1983**, 159–161.

Dynamics of Micellized Radical Pairs. Measurement of Micellar Exit Rates of Benzylic Radicals by Time-Resolved Flash CIDNP and Optical Spectroscopy

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Received June 13, 1983

The dynamics of micellized triplet radical pairs have been investigated recently by time-resolved laser optical flash spectroscopy in several laboratories.[1-5] Usually, the disappearance of the micellized triplet radical pairs consists of a fast decay in the 1–500-ns time domain and a slow decay in the 500–5000-ns time domain. The fast decay is typically sensitive to applied laboratory magnetic fields, whereas the slow decay is not. The fast decay has been attributed to the competition between hyperfine-induced intersystem crossing to a singlet radical pair, which rapidly undergoes reaction and results in loss of radical absorption, and diffusive separation of the radicals to intra- and extramicellar configurations.[3,5] The slow decay has been attributed to uncorrelated micellar recombinations of geminate and nongeminate radical pairs.[3,5] In only one case has a rate constant for micellar exit of a radical been estimated from such experiments.[3] In that case, the exit rate of the cyclohexadienyl radical was found to be similar to the exit rate of singlet excited benzene for SDS micelles. We report the direct measurements of exit rates of radicals from sodium dodecyl sulfate (SDS) micelles by two independent methods: time-resolved laser flash spectroscopy and time-resolved chemically induced dynamic nuclear polarization (CIDNP). Our results are consistent with mechanisms that include radical exit from the micelle as a kinetically important process in the slow decay of micellized triplet radical pairs.

We have used the stable nitroxide radical Fremy's salt (FS), a selective water-soluble anionic scavenger, to react with radicals that exit from SDS micelles. Reaction of benzyl radicals with

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(1) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Tanimoto, Y.; Weed, G. C. *J. Am. Chem. Soc.* **1981**, *103*, 4574.

(2) Sakaguchi, Y.; Nagakura, S.; Minoh, A.; Hayashi, H. *Chem. Phys. Lett.* **1981**, *82*, 213.

(3) Scaiano, J. C.; Abuin, E. B.; Stewart, L. C. *J. Am. Chem. Soc.* **1982**, *104*, 5673.

(4) Tanimoto, Y.; Itoh, M. *Chem. Phys. Lett.* **1981**, *83*, 626.

(5) Turro, N. J.; Baretz, B. H.; Gould, I. R.; Lehr, G. F. *J. Am. Chem. Soc.*, submitted for publication.