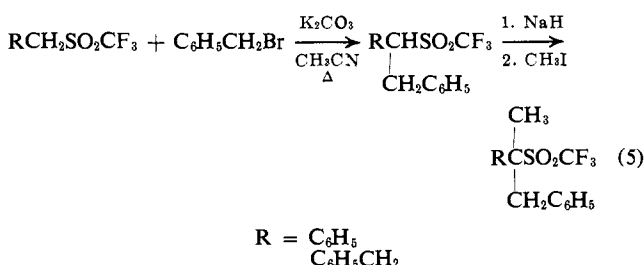
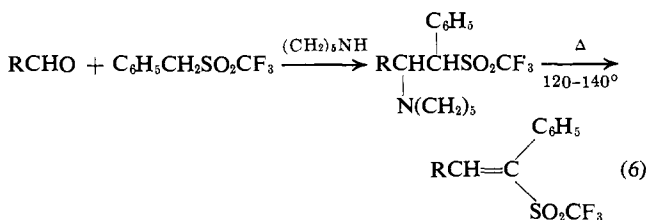


benzylic 2-benzylethylene triflone proceeded without hydrogenolysis.

**B. Triflone  $\alpha$ -Carbanions.** Simple monoalkylation of  $\alpha$ -methylene triflones (5) occurs readily with refluxing  $K_2CO_3$ - $CH_3CN$  with no evidence of dialkylation, the mild base required implying the considerable acidifying influence of the triflyl group. A second alkylation of the  $\alpha$ -methine, however, was easily achieved *via* prior carbanion formation using sodium hydride (in tetrahydrofuran); carbanion formation is rapid and alkylation proceeds at room temperature in excellent yields.<sup>7</sup>



Extended to conjugate addition, benzyl triflone yielded simple adducts with methyl vinyl ketone ( $Et_3N$ - $EtOH$ , reflux, 30 hr; 70%; bp 120–140° (0.07 mm)) or acrylonitrile ( $EtO^-$ - $EtOH$ , 25°, 2 hr; mp 49–51°), the former proceeding with ethoxide *via* internal displacement of triflate to a cyclopropyl ketone (4). At the next oxidation state, benzyl triflone undergoes the Mannich reaction with aldehydes in the presence of piperidine in refluxing benzene (6). Heating the adduct (with R =  $C_6H_5$ , or its salt with R = H) smoothly eliminated piperidine<sup>7</sup> to form the vinyl triflones (6).



R =  $C_6H_5$ : mp 108–112° (75%) mp 100–101° (80%)  
R = H: mp 64–65° (65%) bp 130° (20 mm)(100%)

**C. Additions to Vinyl Triflones.** Piperidine adds smoothly to  $PhCH_2CH=CHSO_2CF_3$ , but reactive anions (cyanide, malonate) create more complex products, presumably through formation of the stabilized triflone carbanion. 1,2-Diphenylethylene triflone, however, adds butyllithium instantly to form 1,2-diphenylhexyl triflone and reacts with cyanide (12 hr, 40° in ethanol-water-ether with ammonium chloride) *via* addition and triflate elimination to cyanodiphenylethylene<sup>9</sup> in 75% yield.  $\alpha$ -Styryl triflone (see (6), R = H) reacted quickly in ethanol with diethyl malonate and triethylamine to form a 1:2 molar mixture of mono- and dialkylated malonates in 88% overall yield; the dialkylated product was  $(C_6H_5CH(SO_2CF_3)CH_2)_2C(COOC_2H_5)_2$ , isolated crystalline, mp 134–135°. The mixture proceeded to cyclize as in (4) on long refluxing in the same medium to the known cyclopropane diester.<sup>11</sup>

Finally, the vinyl triflone (6, R = H) acted as a facile dienophile with butadiene; after several days at room temperature the elimination product of the adduct, 1-

(11) J. Gosselck, H. Ahlbrecht, F. Dost, H. Schenk, and G. Schmidt, *Tetrahedron Lett.*, 995 (1968).

phenyl-1,3-cyclohexadiene, mp 83–85°,  $\lambda_{max}$  248 nm ( $\epsilon$  8200) (lit.<sup>12</sup> 85°, 248 nm ( $\epsilon$  9000)) was isolated in 75% yield. An adduct retaining the triflyl group was similarly obtained with cyclopentadiene.

Further exploration of these triflones as versatile synthetic tools is under active study, but it is already clear that their 1,2- and 1,3-eliminations are significantly more facile than those of other sulfones<sup>13–15</sup> and their ease of alkylation with mild bases offers considerable synthetic advantage.

(12) G. F. Woods, N. C. Bolgiano, and D. E. Duggan, *J. Amer. Chem. Soc.*, 77, 1800 (1955).

(13) Thermal elimination of other sulfones is uncommon while 1,3-elimination of toluene sulfinate requires much more active base (*tert*-butoxide in dimethylformamide).<sup>14,15</sup>

(14) W. L. Parker and R. B. Woodward, *J. Org. Chem.*, 34, 3085 (1969).

(15) R. V. M. Campbell, L. Crombie, and G. Pattenden, *Chem. Commun.*, 218 (1971).

James B. Hendrickson,\* Aziz Giga, James Wareing

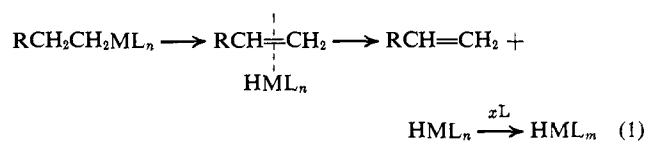
Edison Chemical Laboratory, Brandeis University  
Waltham, Massachusetts 02154

Received September 24, 1973

### Thermal Decomposition of Bis(triphenylphosphine)-(carbonyl)octyliridium(I). A New Decomposition Mechanism for Transition Metal Long Chain Alkyls

Sir:

Transition metal alkyls are of widespread use both as reagents and as unisolable intermediates in organic synthesis. The mechanism of thermal decomposition of transition metal alkyls has been extensively studied because of the insights afforded by such investigations into the electronic structure of these complexes and into reactivity patterns available to them.<sup>1–10</sup> Significant among the observations thus far reported is that  $\beta$ -elimination of metal hydride constitutes the lowest energy decomposition pathway for coordinatively unsaturated long chain alkyl metal complexes (reaction 1).<sup>1–3</sup> Degradation through intramolecular oxidative



addition of a C–H bond of a coordinated ligand followed by reductive elimination of alkane is common when  $\beta$ -hydride elimination is either impossible (no  $\beta$ -

(1) G. M. Whitesides, J. San Filippo, Jr., E. R. Stedronsky, and C. P. Casey, *J. Amer. Chem. Soc.*, 91, 6542 (1969); 92, 1426 (1970), and references cited therein.

(2) (a) G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 94, 5258 (1972); (b) J. X. McDermott, J. F. White, and G. M. Whitesides, *ibid.*, 95, 4452 (1973).

(3) G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. A*, 1392 (1970).

(4) J. Schwartz and J. B. Cannon, *J. Amer. Chem. Soc.*, 94, 6226 (1972).

(5) G. M. Whitesides and W. J. Ehmann, *J. Amer. Chem. Soc.*, 92, 5625 (1970); W. Keim, *J. Organometal. Chem.*, 14, 179 (1968).

(6) G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Amer. Chem. Soc.*, 91, 4990 (1969).

(7) G. W. Parshall, *Accounts Chem. Res.*, 3, 139 (1970).

(8) G. M. Whitesides, E. J. Panek, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 94, 232 (1972).

(9) G. Wilkinson, *et al.*, *J. Chem. Soc., Dalton Trans.*, 533 (1972); P. S. Braterman and R. J. Cross, *ibid.*, 657 (1972).

(10) B. K. Bower and H. G. Tennent, *J. Amer. Chem. Soc.*, 94, 2512 (1972).

hydrogen is present)<sup>4,5</sup> or when rapid readdition of the metal hydride occurs to regenerate the long chain alkyl.<sup>6,7</sup> Indeed, for complexes in which decomposition by either  $\beta$ -hydride elimination or oxidative addition does not readily occur, remarkable thermal stability toward homolysis (the other recognized major pathway for thermal decomposition) is often exhibited.<sup>8-10</sup> Noteworthy among these observations, too, is that ready formation of alkane occurs by coupling of alkyl and hydride ligands when these ligands are coordinated either to a single metal center of monomeric species<sup>2</sup> or to the surface of postulated metal clusters (e.g.,  $(\text{RCu} \leftarrow \text{PBU}_3)_n$ )<sup>1</sup> in compounds where clustering of analogs (e.g.,  $(\text{ICu} \leftarrow \text{PBU}_3)_4$ ) is directly observable.

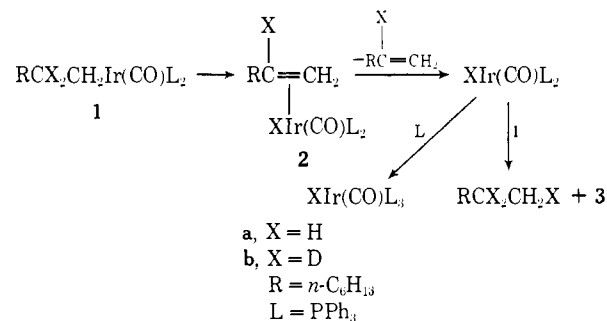
We have studied the thermal decomposition of bis(triphenylphosphine)(carbonyl)octyliridium(I) (**1**) and have observed that octene is the predominant organic product.  $\text{HIr}(\text{CO})\text{L}_3$  is also obtained. Surprisingly, octane is also produced in substantial amounts which depend on the concentration of triphenylphosphine (L) added initially to the reaction mixture.

In typical experiments, **1** was prepared<sup>4</sup> *in situ* from 0.10 mmol of *trans*- $\text{L}_2\text{Ir}(\text{CO})\text{Cl}$  and excess octyllithium at 0° in ether containing 0.14 mmol of dioxane and varying amounts of other reagents as described below. Aliquots were quenched with 1,2-dibromoethane and were analyzed by gas chromatography<sup>11</sup> for octane and octene-1 produced from **1**. In each case, the light yellow suspension of *trans*- $\text{L}_2\text{Ir}(\text{CO})\text{Cl}$  rapidly dissolved when the lithium reagent was added to give a deep yellow solution. The color of this solution slowly became more orange as the generated octyliridium(I) species decomposed. That both octane and octene-1 arise from the same iridium species was demonstrated by the observation that production of both compounds occurred simultaneously, only. Several possible sources of the observed octane can be ruled out immediately. (1) Octane is not produced by reaction of octyllithium with **1**. The relative rate of formation of octane and octene-1 was independent of the concentration of octyllithium. (2) Octane does not result from reductive elimination of the alkane from a hydrido-octyliridium(III) species generated by intramolecular oxidative addition<sup>4,5</sup> to octyliridium(I) of an ortho C-H bond of coordinated L. No octane-*d*<sub>1</sub> was produced<sup>12</sup> when triphenylphosphine-*d*<sub>15</sub> was used throughout in the above described sequence. (3) Octane is not formed by reaction of octyllithium and  $\text{HIr}(\text{CO})\text{L}_3$  (see eq 1). This can be observed directly. (4) Octane is not generated by reaction of **1** and the coordinatively saturated species  $\text{HIr}(\text{CO})\text{L}_3$ . Addition of 3.0 equiv of  $\text{HIr}(\text{CO})\text{L}_3$  to the reaction mixture does not affect the rate of octane formation, and no octane-*d*<sub>1</sub> is formed when 2.6 equiv of  $\text{DIr}(\text{CO})\text{L}_3$  is present in the reaction mixture.

The octane produced by decomposition of  $\beta,\beta$ -deuterio species **1b** in ether is approximately 95% octane-*d*<sub>3</sub>. Thus, the  $\beta$ -hydrogen atom from one octyl group appears in the octane which results from another.<sup>13</sup> Furthermore, the octene-1 produced in this

experiment is approximately 95% octene-1-*d*<sub>1</sub>. No octene-1-*d*<sub>2</sub> was detected. In no case was octene-2 observed.<sup>11</sup> These observations suggest that, under the reaction conditions, formation of olefin by  $\beta$ -hydride elimination is either irreversible or proceeds to yield overwhelmingly the *n*-alkyl species.<sup>14</sup>

The relative yields of octane and octene-1 produced from **1** are strongly dependent on the concentration of added L. With 15 equiv of added L, 7% octane and 93% octene-1 are formed. In the presence of 1.5 equiv and no added L, the yield of octane rises to 28 and 32%, respectively, with concomitant decrease in the yield of octene-1. We propose that a bimolecular reaction between **1** and coordinatively unsaturated  $\text{HIr}(\text{CO})\text{L}_2$  occurs to yield octane and diiridium(0) species **3**<sup>15</sup> as shown in reaction 2. Further substantiation of the bimolecular pathway lies in the observation that reaction of  $(\sigma\text{-C}_6\text{H}_5)\text{Ir}(\text{CO})\text{L}_2$  with **1b** yields  $\text{C}_6\text{H}_5\text{D}$  as well as octene-1-*d*<sub>1</sub> and octane-*d*<sub>3</sub>.



The existence of  $\text{HIr}(\text{CO})\text{L}_2$  as an isolable intermediate has been implicated in hydrogenation<sup>17</sup> and oxidative addition<sup>18</sup> reactions in which it is produced by slow<sup>19</sup> dissociation of L from  $\text{HIr}(\text{CO})\text{L}_3$ . The equilibrium constant for this dissociation has been shown to be small.<sup>17</sup> Our observation of the lack of deuterium incorporation into octane produced from **1** in the presence of added  $\text{DIr}(\text{CO})\text{L}_3$  is consistent with these observations.

That a bimolecular reaction can occur between **1** and  $\text{HIr}(\text{CO})\text{L}_2$  but not  $\text{HIr}(\text{CO})\text{L}_3$  is understandable in

(13) This shows that octane does not arise from **1** *via* octyl radicals which would react with solvent to yield octane-*d*<sub>2</sub>.

(14) This result is in contrast to that reported<sup>2a</sup> for the decomposition of alkylplatinum(II) species in which rapid, reversible Pt-H insertion into coordinated terminal olefin produced large amounts of both internal and terminal alkyl Pt(II) species but from which only terminal olefin was eventually ejected. Were Ir-H insertion to occur to yield mixtures of internal and terminal alkyl, subsequent  $\beta$ -elimination, if only of terminal olefin, would have yielded octene-1-*d*<sub>1</sub> and octene-1-*d*<sub>2</sub>.

(15) In the presence of no added L, a yield of 50% octane and 50% octene-1 is expected on the basis of the scheme shown in eq 2. In addition to the observation of a lower yield of octane than that expected when no L was added,  $\text{HIr}(\text{CO})\text{L}_3$  was also produced. Analysis of the reaction mixture at completion revealed the presence of uncoordinated triphenylphosphine. We have been unable to purify **3**, the iridium-containing product of octane formation. Such attempts result only in decomposition of this orange material with liberation of triphenylphosphine. Thus it seems reasonable to assert that, even though L may not be added intentionally, free L is always present due to decomposition of **3**. Based on the observation that **3** reacts with H<sub>2</sub> at low pressure to form  $\text{H}_2\text{Ir}(\text{CO})\text{L}_2$  and in analogy with the reported dimerization<sup>16</sup> of  $\text{HRh}(\text{CO})\text{L}_2$  with loss of H<sub>2</sub> and 2CO, we postulate that the composition of **3** is  $\text{Ir}_2(\text{CO})_2\text{L}_4$ .

(16) D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. A*, 2660 (1968).

(17) M. G. Burnett and R. J. Morrison, *J. Chem. Soc., Dalton Trans.*, 2325 (1971).

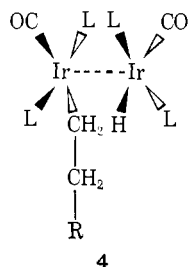
(18) J. F. Harrod, C. A. Smith, and K. A. Than, *J. Amer. Chem. Soc.*, 94, 8321 (1972).

(19) D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 3133 (1968).

(11) Determinations were made using a Hewlett-Packard 402 gas chromatograph equipped with a 6 ft  $\times$  1/4 in. column packed with 5% Carbowax 20M on 60/80 Chromosorb P.

(12) Isotopic ratios were determined both on isolated compounds (MS-9) and on unisolated species using a Du Pont 21-490 mass spectrometer gas chromatography assembly.

terms of the coordinative unsaturation of  $\text{HIr}(\text{CO})\text{L}_2$ . This species, postulated to be generated *in situ*, would be expected to rapidly coordinate a fifth ligand (*e.g.*, L), and the bimolecular reaction discussed can be envisioned as one in which, initially, a metal-metal bond forms by coordination of nucleophilic species 1 to the unsaturated hydride. Such an interaction leads to short-lived intermediate 4, a species whose structure is



reminiscent of  $d^8$  stacked Ir(I) complexes which have been observed crystallographically.<sup>20</sup> Loss of octane from this aggregate might be accomplished through intermediacy of bridging hydride and/or alkyl ligands.<sup>21</sup>

**Acknowledgment.** The authors gratefully acknowledge support for this work given by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the Research Corporation. They also thank Professor Jack R. Norton and Dr. Jay A. Labinger for helpful comments and suggestions.

(20) L. V. Interrante and F. P. Bundy, *Chem. Commun.*, 584 (1970).

(21) Such a process has recently been suggested: P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, 2, 271 (1973).

Jeffrey Schwartz,\* John B. Cannon

Department of Chemistry, Princeton University  
Princeton, New Jersey 08540

Received December 4, 1973

### Evidence for the Generation of Silicon-Silicon, Silicon-Oxygen, and Silicon-Carbon Double Bonds in a Single Reaction

Sir:

Evidence consistent with the transient existence of molecules containing (p-p) $\pi$  bonded silicon<sup>1-3</sup> and germanium<sup>4,2d</sup> has accumulated in the last few years to a degree that little doubt remains, although the nature of bonding (*e.g.*, diradical character) remains in question. We wish to report a novel reaction which can

(1)  $\text{Si}=\text{Si}$ : D. N. Roark and G. J. D. Peddle, *J. Amer. Chem. Soc.*, **94**, 5837 (1972).

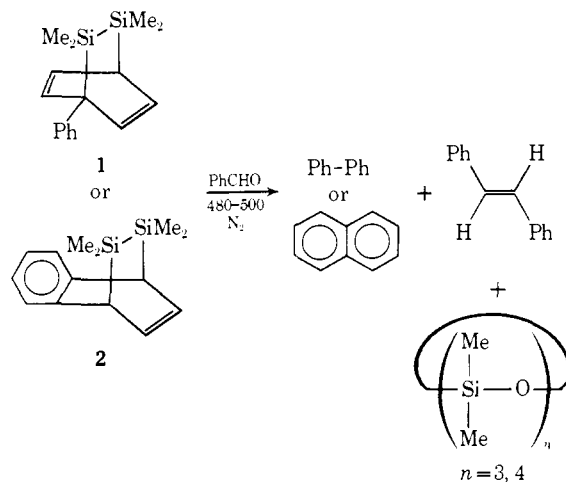
(2)  $\text{Si}=\text{O}$ : (a) L. E. Gusel'nikov, *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 6, 84 (1971); (b) I. M. T. Davidson and J. F. Thompson, *Chem. Commun.*, 251 (1971); (c) T. J. Barton, C. L. McIntosh, and E. A. Kline, 3rd International Symposium on Organosilicon Chemistry, Madison, Wis., Aug 1972; (d) T. J. Barton, E. A. Kline, and P. M. Garvey, *J. Amer. Chem. Soc.*, **95**, 3078 (1973); (e) P. Boudjouk and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, 54 (1973); (f) D. N. Roark and L. H. Sommer, *ibid.*, 167 (1973).

(3)  $\text{Si}=\text{C}$ : (a) N. S. Nametkin, V. M. Vdovin, L. E. Gusel'nikov, and V. I. Zavyalov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 3, 534 (1966); (b) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968); (c) R. P. Clifford, B. G. Gowenlock, C. A. F. Johnson, and J. Stevenson, *J. Organometal. Chem.*, **34**, 53 (1972); (d) I. M. T. Davidson and C. A. Lambert, *J. Chem. Soc. A*, 882 (1971); (e) T. J. Barton and C. L. McIntosh, *J. Chem. Soc., Chem. Commun.*, 861 (1972); (f) T. J. Barton and E. A. Kline, *J. Organometal. Chem.*, **42**, C21 (1972); (g) P. Boudjouk, J. R. Roberts, C. M. Golino, and L. H. Sommer, *J. Amer. Chem. Soc.*, **94**, 7926 (1972); (h) ref 2c; (i) ref 2f.

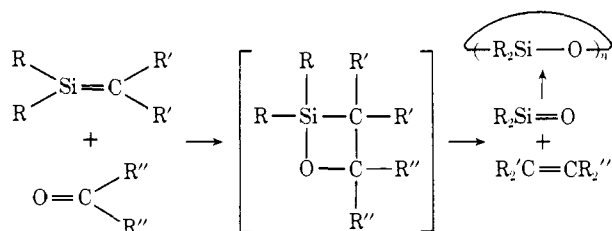
(4) M. D. Curtis, *J. Amer. Chem. Soc.*, **91**, 6011 (1969).

best be explained by invoking the intermediacy of compounds containing the silicon-silicon, silicon-oxygen, and silicon-carbon double bonds, respectively.

Roark and Peddle<sup>1</sup> have reported strong evidence that 7,8-disilabicyclo[2.2.2]octa-2,5-dienes thermally aromatize through extrusion of a disilene ( $\text{R}_2\text{Si}=\text{SiR}_2$ ). We find that copyrolysis of either 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene<sup>1</sup> (1) or 5,6-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (2) and an excess (20:1) of benzaldehyde in a flow system ( $\text{N}_2$ , 480-500°) affords the expected biphenyl or naphthalene together with *trans*-stilbene (23.9%)<sup>5</sup> and a mixture of hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane (16 and 13.8%, respectively).<sup>5</sup>



The recent demonstration<sup>2e-f</sup> that silaalkenes ( $\text{R}_2\text{Si}=\text{CR}_2'$ ) undergo cycloaddition to the carbonyl group to produce an unstable silaoxetane which thermally decomposes to an olefin and a silanone ( $\text{R}_2\text{Si}=\text{O}$ ) which undergoes cyclic oligomerization is crucial in understanding the reaction of 1 or 2 with benzaldehyde.



In view of this sequence we propose a mechanism (Scheme I) where initially formed tetramethyldisilene (3) adds to benzaldehyde to form an intermediate disilaoxetane (4). Thermal cleavage of 4 generates both a silanone (5) and a silaalkene, 1-phenyl-2-methyl-2-silapropene (6). Oligomerization of 5 leads to the observed mixture of cyclotrisiloxanes while 6 can react further with benzaldehyde to form silaoxetane, 7. Finally, extrusion of a second molecule of 5 from 7 affords *trans*-stilbene.

It is difficult to exclude the possibility that *trans*-stilbene arises from dimerization of phenylcarbene (8). Indeed a reasonable route can be written by assuming stepwise attack by 3 on carbonyl followed by extrusion of 8. The cyclotrisiloxanes could again be formed

(5) Positive identification of products was made by spectral comparison with authentic samples. Yields are taken from calibrated gc traces.