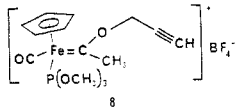
Table I. Summary of Rearrangement Results

entry	carbene complex	solv	temp, °C	time, h	product (%)[a]
1	$R^1 = R^2 = R^3 = R^4 = H$, $R^5 =$ Ph, X = BF^4 (**5a**)	C_6H_6	68	120	**7a** (10)[b]
2	$R^1 = R^2 = R^3 = R^4 = H$, $R^5 = OCH_3$, X = BF^4 (**5b**)	xylenes	118–120	24	**7b** (33)
3	$R^1 = R^2 = R^3 = H$, $R^4 = CH_3$, $R^5 = OCH_3$, X = BF_4 (**5c**)	PhMe	114	25	**7c** (22)[c]
4	$R^1 = R^2 = R^4 = H$, $R^3 = CH_3$, $R^5 = OCH_3$, X = BF_4 (**5d**)	C_6H_6	reflux	26	**7d** (60)[d]
5	$R^1 = R^3 = R^4 = H$, $R^2 = CH_3$, $R^5 = OCH_3$, X = BF_4 (**5e**)	C_6H_6	76–78	26	**7e** (13)[e]
6	$R^1 = R^3 = H$, $R^2 = R^4 = CH_3$, $R^5 = OCH_3$, X = BF_4 (**5f**)	C_6H_6	reflux	26	**7f** (34)[f]
7	$R^3 = R^4 = H$, $R^1 = R^2 = CH_3$, $R^5 = OCH_3$, X = OSO_2CF_3 (**5g**)	C_6H_6	reflux	21	**7g** (21)
8	**8**	C_6H_6	reflux	20	**9** (28)

[a] Yield calculated from the starting saturated iron acyl complex **3**, unless otherwise noted. [b] Yield calculated from the allyloxy carbene complex **5**. [c] Product obtained as a 3:1 mixture of diastereomers. [d] Product obtained exclusively as the *E* isomer. [e] Product obtained as a 1:1 mixture of diastereomers. [f] Product obtained as a complex mixture of diastereomers.

9 H, J = 12 Hz), 4.63 (s, 5 H), 4.87 (d, 1 H, J = 9.2 Hz), 4.94 (dd, 1 H, J = 16.8, 1.6 Hz), 5.75 (m, 1 H)]. Further results are summarized in Table I. It is clear from these examples that a range of simple allylic alcohols (and propargyl alcohol, entry 8) indeed reacted with the cationic iron vinylidenes **4** to produce the desired carbene complexes, and these in turn gave the corresponding rearrangement products **7**. The overall yields from the starting acyl **3** were modest (10–60%).[17] However the method is clearly useful for the preparation of diverse systems including the sterically encumbered product **7g** (entry 7) and the allene **9** (entry 8). The allene **9** readily isomerized to produce the corresponding diene acyl complex **10**. In



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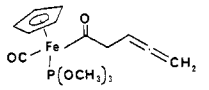
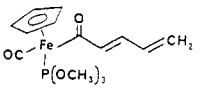


9



10

principle these γ,δ-unsaturated iron acyls **7** should be available from direct allylation of the enolate derived from **3**. Indeed this method has been efficiently used to prepare **7a**,[9] but attempts to apply this strategy to the preparation of the trimethyl phosphite substituted iron acyls failed due to competitive metalation of the cyclopentadienyl ring.[18,19] Thus the Claisen rearrangement provides a valuable route to the γ,δ-unsaturated iron acyls when the alternate alkylation route presents a problem.

In conclusion, these results demonstrate that iron allyloxy carbene complexes, on deprotonation, undergo a [3,3] sigmatropic rearrangement to give the corresponding γ,δ-unsaturated acyl complexes. Further studies are in progress to confirm the intramolecular nature of the rearrangement and to optimize the yield and diastereoselectivity of the transformation. Absolute stereochemical control of the Claisen rearrangement via organometallic intermediates would be a reaction of considerable synthetic importance.

Acknowledgment. We thank the National Science Foundation (CHE-8500890) for the generous support of this program and the Midwest Center for Mass Spectrometry, an NSF Regional Instrument Facility (CHE-8211164), for obtaining mass spectral data.

Supplementary Material Available: Spectroscopic and microanalytical data characterizing vinylidenes, carbenes, and acyls described in this paper (6 pages). Ordering information is given on any current masthead page.

(17) Approximately 5–30% of the starting saturated acyl complex **3** was typically recovered.

(18) Sturgess, M. A., unpublished results.
(19) Heah, P. C.; Patton, A. T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1185.

Thermal Rearrangement of (*S*,*S*)-1-Naphthylphenylmethyl(1-chloroethyl)silane and (*S*)-(1-Chloroethyl)phenyldimethylsilane

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Summary: (*S*,*S*)-1-Naphthylphenylmethyl(1-chloroethyl)-silane (**1**) and (*S*)-(1-chloroethyl)phenyldimethylsilane (**2**) were prepared and employed in a study of the stereochemistry of their thermal rearrangements. Although the stereochemistry at silicon could not be determined due to racemization, the stereochemistry at carbon was found to be inversion with a high degree of stereospecificity. The stereochemistry at carbon is preserved in a subsequent oxidative cleavage of the Si–C bond providing an interesting silicon-mediated preparation of (*S*)-1-phenylethanol and (*S*)-1-(1-naphthyl)ethanol.

The rearrangement of α-haloorganosilanes has been shown to take place under thermal,[2] Lewis acid catalyzed,[3]

(1) (a) University of Puerto Rico and Petrarch Systems. (b) University of Puerto Rico. (c) Louisiana State University. Taken in part from the Ph.D. Thesis of R.K., UPR, Rio Piedras, P.R., 1987.

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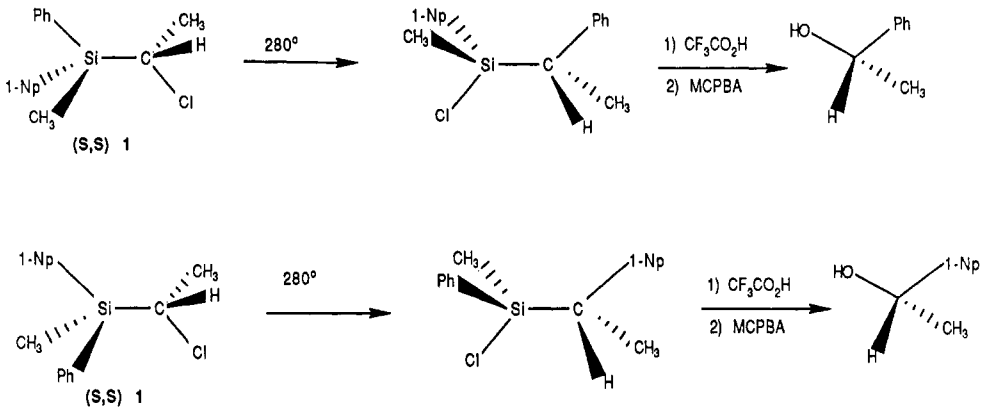
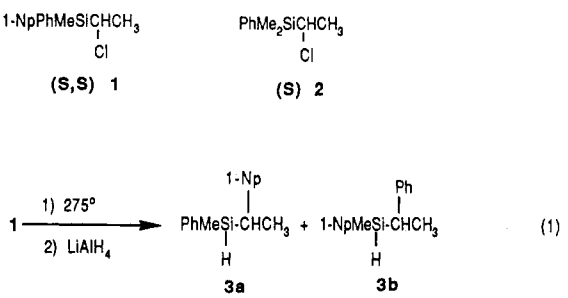
Scheme I



and basic[4] conditions. The reactions proceed best with the chloromethyl group,[5] making a study of their stereochemistry more difficult. We have now prepared the optically active system **1**[5] and converted it to **2** and employed it to study the stereochemistry of the thermal rearrangement.

α-Halosilane **1** was prepared as previously reported[6] as the *S,S* diastereomer. Heating **1** to temperatures of 260 °C for several hours in a sealed NMR tube showed no evidence for a reaction. It was not until the rearrangement was carried out at over 275 °C for 8–10 h that complete reaction was observed. This resulted in the migration of both the phenyl and 1-naphthyl groups in a ratio of ca. 1:4. Since working with the diastereomeric chlorides proved difficult and the attempted separation of the isomers was unproductive, this material was directly reduced with lithium aluminum hydride to the corresponding mixture of silanes **3a** and **3b**. The ^{1}H NMR spectrum of the crude



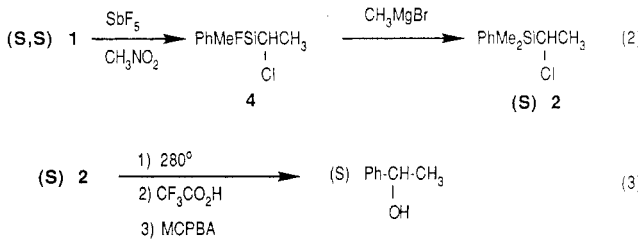
reaction product from the rearrangement–reduction sequence showed two pairs of doublets: the set for **3a** at 0.58 and 0.47 ppm (relative intensity 4) and a separate set for **3b** at 0.38 and 0.32 ppm (relative intensity 1). The presence of two doublets for each new diastereomer formed is due to racemization at silicon under the reaction conditions. Unfortunately, hydrides **3a** and **3b** resisted a variety of attempts at separation, and so a different approach was adopted. Thus, **1** was thermolyzed at 280 °C and the reaction product treated with trifluoroacetic acid and then oxidized with *m*-chloroperbenzoic acid. This oxidation procedure has been shown to occur with retention of configuration at carbon.[7] This provided a mixture of 1-(1-naphthyl)ethanol and 1-phenylethanol, both of which were shown by chiral shift reagent ^{1}H NMR studies[8] to have the *S* configuration[9] and to exist in greater than 95% ee. This sequence is depicted in Scheme I. The stereochemistry indicated at silicon is assumed because, unfortunately, it could not be determined due to the racemization at silicon under the reaction conditions.

It is possible that the reaction proceeds via a carbocation and that the stereoselectivity is a result of preferred conformational effects of the intermediate carbocation. This seems highly unlikely to us since the tributyltin hydride reduction of (*S*)-1-naphthylphenylmethyl(1,1-dichloroethyl)silane, which would pass through a trigonal radical intermediate, shows no diastereoselectivity[6] and also because no vinylsilane was observed in the reaction. A reaction pathway involving simultaneous intramolecular migration of an aryl group and chlorine is a reasonable mechanistic possibility consistent with the observed stereochemical results. Bassindale and co-workers[2] found the thermal rearrangement of $Me_3SiCBrPh_2$ to be first order in silane with $\Delta S = -1.3 + 3$ eu, the latter being considered inconsistent with a doubly bridged transition state. Consequently, an inverse ylide intermediate was proposed. The inversion stereochemistry at carbon observed here argues against the inverse ylide. It is possible, of course, that very stable carbocations, such as Bassindale's benzhydryl case, can be formed via the inverse ylide route, while the more normal mechanistic pathway does not involve a cationic intermediate.

In an attempt to bring about the rearrangement with antimony pentafluoride in nitromethane a very interesting and selective denaphthalenation to give **4** was found to occur. This material proved to be an equimolar mixture of diastereomers as evidenced by ^{1}H, ^{13}C, and ^{19}F NMR. We believe that this is the result of racemization of the resulting fluorosilane under the reaction conditions and does not necessarily have mechanistic implications concerning the denaphthalenation reaction itself. In order to determine that racemization takes place only at the silicon center **4** was treated with methylmagnesium bromide (methyllithium gives a mixture of products) to provide **2**,

(2) Bassindale, A. R.; Brook, A. G.; Jones, P. F.; Lennon, J. M. *Can. J. Chem.* **1975**, *53*, 332.
(3) Bott, R. W.; Eaborn, C.; Rushton, B. M. *J. Organomet. Chem.* **1965**, *3*, 455.
(4) Damrauer, R.; Yost, V. E.; Danahey, S. E.; O'Connell, K. *Organometallics* **1985**, *4*, 1779.
(5) Hairston, T. J.; O'Brien, D. H. *J. Organomet. Chem.* **1970**, *23*, C41.
(6) Larson, G. L.; Sandoval, S.; Cartledge, F.; Fronczek, F. R. *Organometallics* **1983**, *2*, 810.
(7) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694.
(8) The chiral shift reagents tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) and tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium(III) were employed for these analyses.
(9) Prelog, van V.; Philbin, E.; Watanabe, E.; Wilhelm, M. *Helv. Chim. Acta* **1956**, *3*, 1086.

which showed a specific rotation of −3.46° (*c* 7.22, cyclohexane) (eq 2). Thermolysis-oxidation of **2** also provided



(*S*)-1-phenylethanol, this time in 86% ee (eq 3). These results, together with those shown in Scheme I, provide the first stereochemical studies carried out on the thermal rearrangement of α-haloorganosilanes. The reactions proceed with inversion of configuration at carbon, a result which is inconsistent with the formation of an open carbocation intermediate and consistent with an intramolecular, simultaneous migration of the chlorine and aryl groups.

Acknowledgment. G.L.L. thanks the NIH-MBRS (RR-8102) for partial support of this work. The Petroleum Research Fund administered by the American Chemical Society is thanked for their support. Drs. Sydia Sandoval and J. A. Prieto are thanked for helpful discussions.

Registry No. (*S,S*)-1, 85082-06-0; **2**, 110079-44-2; **3a**, 110079-45-3; **3b**, 110079-46-4; **4** (isomer 1), 110079-47-5; **4** (isomer 2), 110079-48-6; (*S*)-1-phenylethanol, 1445-91-6; (*S*)-1-(1-naphthyl)ethanol, 15914-84-8.

Differentiating Metal Centers in Homopolynuclear Systems: Use of the Oxodiphenylphosphoranido (Diphenylphosphidoxo, μ-Ph_2P=O) Ligand as a Versatile Bridging Group and a Comparison with Related μ-Diphenylphosphido (μ-PPh_2) Complexes

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Summary: The novel diphenylphosphidoxo complexes $Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu\text{-}Ph_2P{=}O)$ and $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu\text{-}Ph_2P{=}O)$ have been synthesized from the phosphine oxide $Ph_2P(O)C{\equiv}C\text{-}t\text{-}Bu$ and $Ru_3(CO)_{12}$ or $Fe_2(CO)_9$; X-ray structural analyses of $Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu\text{-}Ph_2P{=}O)$ (**1**) and $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu\text{-}Ph_2P{=}O)$ (**2**) revealed phosphidoxo ligands bridging a strong metal–metal bond in **1** (Ru(1)–Ru(2) = 2.7729 (3) Å) and two noninteracting metals in **2** (Fe(1)–Fe(3) = 3.6064 (6) Å).

There are a number of reasons for anticipating an interesting chemistry for polynuclear complexes containing bridging phosphidoxo groups μ-R_2P=O;[1b] (i) the combination of a soft donor (P) and a hard ligand (=O) differentiates metal centers even in homobinuclear systems; (ii) the μ-R_2P=O moiety should, like the μ-R_2P group, be capable of bridging both bonding and nonbonding metals; (iii) there is evidence that phosphine oxides exert a labilizing influence on metal–carbonyl bonds.[2] Thus the oxygen end of the μ-phosphidoxo ligand may exercise control over the sites of substitution in polynuclear complexes. We describe herein a facile route to polynuclear carbonyl complexes of iron and ruthenium containing a single μ-Ph_2P=O ligand. X-ray analyses of $Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu\text{-}Ph_2P{=}O)$ (**1**) and $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu\text{-}Ph_2P{=}O)$ (**2**) have allowed a detailed comparison of structural parameters for closely related diphenylphosphidoxo and diphenylphosphido complexes, suggesting that μ-Ph_2PO ligands may be equally as versatile as their μ-Ph_2P counterparts. Although bridging phosphonato and phosphinito complexes are known[3] including several obtained by thermal degradation of phosphites,[3c–e] there are to our knowledge no structurally characterized examples of μ-Ph_2P=O ligands bridging strong metal–metal bonds.[4]

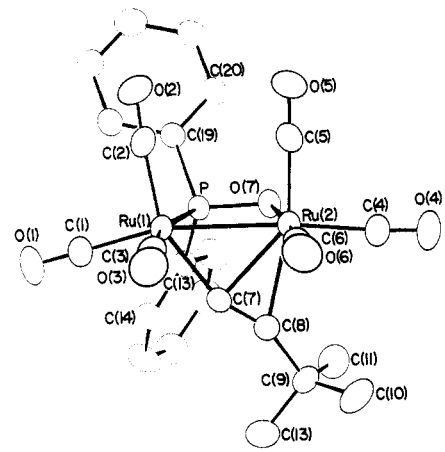

Figure 1. An ORTEP II plot of the molecular structure of $Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}(Bu)(\mu\text{-}Ph_2P{=}O)$ (**1**) showing the atomic numbering.

In a typical reaction diphenyl(*tert*-butylethynyl)phosphine oxide[5] (1.1 g, 3.9 mmol), a few drops of sodium benzophenone ketyl, and $Ru_3(CO)_{12}$ (1.5 g, 2.3 mmol) in dry degassed THF (150 mL) were refluxed for 30 h giving an orange-red solution. Solvent was removed in vacuo and the residue chromatographed on Florisil. Elution with *n*-heptane afforded unreacted $Ru_3(CO)_{12}$ (0.4 g); yellow **1** (1.3 g, 76%) was eluted with benzene.[6] The $^{31}P\{^1H\}$ NMR

(1) (a) On leave from Le Laboratoire de Chimie Organométallique, L'Université de Rennes, Campus de Beaulieu, Rennes, France. (b) We have chosen to describe these ligands simply as diorganophosphidoxo groups to emphasize the relationship to diorganophosphido complexes. Thus the diphenylphosphide anion Ph_2P^- is derived from diphenylphosphine Ph_2PH. The diphenylphosphidoxo anion $Ph_2P{=}O^-$ (oxodiphenylphosphoranide) relates to diphenylphosphine oxide $Ph_2P(O)H$ via deprotonation at phosphorus.

(2) Darensbourg, D. J.; Darensbourg, M. Y.; Walker, N. *Inorg. Chem.* **1981**, *20*, 1918.

(3) See, for example: (a) Berry, D. E.; Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R.; Pidcock, A. *Can. J. Chem.* **1986**, *64*, 343 and references therein. (b) Duncan, J. A. S.; Hedden, D.; Roundhill, D. M.; Stephenson, T. A.; Walkinshaw, M. D. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 452. (c) Burch, R. R.; Muetterties, E. L.; Thompson, M. R.; Day, V. W. *Organometallics* **1983**, *2*, 474. (d) Fernandez, J. M.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc. Dalton Trans.* **1981**, 2250. (e) Bruce, M. I.; Shaw, G.; Stone, F. G. A.; *J. Chem. Soc., Dalton Trans.* **1973**, 1667. (f) Klaui, W.; Otto, H.; Eberspach, W.; Bucholz, E. *Chem. Ber.* **1982**, *115*, 1922.

(4) A few μ-Me_2PO complexes have been synthesized via oxygen insertion into a μ-Me_2P bridge. See: Klingert, B.; Werner, H. *J. Organomet. Chem.* **1983**, *252*, C47.

(5) (a) Charrier, C.; Chodkiewicz, W.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1966**, 1002. (b) Carty, A. J.; Hota, N. K.; Ng, T. W.; Patel, H. A.; O'Connor, T. J. *Can. J. Chem.* **1971**, *49*, 2706.

(6) **1**: IR (C_6H_{12}) ν(CO) 2087 (m), 2057 (s), 2021 (s), 2012 (m), 1992 (m); IR (Nujol) ν(P=O) 980 (m) cm^{-1}; ^{31}P NMR (C_6D_6) δ +83.2; ^1H NMR ($CDCl_3$) δ 7.5–7.1 (m, 10 H), 1.2 (s, 9 H).

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