

**Supplementary Material Available:** Tables of ruthenium pyrochlore oxide synthesis and characterization and of reactor data (11 pages). Ordering information is given on any current masthead page.

## Direct Conversion of 2,3-Dihydrofurans to Silylsiloxyalkynes and Bis(silyl)ketenes

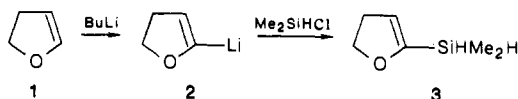
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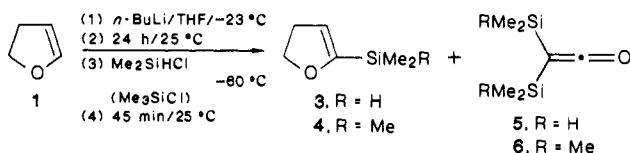
The recent independent reports by Stang<sup>1</sup> and Kowalski<sup>2</sup> on the first silylations of ynoate anions on oxygen prompt us to disclose our preliminary results on the generation and trapping of ynoate dianions directly generated from the readily available precursor, 2,3-dihydrofuran (**1**).

Metalation of 2,3-dihydrofuran (**1**) to produce  $\alpha$ -lithiodihydrofuran (**2**) is a well-established reaction, and the carbanion structure has been studied by <sup>13</sup>C NMR.<sup>3</sup> Boeckman<sup>4</sup> has used



this carbanion to react with a variety of electrophiles, while Sebastian<sup>3</sup> reports that **2** is conveniently prepared at ambient temperatures with *n*-BuLi in hexane and a catalytic amount of TMEDA. We desired a sample of 5-(dimethylsilyl)-2,3-dihydrofuran (**3**) for flash pyrolytic studies<sup>5</sup> and found that its preparation was reported by Lukevics<sup>6</sup> to be achieved in 50% yield by metalation of **1** with *n*-BuLi/THF at -30 °C and quenching with Me<sub>2</sub>HSiCl at -45 °C.

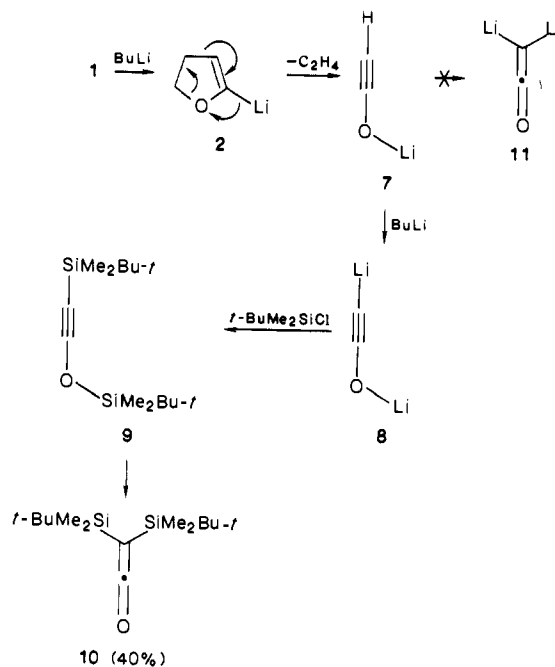
Thus, we were surprised to find that upon deprotonation of **1** with *n*-BuLi in THF (-23 °C, 24 h at 25 °C), quenching with Me<sub>2</sub>HSiCl (-60 °C, 45 min at 25 °C), and vacuum distillation, the product **3** was severely contaminated with bis(dimethyl-



silyl)ketene (**5**).<sup>7</sup> The yield of **5** was 28% or 56% based on the limiting reagent, *n*-BuLi. The same procedure, substituting Me<sub>3</sub>SiCl for Me<sub>2</sub>HSiCl, afforded bis(trimethylsilyl)ketene (**6**)<sup>7</sup> [21% (42%) yield] which was readily separable from the accompanying **4**.

A variety of experimental modifications were employed in attempts to maximize the yield of ketene from **1**. TMEDA had

## Scheme I



no effect on the ratios of ketene and dihydrofuran products, and changing the solvent to Et<sub>2</sub>O and quenching with Me<sub>3</sub>SiCl produced **only 4** (51%). Metalation with 1 equiv each of *n*-BuLi and potassium *tert*-butoxide in a solution of THF and hexane (4:3) at -23 °C produced **only 4** upon quenching with Me<sub>3</sub>SiCl at -23 °C, while allowing the reaction to warm to room temperature resulted in the destruction of even this product. Reaction of **1** with *n*-BuLi/*t*-BuOK in only hexane at -23 °C and then 1 h at 25 °C afforded, upon addition of Me<sub>3</sub>SiCl, both **4** and **6** (17% and 13%). Two equivalents of BuLi are obviously required for the production of ketenes **5** or **6**, but because BuLi will react with THF under these conditions both equivalents cannot be added simultaneously. Maximum yields to date have been obtained by reacting **1** with a single equivalent of *n*-BuLi for 24 h, addition of a second equivalent, and stirring for an additional 10 h at room temperature. Quenching this mixture with Me<sub>3</sub>SiCl produced **4** in 33% yield and **6** in 38% yield.

Formation of ketenes **5** and **6** obviously involves loss of ethylene, and this might occur by decomposition of **2** (Scheme I)<sup>9</sup> to afford lithium alkynolate **7**. Alternatively, elimination may occur from a dimetalated dihydrofuran and our data to date do not allow for other than speculation. The nature of the products make it tempting to invoke the intermediacy of dilithioacetene (**11**) which is then silylated. However, we find (following the observations of Kowalski<sup>2</sup>) that if 1 h or less after quenching with *tert*-butyldimethylsilyl chloride the reaction mixture is diluted with pentane, followed by washing with aqueous bicarbonate, IR analysis reveals **only** siloxyacetylene **9** (2185 cm<sup>-1</sup>)<sup>7</sup> and no ketene **10** (2075 cm<sup>-1</sup>).<sup>11</sup> If the reaction mixture is allowed to stand for 8 h before pentane/aqueous NaHCO<sub>3</sub> workup, the IR showed both acetylenic and ketene stretches (ca. 1:1). After 20 h, the ratio is ca. 1:3, and if the pentane/NaHCO<sub>3</sub> workup is not employed for 36 h after quenching with *t*-BuMe<sub>2</sub>SiCl, only the ketene stretch at 2075 cm<sup>-1</sup> is present. However, a dried pentane solution of the reaction products worked up with pentane/aqueous NaHCO<sub>3</sub>

(1) Stang, P. J.; Roberts, K. A. *J. Am. Chem. Soc.* **1986**, *108*, 7125.  
(2) Kowalski, C. J.; Lal, G. S.; Haque, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 7127.

(3) Oakes, F. T.; Sebastian, J. F. *J. Org. Chem.* **1980**, *45*, 4959.  
(4) Boeckman, R. K., Jr.; Bruza, K. J. *Tetrahedron Lett.* **1977**, 4187.  
(5) Barton, T. J.; Groh, B. L. *J. Am. Chem. Soc.* **1985**, *107*, 8297.  
(6) Lukevics, E.; Gevorgyan, V.; Goldberg, Y.; Popelis, J.; Gavars, M.; Gaukhman, A.; Shimanska, M. *Heterocycles* **1984**, *22*, 987.

(7) Products **3**, **5**, and **9** were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, IR, high resolution mass spectroscopy, and combustion analysis. Identification of **5** when a mixture with **3** was complicated by the accidental identity of the C=C=O and Si-H stretching frequencies of **5** and **3**, respectively, and by the unusual <sup>13</sup>C chemical shift of the sp<sup>2</sup>-hybridized carbon of **5** (δ -4.21). The unusual spectral features (IR and CMR) of silylketenes caused considerable difficulty in the earlier literature with original misassignment to the siloxyacetylene structure.<sup>8</sup>

(8) Shchukovskaya, L. L.; Kol'tsov, A. I.; Lazarev, A. N.; Pal'chik, R. I. *Dokl. Akad. Nauk SSSR* **1968**, *179*, 892.

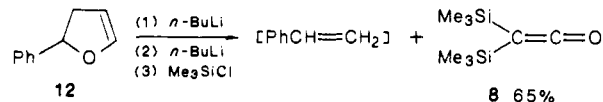
(9) There are a number of precedents for this type of decomposition in heterocyclopentadienes— isoxazoles, oxadiazoles, triazoles, tetrazoles, thia-diazoles, and selenadiazoles.<sup>10</sup>

(10) *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; 1987; Vol. 41, pp 58-64.

(11) This experiment is only sporadically successful suggesting that often we are unable to completely remove whatever is inducing the isomerization of **9** to **10**.

showed no evidence of isomerization of **9** to ketene **10** after 10 days. Thus, we conclude that the actual dianion is dilithioynolate **8** and not dilithioacetene (**11**) and that the ketene products arise from a salt-promoted isomerization rather than a purely thermal rearrangement.<sup>12,14</sup>

Since a mixture of silylated ketene (and/or siloxyacetylene) and silylated dihydrofuran (e.g., **3** and **4**) is always obtained, we modified the starting material so as to make olefin extrusion more favorable. Use of 2-phenyl-2,3-dihydrofuran (**12**)<sup>16</sup> has the ad-



vantage of styrene extrusion rather than ethylene, and indeed sequential metalation of **12** with 2 equiv of *n*-BuLi followed by quenching with Me<sub>3</sub>SiCl afforded ketene **6** in 65% yield uncontaminated by silylated dihydrofuran or styrene which is polymerized under these conditions.

**Acknowledgment.** The support of this work by the National Science Foundation is gratefully acknowledged. We thank Professor Richard C. Larock for supplying us with the procedure for the synthesis of **12** before publication.

(12) These observations call into question the sole report<sup>13</sup> of the generation of dilithioacetene (**12**).

(13) Hoppe, I.; Schöllkopf, U. *Leibigs Ann. Chem.* **1979**, 219.

(14) Theoretical calculations<sup>15</sup> place alkynols significantly higher in energy than the corresponding ketenes.

(15) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 289.

(16) Although **12** is a known compound,<sup>17</sup> we have used a convenient synthetic procedure involving the Pd(OAc)<sub>2</sub> initiated reaction of dihydrofuran and iodobenzene.<sup>18</sup>

(17) Scribe, P.; Wiemann, J. *Bull. Soc. Chim. Fr.* **1971**, 2268.

(18) Private communication from Professor Richard C. Larock, who will soon publish this procedure.

### A Trans Effect on Methyl Migration from Iridium(III) to Carbon Monoxide. The Influence of $\pi$ Acceptor Ligands on the Methyl Migration Reaction

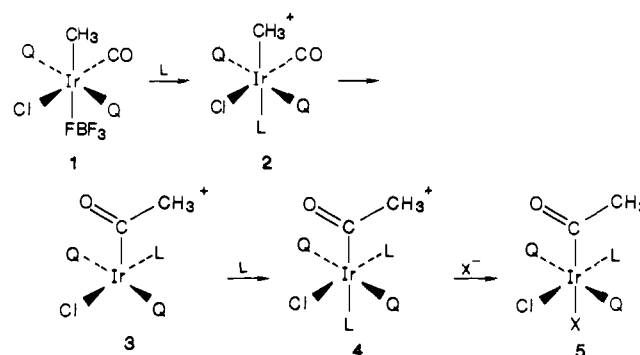
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The migratory insertion of carbon monoxide into a metal-carbon bond has been intensively studied because of its significance in metal-catalyzed processes for forming carbon-carbon bonds.<sup>1</sup> Many aspects of the migration reaction including stereochemistry at carbon and the metal,<sup>2</sup> the effects of solvents<sup>3</sup> and incoming ligands, the migratory aptitudes of the migrating group, the acceleration of the migration reaction by Lewis acids<sup>4</sup> and oxidation-reduction,<sup>5</sup> and the characterization of unsaturated inter-

Scheme I<sup>a</sup>



<sup>a</sup> Q is PPh<sub>3</sub>. L is H<sub>2</sub>O for **2A**. L is CO for **2B**, **3B**, **4B**, and **5B**. L is RNC for **2C**, **3C**, and **4C**. X is NCO for **5B-1** and NCS for **5B-2**. L is PhCN for **2D**. L is Cl<sup>-</sup> for **2E**.

mediates formed upon migration have been previously examined in great detail, but experimental studies on the influence of ligands on the primary migration step have not been reported. Berke and Hoffmann on the basis of molecular orbital calculations predicted in 1978 that  $\pi$  acceptor ligands L in the migrating plane should lower the activation energy for the primary migration step in the Mn(CO)(CH<sub>3</sub>)L system and that  $\sigma$  donor ligands should raise the activation energy,<sup>6</sup> but these predictions have not been verified. We report experiments which indicate that  $\pi$  acceptor ligands CO and isonitriles which are trans to the migrating methyl ligand do indeed promote migratory insertion and that  $\sigma$  donor ligands trans to the migrating methyl ligand do not promote migration.

Addition of (CH<sub>3</sub>)<sub>3</sub>OBF<sub>4</sub> to *trans*-[Ir(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>] gave [Ir(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl(CH<sub>3</sub>)BF<sub>4</sub>], **1** [Anal. (C<sub>38</sub>H<sub>33</sub>OP<sub>2</sub>IrClBF<sub>4</sub>) C, H, Cl; IR (cm<sup>-1</sup>, Nujol) 2067 (CO), 1060-1100 vs b (BF<sub>4</sub>)]. Compound **1** in CDCl<sub>3</sub> rapidly reacts with water to give **2A** (L = H<sub>2</sub>O) [<sup>1</sup>H NMR  $\delta$  0.82 (t, *J* = 4.7 Hz, 3 H), 4.9 (s, 2 H, H<sub>2</sub>O), 7.5-7.8 (m, 30H, 6 Ph); <sup>31</sup>P{<sup>1</sup>H} NMR  $\delta$  18.6 s; IR (cm<sup>-1</sup>, CDCl<sub>3</sub>) 2038 (CO), 1072-1110 vs b (BF<sub>4</sub>), 3532, 1616 (OH)]. The triplet at 0.82 ppm is due to the coupling of the methyl hydrogen atoms with the two phosphorus atoms which as shown by the singlet <sup>31</sup>P NMR are trans to each other, and the assignment of the resonance at 4.9 ppm to water is verified by its immediate disappearance upon the addition of D<sub>2</sub>O, CO, and isonitriles (see Scheme I). Addition of CO (30 psi) to **2A** initially gives **2B** characterized by <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.08 (t, *J* = 6.8 Hz), IR (cm<sup>-1</sup>, CDCl<sub>3</sub>) 2097, 2071(CO), and gradual formation of singlet proton resonances at 1.21 and 1.25 ppm. These singlet proton resonances along with IR absorptions at 1732 and 1629 cm<sup>-1</sup> are assigned to the acetylated species **3B** and **4B**. The neutral five coordinate phenylacetyl complex [Ir(PPh<sub>3</sub>)<sub>2</sub>(PhCH<sub>2</sub>CO)Cl<sub>2</sub>], which is analogous to **3B** in which L is Cl, has been previously reported.<sup>7</sup> The structure for **3** is likely to be square pyramidal with the acyl ligand in the apical position analogous to the structure of [Rh-(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>(PhCH<sub>2</sub>CH<sub>2</sub>CO)].<sup>8</sup> Reversible addition of CO to acylated 16-electron complexes analogous to **3** has been reported,<sup>7</sup> and the addition of anions X<sup>-</sup> = NCO<sup>-</sup> and NCS<sup>-</sup> to **4B** led to the isolation of crystalline **5B-1** and **5B-2** [Anal. (C<sub>40</sub>H<sub>33</sub>NO<sub>3</sub>-ClIrP<sub>2</sub>) C, H, N; IR (cm<sup>-1</sup>, Nujol) 2218, 1335 (NCO), 2088 vs, 2059 sh, 1610 (CO). Anal. (C<sub>40</sub>H<sub>33</sub>NO<sub>2</sub>ClIrP<sub>2</sub>S) C, H, N; IR (cm<sup>-1</sup>, Nujol) 2066 (NCS), 2028, 1612 (CO)]. Addition of <sup>13</sup>CO to **1** and CO to <sup>13</sup>CO labeled **1** established that the methyl carbon is bonded to the initially coordinated CO rather than the CO which is added.<sup>9</sup>

(6) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

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(8) Egglestone, D. L.; Baird, M. C.; Lock, J. L.; Turner, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1576.

(9) Addition of <sup>13</sup>CO to **2A** gave **3B** with  $\nu$ (CO) shifted from 2067 to 2017 cm<sup>-1</sup> and bands at 1732 and 1629 cm<sup>-1</sup> unshifted. Addition of CO to <sup>13</sup>CO labeled **1** gave a spectrum with bands at 1697 and 1598 cm<sup>-1</sup> shifted from 1733 and 1626 cm<sup>-1</sup> in the unlabeled complex.

(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books, 1987; Chapter 6. (b) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. (c) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (d) Kuhlman, E. J.; Alexander, J. *J. Coord. Chem. Rev.* **1980**, *33*, 195.

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(3) (a) Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028. (b) Webb, S. L.; Giandomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* **1986**, *108*, 345.

(4) (a) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093. Richmond, T. G.; Basolo, F.; Shriver, D. F. *Inorg. Chem.* **1982**, *21*, 1272.

(5) (a) Magnuson, R. H.; Meirowitz, R.; Zulu, S. J.; Giering, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 5790. (b) Magnuson, R. H.; Meirowitz, R.; Zulu, S. J.; Giering, W. P. *Organometallics* **1983**, *2*, 460.