demonstrated by the formation of CH_3COCH_2OBz in 46% yield in this reaction. Further experimental studies designed to establish the details of these reactions are in progress.

Acknowledgment. Support in Toronto by the Natural Sciences and Engineering Research Council of Canada and in Utah by the National Cancer Institute of the National Institutes of Health (Grant 1ROCA16903) is gratefully acknowledged.

Supplementary Material Available: Tables II-IV containing rate constants and solvent isotope effect calculations for **1-3** (5 pages). Ordering information is given on any current masthead page.

Reaction of Phosphorus Ylides with Elemental Selenium: Generation of Selenoaldehydes and Selenium-Catalyzed $Ph_3P{=}CHR$ Cleavage To Give $RHC{=}CHR$ and Triphenylphosphine

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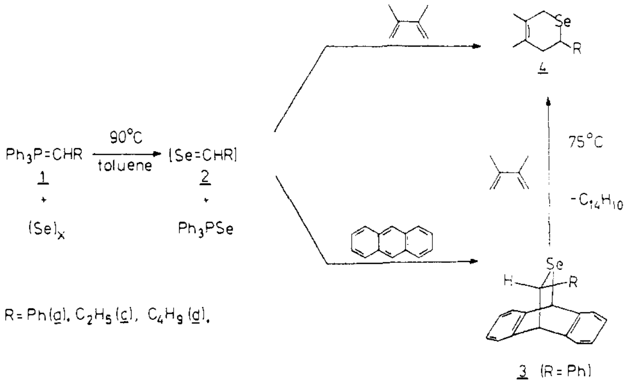
Received August 3, 1987

Selenoaldehydes (RCHSe) **2** are more reactive than their oxygen analogues RCHO. With very few exceptions, this has prevented the isolation of the monomeric RCHSe species.[1-3] The enhanced and often different reactivity makes selenoaldehydes objects of general interest and indicates some special synthetic potential. In situ generated selenocarbonyl compounds **2** undergo thermally induced [4 + 2] cycloaddition reactions with conjugated dienes to form 3,6-dihydro-2*H*-selenapyran derivatives **4**.[4] When carried out with aldehydes, the analogous reactions require strong acid catalysis.[5]

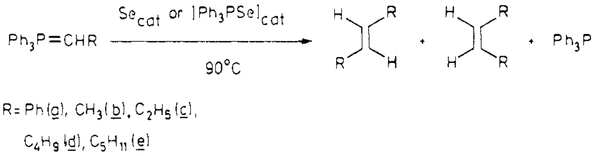
Several methods to generate selenoaldehydes have been reported, most of which are variants of 1,2-elimination reactions employing suitably substituted precursors X-RCHSe-Y.[2,4] We report here a fundamentally different way of generating the RCHSe species **2** by treating alkylidene triphenylphosphoranes $Ph_3P{=}CHR$ **1** with elemental selenium.[6]

The reaction between elemental selenium (2.1 equiv) and $Ph_3P{=}CHR$ was carried out at 90 °C with use of an excess of a conjugated diene as a Diels-Alder trapping agent (Scheme I). Typically, a red solution of benzylidene triphenylphosphorane **1a** (12 mmol, in 50 mL of toluene) was added dropwise over a period of 48 h to a hot (90 °C) mixture of 2,3-dimethylbutadiene (177 mmol) and Se (2.0 g) in 50 mL of toluene. Decolorization of the ylide occurred rapidly, and Ph_3PSe precipitated. 3,6-Dihydro-4,5-dimethyl-2-phenyl-2*H*-selenapyran **4a** was isolated from the solution (41% yield after chromatography).[7] The corresponding heterocycles **4c** and **4d** were identified by NMR from the reaction of the ylides $Ph_3P{=}CHR$ ($R{=}C_2H_5$, C_4H_9) with selenium and 2,3-dimethylbutadiene. An analogous reaction was carried out employing $Ph_3P{=}CHPh$ and anthracene to give **3** (21%).[7] Compound **3**, when heated to 75 °C in chloroform in the presence of excess 2,3-dimethylbutadiene, decomposed and transferred the selenobenzaldehyde unit to give **4a** and anthracene.

Scheme I



In the absence of the diene scavenger, a different reaction was observed. At 90 °C $Ph_3P{=}CHPh$ (**1a**) reacted smoothly with excess selenium to yield stilbene and triphenylphosphine selenide[8] (eq 1). Surprisingly, Ph_3PSe itself is capable of inducing the cleavage of nonstabilized ylides $Ph_3P{=}CHR$ **1a-e** to give the alkylidene coupling product $RCH{=}CHR$ and triphenylphosphine. This indicated that alkylidene triphenylphosphoranes $Ph_3P{=}CHR$ can be catalytically cleaved by elemental selenium to give $RCH{=}CHR$ and 2 equiv of PPh_3.[9] We were able to demonstrate this by reacting benzylidene triphenylphosphorane (58 mmol) in 100 mL of toluene with 5.8 mmol of selenium. Reaction took place rapidly. After 6-h reaction time and usual workup, stilbene (64%) and PPh_3 (70%) were isolated. Similar results were obtained reacting ylides $Ph_3P{=}CHR$ **1a-e** each with $^1/_{10}$ equiv of gray selenium or Ph_3PSe in toluene solution. In each case a near-to-thermodynamic mixture of the two geometric isomers of the expected olefin was obtained [(cis/trans ratio (yield): stilbene (**a**) 16/84 (64%); 2-butene (**b**) 20/80 (53%); 3-hexene (**c**) 17/85



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(9) To our knowledge, a pairwise exchange mechanism (of the type $R_3P{=}CHR^a + R_3'P{=}CHR^b \rightleftharpoons R_3P{=}CHR^b + R_3'P{=}CHR^a$) had only once been proposed in the literature (Bestmann, H. J.; Snyder, J. P. *J. Am. Chem. Soc.* **1967**, *89*, 3936). Since this interpretation was later corrected in favor of a trans ylidation mechanism (Crew, P. *J. Am. Chem. Soc.* **1968**, *90*, 2961. Bestmann, H. J.; Liberda, H,. G.; Snyder, J. P. *J. Am. Chem. Soc.* **1968**, *90*, 2963. See, also: Schmidbaur, H.; Tronick, W. *Angew. Chem.* **1967**, *79*, 412), a pairwise ylide alkylidene exchange reaction appears not to have been observed yet experimentally. In view of the close mechanistic similarity to the olefin metathesis reaction[10] one might therefore be tempted to use the term "ylide metathesis" for the here described $2R_3P{=}CHR \rightarrow 2R_3P + RCH{=}CHR$ transformation.

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(50%); 4-octene (**d**) 15/85 (50%); 5-decene (**e**) 15/85 (63%)].[11]

In view of the trapping experiments described above and the widely accepted mechanism of the stoichiometric reactions between ylides and the chalcogen elements sulfur[12] and oxygen,[8] it is likely that selenoaldehydes **2** serve as key intermediates in this *catalytic* olefin forming ylide cleavage reaction.[13,14] In this case, the product-forming step in the catalytic cycle is a Wittig olefination-type reaction of a selenoaldehyde. The rather high trans selectivity observed here contrasts with the Wittig olefination of aldehydes RCHO under similarly salt-free conditions.[15] This might originate from a more facile reversal of the formation of a selenaphosphetane from RCHSe and $Ph_3P{=}CHR$ as compared to the oxaphosphetane analogue[16,17] or a preferred reaction path through a thermally unstable trans disubstituted episelenide stereoselectively decomposing under the reaction conditions.[18]

Acknowledgment. We thank Dr. G. Schomburg for helping us with the GC analyses. Generous financial support of the Fonds der Chemischen Industrie and the Alfried Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged.

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An Unusually Stable $Mn^{II}Mn^{III}$ Complex with Novel EPR Spectra: Synthesis, Structure, Magnetism, and EPR Analysis[†]

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Well-characterized polynuclear Mn complexes that catalytically oxidize H_2O to molecular oxygen are of intense current interest as models for the polynuclear Mn center in photosystem II.[3] The protein center exhibits a rich, hyperfine-structured EPR spectrum in its S_2 state whose interpretation could be facilitated by examining the corresponding spectra of suitable low molecular weight complexes. Earlier, we reported the first structural characterization of valence-trapped $Mn^{II}Mn^{III}$ complexes and demonstrated that the development of Mn hyperfine structure in the low-temperature EPR spectra is related to the strength of the Mn–Mn coupling.[4]

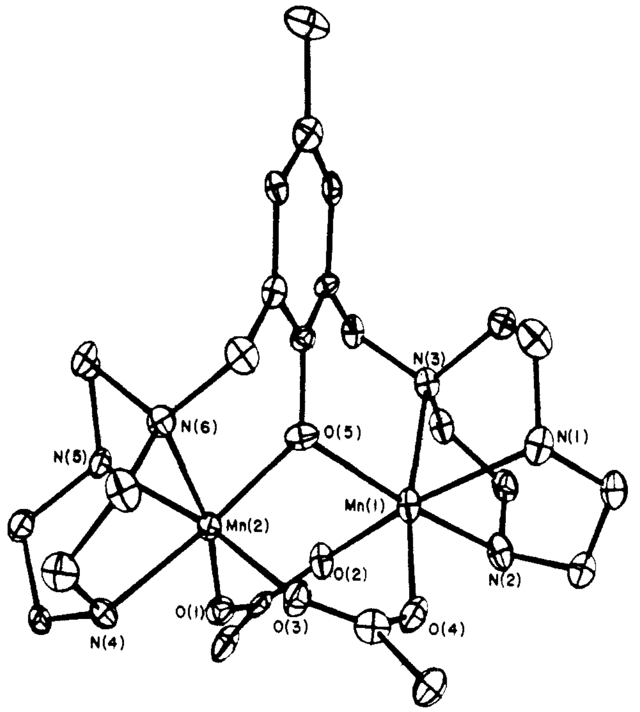

Figure 1. ORTEP plot of the $[Mn_2(bcmp)(\mu\text{-}OAc)_2]^{2+}$ cation in **1**. Selected interatomic distances and angles are as follows: Mn(1) -O(2), 2.135 (9); -O(4), 2.09 (1); -O(5), 2.17 (1); -N(1), 2.26 (1); -N(2), 2.22 (1); -N(3), 2.23 (1); Mn(2)-O(1), 2.01 (1); -O(3), 2.056 (9); -O(5), 1.957 (9); -N(4), 2.11 (1); -N(5), 2.23 (1); -N(6), 2.18 (1); Mn(1)⋯Mn(2), 3.422 (3) Å; Mn(1)-O(5)-Mn(2), 112.1 (4)°.

We report here the preparation and characterization of a new binuclear $Mn^{II}Mn^{III}$ complex (**1**), $[Mn_2(bcmp)(\mu\text{-}OAc)_2](ClO_4)_2{\cdot}CH_2Cl_2$, that exploits the special thermodynamic and kinetic stability associated with the binucleating 1,4,7-triazacyclononane[5] (tacn) ligand bcmp (**2**). We also report a novel

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[†] The synthesis and characterization of the complexes described in this communication are abstracted from the following: Diril, H., Ph.D. Thesis, Rutgers University, 1988.

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