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An unexpected isotope scrambling process accompanies hydrozirconation of styrene

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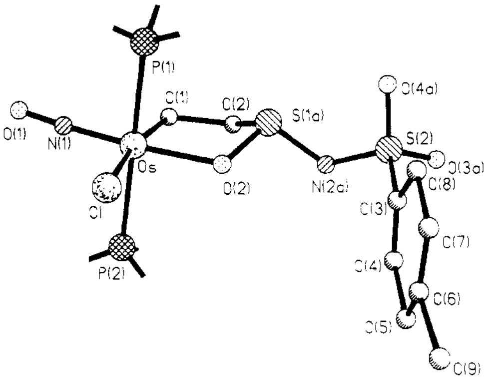

Figure 1. The molecular geometry of 4 showing the (a) arrangement of the sulfane group. Bond distances: Os–P(1), 2.447 (2); Os–P(2), 2.450 (2); Os–Cl, 2.460 (2); Os–N(1), 1.706 (9); Os–O(2), 2.035 (7); Os–C(1), 2.158 (10) Å. S(1a) is displaced from the plane defined by Os, C(1), C(2), O(2), and N(2a) by 0.69 Å while in the (b) molecule this distance is −0.23 Å.

which derives from the coupling of the osmium–alkene moiety with the sulfur–oxygen multiple bond. The complex $[Os\{CH_2CH_2S(NSO_2C_6H_4Me\text{-}4)O\}Cl(NO)PPh_3)_2]$ (4) is characterized by infrared activity (1805 cm^{-1}) typical of a nitrosyl ligand bound to divalent osmium[10] while the osmacycle gives rise to bands at 1026, 1010, and 830 cm^{-1}. Multiplet resonances are observed in the ^1H NMR spectrum of 4 at δ 1.64 and 2.69 ppm, regions typical of transition-metal alkyls and metallacyclic alkylsulfinates.[8b,11,12] These resonances show some simplification upon $\{^{31}P\}$ or selective $\{^1H\}$ decoupling, but not sufficient to resolve the ABCDXY spin system. The characterization of 4[13] included a single-crystal X-ray diffraction analysis (Figure 1) that confirmed the coordination spheres of osmium and sulfur, the metallacycle connectivity, and aplanarity.

The course of the reaction 1 + 2 → 4 presumably proceeds via direct electrophilic attack at the coordinated olefin, formation of the zwitterion $[Os^+\{CH_2CH_2S(NSO_2C_6H_4Me\text{-}4)O^-\}Cl(NO)(PPh_3)_2]$, and subsequent intramolecular ion-pair-collapse cyclization, a process described previously for transition-metal alkyls.[14] The specificity of this ring closure [O(2) exclusively trans to N(1)] is presumably due to steric control. Thus the formation of 4 rather than 3 predominates in situations where olefin dissociation (leading to 3) is less favored, i.e., a nondonor solvent (toluene vs tetrahydrofuran) and a high relative concentration of 1, this being obtained when 2 is suspended rather than completely dissolved. An alternative interpretation should also be noted. The ability of nitrosyl complexes to expand their coordination spheres by bending is well documented, and such a tautomerism in 2 would, according to Hoffmann's treatment,[15] provide a square-pyramidal complex with an apical nitrosyl ligand. Nucleophilic attack at osmium by the oxygen of the iminooxosulfurane moiety would therefore occur trans to the nitrosyl ligand, giving the observed stereochemistry.

The novel formation of 4 involves the combination of an olefin and iminooxosulfane within a transition-metal coordination sphere in a manner which constrasts markedly with that occurring in the absence of ligation and illustrates the control of the fine balance between the processes of substitution or chemical modification of coordinated olefins.

Preliminary results with the alkyne complexes $[OsCl(NO)(PPh_3)_2(PhC{\equiv}CR)]$ (R = H, Ph) and the allene complex $[OsCl(NO)(PPh_3)_2(\eta^2\text{-}CH_2C{=}CH_2)]$ suggest the formation 5-membered metallacycles similar to 4, indicating that the reaction may have some generality.[16]

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(13) Spectroscopic data for **4**: IR (Nujol) 1805 [$\nu(NO)$], 1299, 1284, 1145 ($-SO_2$), 1026, 1010, 830 (metallacycle), 280 cm^{-1} [$\nu(OsCl)$]; ^1H NMR ($CDCl_3$) δ 1.64 (m, 2 H, $OsCH_2$), 2,38 (s, 3 H, Me-4), 2.62–2.69 (m, 2 H, SCH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$), −5.6 (s). Crystal data for $C_{45}H_{41}ClN_2O_4OsP_2S_2$: $M_r = 1025.56$; monoclinic, $P2_1/n$; $a = 10.329$ (2), $b = 33.273$ (3), $c = 12.600$ (1) Å; $\beta = 99.76$ (1)°; $U = 4267.7$ Å^3; $Z = 4$, $D_{calcd} = 1.596$ g cm^{-3}; yellow prisms; $F(000) = 2048$, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu(Mo\ K\alpha) = 34.44$ cm^{-1}; $\theta_{max} = 25°$; 5111 observed reflections [$I > 3\sigma(I)$] were collected on a Nonius CAD4 diffractometer and corrected for absorption. The structure was solved by conventional Patterson and Fourier techniques and by full-matrix least-squares refinement. It was found that the $SNSO_2$–component of the sulfane moiety adopted one of two alternative arrangements while common positions for atoms C(1)–C(9), O(2), and S(2) were maintained. Refinement of the occupancy factors for alternative half atoms indicated that one arrangement (a) occurred two thirds of the time, and the other arrangement (b) occurred one third of the time. Figure 1 shows arrangement a, but there is no significant chemical difference between the two arrangements. Refinement of this model converged with $R = 0.050$. The crystals contain one molecule per asymetric unit. The atomic coordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

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An Unexpected Isotope Scrambling Process Accompanies Hydrozirconation of Styrene[†]

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Summary: Treatment of Cp_2ZrHCl with styrene leads to a mixture of terminal (85%) and internal (15%) insertion products. Attempts to prepare stereospecifically labeled deuterioorganozirconium derivatives result in scrambling of the β-positions of both isomers, yielding a statistical distribution of isotopomers. The features of this scrambling process are described, and a mechanism is proposed.

The use of NMR stereochemical probes such as $Me_3CCHDCHDX$ as a mechanistic tool was introduced to organometallic chemistry by Whitesides.[1] In subsequent application of this technique to electrophilic cleavage reactions of organozirconium compounds, it was recognized that hydrozirconation itself provides a particularly con-

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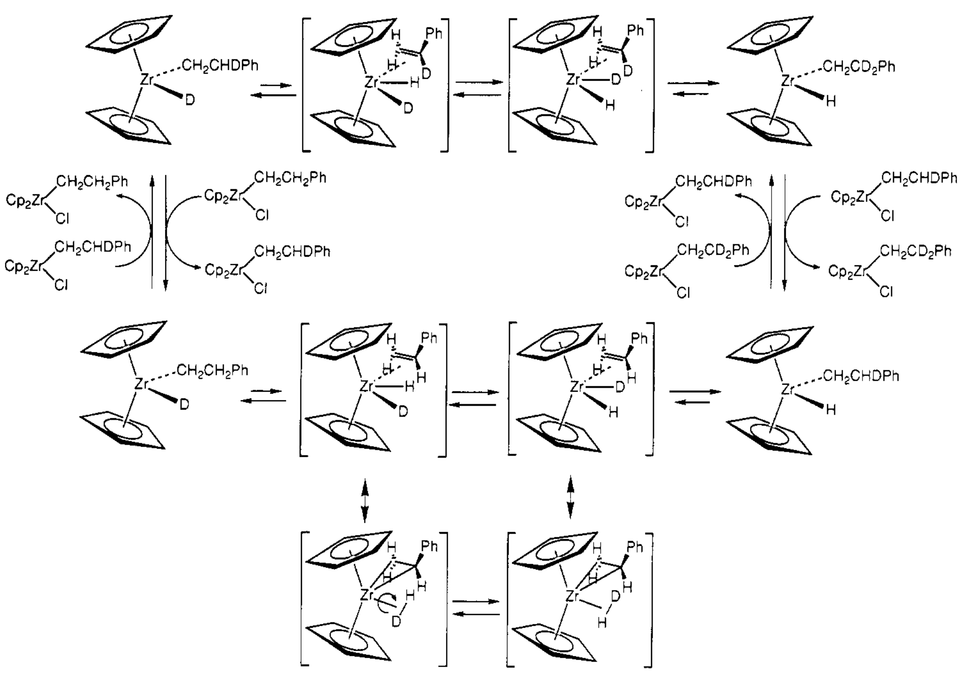
[†] Contribution Number 7944.

(1) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814.

Scheme I



venient synthetic route to the desired stereolabeled compound,[2] as it generally proceeds with high stereo- and regioselectivity.[3] For a mechanistic study of α-alkyl migration from sulfur to tantalum in $[(\eta^5\text{-}C_5Me_5)_2TaSR]$,[4] we required pure diastereomers of the analogous phenethyl mercaptan, PhCHDCHDSH. However, initial attempts to make either pure *erythro-* or pure *threo-*PhCHDCHDBr from PhC≡CH, following the routes established for the neohexyl analogues,[2] failed: both products gave the *same* complex NMR spectrum. In trying to determine the cause of this failure, we discovered a novel isotopic scrambling process. We report herein on its features.

It has been reported that hydrozirconation of styrene, in contrast to most olefins, gives *both* terminal (**1**) and internal (**2**) products (eq 1).[5] Monitoring the reaction

$$Cp_2(Cl)ZrH + CH_2{=}CHPh \xrightarrow{25\ ^\circ C} \underset{\mathbf{1}\ (85\%)}{Cp_2(Cl)ZrCH_2CH_2Ph} + \underset{\mathbf{2}\ (15\%)}{Cp_2(Cl)ZrCHPhCH_3} \quad (1)$$

between $Cp_2(Cl)ZrH$[6] and styrene by high-field ^1H NMR spectroscopy (Figure 1a) reveals that at room temperature **1** and **2** are formed in a ratio of 85:15, and on prolonged standing at room temperature this ratio does not change appreciably. The peaks attributable to **1** are as reported previously,[7] and the AA′XX′ pattern may be fully analyzed.[8] The peaks due to **2** also may be assigned straightforwardly.

Surprisingly, the ^1H NMR spectrum of the products of the reaction of $Cp_2(Cl)ZrD$ with $CH_2{=}CHPh$ *is not* that predicted for simple replacement of D for H in the β-positions of **1** and **2** (Figure 1b). Rather, the signals clearly include as well patterns for $Cp_2(Cl)ZrCH_2CH_2Ph$ (**1**-d_0) and $Cp_2(Cl)ZrCH_2CD_2Ph$ (**1**-β-d_2) together with $Cp_2(Cl)ZrCHPhCH_3$ (**2**-d_0), $Cp_2(Cl)ZrCHPhCHD_2$ (**2**-β-d_2), and $Cp_2(Cl)ZrCHPhCD_3$ (**2**-β-d_3), in roughly statistical amounts (**1**-d_0:**1**-β-d_1:**1**-β-d_2 ≈ 1:2:1, **2**-d_0:**2**-β-d_1:**2**-β-d_2:**2**-β-d_3 ≈ 8:12:6:1) (eq 2). Significantly, ^2H NMR spectroscopy

$$\begin{aligned}&Cp_2(Cl)ZrD + CH_2{=}CHPh \rightarrow\\ &\quad \underset{(\mathbf{1}\text{-}d_0,\ \mathbf{1}\text{-}\beta\text{-}d_1,\ \mathbf{1}\text{-}\beta\text{-}d_2)}{Cp_2(Cl)ZrCH_2CH_nD_{2-n}Ph}\ (n = 0\text{–}2) +\\ &\quad\quad \underset{(\mathbf{2}\text{-}d_0,\ \mathbf{2}\text{-}\beta\text{-}d_1,\ \mathbf{2}\text{-}\beta\text{-}d_2,\ \mathbf{2}\text{-}\beta\text{-}d_3)}{Cp_2(Cl)ZrCHPhCH_nD_{3-n}}\ (n = 0\text{–}3) \quad (2)\end{aligned}$$

reveals that *isotopomers which contain deuterium in the α-positions* (**1**-α-d_1, **1**-α-d_2, or **2**-α-d_1) *are initially obtained in no more than 10% yield.* Deuterium scrambling into the α-positions is very slow, so that even after 1 week at room temperature the amount of deuterium in the α-positions of **1** and **2** is less than 20% of statistical.

Thus, two distinct exchange processes are operating: (1) a fast exchange of (only) β-hydrogens between various alkyl derivatives and (2) a much slower exchange that eventually exchanges α- and β-hydrogens, most likely via the reverse of eq 1. With regard to the fast exchange process we have made the following observations: (i) a mixture of $Cp_2(Cl)ZrCH_2CH_2C_6H_5$ (**1**-d_0) and $Cp_2(Cl)ZrCD_2CD_2C_6D_5$ (**1**-d_9) (isolated separately from $Cp_2(Cl)ZrH$ and $CH_2{=}CHC_6H_5$ and from $Cp_2(Cl)ZrD$ and $CD_2{=}CDC_6D_5$, respectively) shows complete (β) scrambling within 30 min in benzene at 25 °C;[9] (ii) over the same period no deuterium

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[5] This conclusion was based only upon analysis of cleavage products such as halides or alcohols, not direct NMR examination of the organozirconium product(s); the sole report of the latter showed evidence for **1** only. (a) Gibson, T. *Organometallics* **1987**, *6*, 918. (b) Negishi, E.; Miller, J.; Yoshida, T. *Tetrahedron Lett.* **1984**, *25*, 3407. (c) Buchwald, S. L.; LaMaire, S. J. *Tetrahedron Lett.* **1987**, *28*, 295. (d) Liu, Y.; Guo, Q.; Lei, X. *Youji Huaxue* **1984**, *33* (*Chem. Abstr.* **1984**, *101*, 37 981.)

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[9] These isolated samples also contained ca. 15% **2**-d_0 and **2**-d_9. Faster exchange of the β-positions of **1**-d_0 and **1**-d_9 is observed, almost certainly because **2** dissolves much slower in benzene than **1**. When this sample was examined 12 h later, **2** was in solution and exchange was complete.

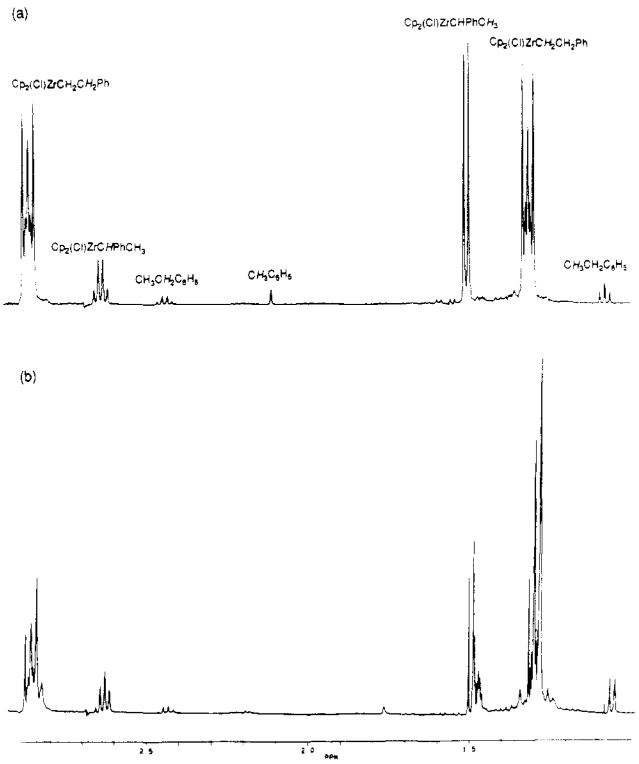

Figure 1. 500-MHz ^1H NMR spectra (in benzene-d_6) of (a) products of reaction of $Cp_2(Cl)ZrH$ and $CH_2{=}CHPh$ and (b) products of reaction of $Cp_2(Cl)ZrD$ and $CH_2{=}CHPh$.

incorporation into $Cp_2(Cl)ZrCH_2CH_2Ph$ is observed when it is treated with an equivalent of $CHD{=}CDPh$ (benzene-d_6, 25 °C; ^1H NMR).

The fast process is remarkable, not only because it is specific for exchange between β-positions but also because it occurs rapidly after hydrozirconation is complete and without exchange with free styrene. Given these very restrictive requirements, we suggest the mechanism in Scheme I (shown for 1 only). The following points are particularly notable: (i) scrambling is catalyzed by a small amount of a zirconium alkyl *hydride* complex, $Cp_2(H)ZrR$, produced from the Cp_2ZrH_2 present in the initial preparation of $Cp_2(Cl)ZrH$[6] (exchange between metal and β-alkyl positions has previously been demonstrated in such a compound);[10] (ii) the geometry of the olefin–dihydride intermediate must be that shown (otherwise this mechanism would interconvert 1 and 2 and thus provide facile α-exchange),[11] (iii) chain-propagating hydride-for-chloride exchange proceeds via bridged dimers (all such $Cp_2(X)ZrH$ species are at least dimeric). In accord with the proposed mechanism, when solutions of 1-d_0 and 1-d_9 in benzene-d_6, each containing ca. 0.5 equiv of acetone to convert any [Zr–H] to [Zr–$OCHMe_2$], are mixed, *no H/D exchange is observed*, even after 12 h.

Since stereospecific hydrozirconation *can* be effected in the neohexyl system,[2] scrambling must not take place there; we have verified that the reaction of $Cp_2(Cl)ZrD$ with $CH_2{=}CHCMe_3$ gives no detectable isotopomers other than the expected $Cp_2(Cl)ZrCH_2CHDCMe_3$. Which result is the anomaly: scrambling for styrene or the failure to scramble for neohexene? Although a thorough study has not yet been carried out, *no scrambling* is found in the reactions of $Cp_2(Cl)ZrD$ with $CH_2{=}CHCH_2Ph$ or $PhCH{=}CHCH_3$.[12] These preliminary results suggest that styrene is the special case; perhaps the olefin complex is stabilized by conjugation relative to alkyls 1 and 2,[13] thus accelerating the β-elimination steps in Scheme I. It is striking that styrene is also special in that it gives significant amounts of the nonterminal hydrozirconation product, but this work suggests that these two manifestations of special behavior are *not* interconnected in any obvious manner.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE-8600875) and by Shell Companies Foundation, which are gratefully acknowledged.

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(11) Since this result apparently requires that H-D exchange is facile but olefin rotation is very slow, one might speculate that the bonding is better described as metallacyclopropane–dihydrogen than as olefin–dihydride as shown in Scheme I. Alternatively, the interchange of H and D in the olefin–dihydride complex might occur by the "Tarzan swing" mechanism described for $[(\eta^5\text{-}C_5Me_5)_2WH_2D]^+$; Parkin, G.; Bercaw, J. E. *Polyhedron* 1988, *7*, 2053–2082.

(12) NMR of the hydrozirconation products confirms Gibson's inference, again based only on derived alcohols,[5a] that $PhCH_2CH{=}CH_2$ gives mostly the terminal and $PhCH{=}CHCH_3$ initially the benzylic which slowly rearranges to the terminal product. Full details, including the fate of a D label during the rearrangement, will be reported later.

(13) Stabilization of olefin–hydride relative to inserted alkyl by phenyl has been inferred for the sterically (but *not* electronically) similar systems $Cp_2NbH(CH_2{=}CHR)$: Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* 1988, *110*, 3134.

Synthesis and Spectroscopic Investigations of Optically Active Alkylaluminum Compounds of *l*-Ephedrine. The Crystal Structure of the $[Me_2Al(O\text{-}(R)\text{-}CHC_6H_5((S)\text{-}CH((S)\text{-}NHCH_3)CH_3)]_2$ Dimer: An Optically Active Five-Coordinate Aluminum Complex

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Summary: The reaction of *l*-ephedrine with a trialkylaluminum affords the compound $[R_2Al(O\text{-}(R)\text{-}CHC_6H_5\text{-}((S)\text{-}CH((S)\text{-}NHCH_3)CH_3)]_2$ (R = Me, **1**; R = Et, **2**) in high yield. Compounds **1** and **2** contain a five-coordinate aluminum center with a central Al_2O_2 ring and an Al–N dative bond. The formation of the Al–N dative bond is stereospecific, resulting in 100% induction of optical activity at the nitrogen center. This is indicated from the optical rotations, $[\alpha]^{25}$, and confirmed by the crystal structure of **1**. Compound **1** crystallizes in the tetragonal space group $P4_12_12$ with unit cell parameters $a = b = 8.614$ (1) Å, $c = 35.348$ (5) Å, $V = 2622.61$ (6) Å^3, and $D_{calcd} = 1.12$ g cm^{-3} for $Z = 4$. Least-squares refinement based on 891 observed reflections ($F_o \geq 2.5\sigma(F)$) converged at $R = 6.3\%$ ($R_w = 4.0\%$). The Al_2O_2 ring system is unsymmetrical with Al–O and Al–O′ distances of 1.86 and 1.95 Å, respectively. The coordination around the Al atom can be further described as a distorted trigonal bipyramid with an exceptionally long Al–N bond of 2.19 Å. The molecules undergo a dynamic process which averages the nonequivalent Al–Me and Al–Et groups. This averaging process is thought to result from the dissociation of the Al–N bond without disruption of the Al_2O_2 ring and occurs with an activation energy of 24.4 kcal/mol for **1**.

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