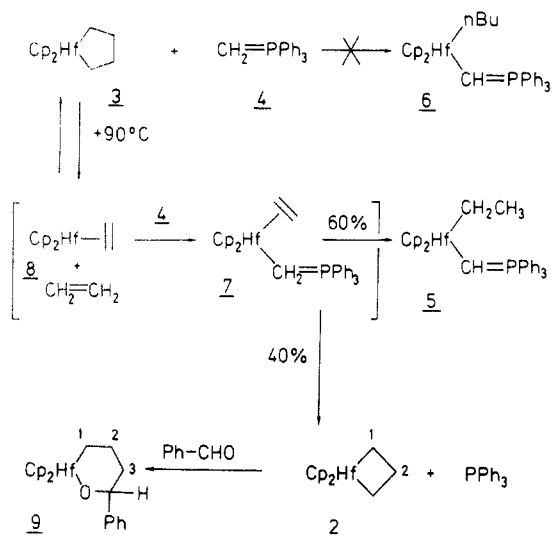


Scheme I



halides with a large excess of  $\text{CH}_2=\text{PPh}_3$ . In this reaction the ylide serves as both a nucleophile and a base in subsequent second-order reaction steps.<sup>8</sup> The complete absence of the *n*-butylhafnocene ylide **6** shows that the metallocene ylide formation from **3** and  $\text{CH}_2=\text{PPh}_3$  represents a fundamentally different reaction type. Intramolecular hydrogen transfer from the ylide carbon to a coordinated olefinic ligand in the intermediate  $\text{Cp}_2\text{Hf}(\text{CH}_2=\text{CH}_2)(\text{CH}_2=\text{PPh}_3)$  (**7**) accounts for the formation of the ethylhafnocene ylide **5**.<sup>9</sup>

A competing reaction path (40%), probably through the same intermediate **7**, leads to the formation of a 1:1 mixture of triphenylphosphine and bis(cyclopentadienyl)-hafnacyclobutane (**2**), the product of a methylene transfer reaction from methylene triphenylphosphorane to the 16-electron  $d^2$  species ethylhafnocene (**8**). Like **5**, the metallacyclobutane **2** has been isolated from the reaction mixture by fractional crystallization. It has been characterized spectroscopically, by elemental analysis, and chemical reactions.<sup>10</sup> **2** exhibits NMR spectra consistent with a planar metallacyclic ring system.<sup>11</sup> Observed coupling constants (Hz) are as follows:  $^2J(\text{H}, \text{H}) = -10.8$  (H1, H1'),  $-10.7$  (H2, H2');  $^3J(\text{H}, \text{H}) = 5.2$  (H1, H2, "cis"),  $12.4$  (H1, H2', "trans");  $^1J(\text{C}, \text{H}) = 134$  (C1, H1),  $138$  (C2, H2).

**2** turns out to be completely stable at room temperature in the absence of air and moisture. It has even remained unaffected by thermolysis in the presence of di-

phenylacetylene to  $150^\circ\text{C}$  for a period of 4 h. Treatment with bromine (stoichiometric) yields  $\text{Cp}_2\text{HfBr}_2$  and 1,3-dibromopropane. With equimolar amounts of benzaldehyde **2** reacts at ambient temperature to give a single organometallic product **9**,<sup>12</sup> which is formed by a formal insertion of the organic carbonyl compound into the hafnium-carbon  $\sigma$ -bond of **2**. We have not obtained any experimental evidence for a retro [2 + 2] cleavage of the hafnacyclobutane.<sup>13</sup>

Finally, let us speculate about the scope of this new metallacyclobutane formation. It is clear that an increasing metal-alkylidene character in the metal ylide linkage in the intermediate **7** should favor the formation of the four-membered ring system at the expense of the hydrogen transfer reaction leading to the metal ylide **5**. Therefore, we expect metallacyclobutane formation according to Scheme I to become increasingly important on going from hafnium to titanium.<sup>11</sup> Equally, sufficiently reactive mono(olefin) complexes of the later transition elements, which tend to form more stable carbene complexes than the group 4<sup>14</sup> metals, should be good candidates to undergo four-membered ring formation upon treatment with an alkylidene ylide.

**Acknowledgment.** Financial aid from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Max-Planck-Gesellschaft is gratefully acknowledged. We thank Drs. R. Benn and R. Mynott and their co-workers for the NMR spectra.

**Registry No.** **2**, 98395-20-1; **3**, 83719-75-9; **4**, 3487-44-3; **5**, 98395-19-8; **9**, 98395-21-2;  $\text{Cp}_2\text{HfBr}_2$ , 37260-83-6; Ph-CHO, 100-52-7; 1,3-dibromopropane, 109-64-8.

**Supplementary Material Available:** Tables of atomic coordinates and thermal parameters and a table of selected interatomic distances and angles, as well as a list of observed and calculated structure factors for **5** (20 pages). Ordering information is given on any current masthead page.

(12)  $^1\text{H}$  NMR of **9** (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  5.71, 5.80 (s, each 5 H, Cp), 4.81 (dd,  $^3J_{\text{aa}} = 11.1$  Hz,  $^3J_{\text{ae}} = 2.6$  Hz, 1 H, H4), 0.96 (m,  $^2J_{\text{H}_3\text{H}_3'} = -13.7$  Hz,  $^3J_{\text{aa}} = 12.8$  Hz,  $^3J_{\text{ae}} = 2.3$  Hz, 1 H, H3'), 1.90 (m,  $^3J_{\text{ee}} = 4.7$  Hz,  $^3J_{\text{ae}} = 1.9$  Hz, 1 H, H3), 2.80 (m,  $^2J_{\text{H}_2\text{H}_2'} = -14.0$  Hz,  $^3J_{\text{ae}} = 3.9$  Hz,  $^3J_{\text{ee}} = 6.1$  Hz, 1 H, H2'), 1.52 (m,  $^3J_{\text{aa}} = 13.5$  Hz,  $^3J_{\text{ae}} = 2.3$  Hz, 1 H, H2), 1.39 (m,  $^2J_{\text{H}_1\text{H}_1'} = -13.3$  Hz, 1 H, H1'), 0.83 (m, H1); Ph,  $\delta$  7.37 (ortho-CH), 7.30 (meta-CH), 7.05 (para-CH) (a = axial; e = equatorial).

(13) For an analogous behavior of a four-membered metallacyclic zirconium complex, see: Tikkanen, W. R.; Petersen, J. L. *Organometallics* 1984, 3, 1651.

(14) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III  $\rightarrow$  3 and 13.)

(8) Baldwin, J. C.; Keder, N. L.; Strouse, C. F.; Kaska, W. C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1980, 35B, 1289.

(9) The reactions of  $\text{CH}_2=\text{PPh}_3$  with (dihydrobenzene) $\text{ZrCp}_2$  or (butadiene) $\text{ZrCp}_2$ , respectively, may represent further examples of this reaction type: Erker, G.; Czisch, P.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Organometallics* 1985, 4, 1310.

(10) After separation of **5** from the reaction mixture (see ref 6a) hafnacyclobutane **2** was obtained free of  $\text{PPh}_3$  by a second extraction with pentane. After removal of the solvent, 10–15 mL of pentane was added and a colorless precipitate of pure **2** was obtained (510 mg, 20%; mp  $105^\circ\text{C}$  dec). As this procedure turned out to be difficult to reproduce, mixtures of **2** with  $\text{PPh}_3$  were used for chemical reactions:  $^1\text{H}$  NMR (400 MHz,  $\text{C}_7\text{D}_8$ )  $\delta$  5.34 (s, 10 H Cp), 1.89 (m, 4 H,  $\alpha\text{-CH}_2$ ),  $-0.05$  (m, 2 H,  $\beta\text{-CH}_2$ );  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  107.4 (Cp), 56.0 ( $\alpha\text{-CH}_2$ ),  $-10.3$  ( $\beta\text{-CH}_2$ ); MS,  $m/e$  352 ( $\text{M}^+$ ), 325 ( $\text{M}^+ - \text{C}_2\text{H}_4$ ), 324 ( $\text{M}^+ - \text{C}_2\text{H}_2$ ), 310 ( $\text{M}^+ - \text{C}_3\text{H}_6$ ). Anal. Calcd for  $\text{C}_{15}\text{H}_{16}\text{Hf}$ : C, 44.52; H, 4.60. Found: C, 44.84; H, 4.14.

(11) Planar structures seem to be favored for the group 4 metallacyclobutanes; for experimental evidence, see: Lee, J. B.; Gajda, G. L.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* 1981, 103, 7358. Tikkanen, W. R.; Egan, J. W., Jr.; Petersen, J. L. *Organometallics* 1984, 3, 1646. See also ref. 4b); for a theoretical treatment see: Rappé, A. K.; Goddard III, W. A. *J. Am. Chem. Soc.* 1982, 104, 297.



## The Kinetics of Some Gas-Phase Reactions of Dimethylsilanone

Iain M. T. Davidson\* and Andrew Fenton  
Department of Chemistry, The University  
Leicester LE1 7RH, Great Britain

Received July 23, 1985

**Summary:** The first results of a study of the reactions of dimethylsilanone with various substrates are reported, including some kinetic measurements. Comparisons are drawn with analogous reactions of dimethylsilene, and it is suggested that some reactions of both intermediates proceed stepwise, by addition followed by 1,3-silyl shifts.

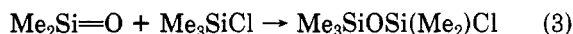
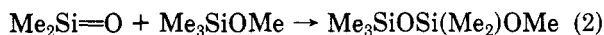
Table I. Reactions of Dimethylsilanone with Substrates

substr	product	reacting bond	Me <sub>2</sub> Si=CH <sub>2</sub> reacts with substr
HCl	HOSi(Me <sub>2</sub> )Cl	H—Cl	yes
H <sub>2</sub> O	Me <sub>2</sub> Si(OH) <sub>2</sub>	O—H	yes
MeOH	MeOSi(Me <sub>2</sub> )OH	O—H	yes
Me <sub>3</sub> SiOMe	Me <sub>3</sub> SiOSi(Me <sub>2</sub> )OMe	Si—O	yes
Me <sub>3</sub> SiCl	Me <sub>3</sub> SiOSi(Me <sub>2</sub> )Cl	Si—Cl	no
Me <sub>2</sub> C=O	1:1 adduct <sup>a</sup>	C=O?	yes
MeCHO	1:1 adduct <sup>a</sup>	C=O?	yes
Et <sub>2</sub> O	none obsd		no
CH <sub>2</sub> Cl <sub>2</sub>	none obsd		no
Me <sub>3</sub> SiH	none obsd		no
	none obsd		yes
	none obsd		yes

<sup>a</sup> Adduct decomposes slowly at 440 °C.

Although we have long been interested in the kinetics of reactions involving silanones,<sup>1-3</sup> progress has been hampered by the lack of suitable silanone sources. We recently demonstrated by kinetic studies<sup>4</sup> that 6-oxa-3-dimethylsilabicyclo[3.1.0]hexane (1) is a convenient new thermal source of dimethylsilanone, Me<sub>2</sub>Si=O (2). We now report the results of some kinetic and other experiments on the reactions of dimethylsilanone, 2 (generated from 1), with several substrates. We know of no other published kinetic data for reactions of dimethylsilanone, although there are some for a few reactions of the related intermediate dimethylsilene, Me<sub>2</sub>Si=CH<sub>2</sub> (3).<sup>5-7</sup> Interpretation of our results is greatly assisted by recent theoretical studies<sup>8,9</sup> on silanone, H<sub>2</sub>Si=O.

A general impression of the reactivity of 2 was obtained by pyrolyzing 1 at ca. 440 °C in our low-pressure pyrolysis apparatus in the presence of a number of substrates. The results are in Table I, which also shows whether or not a similar reaction occurs with the silene 3. In every experiment involving 2, irrespective of whether it reacted with the substrate or not, substantial quantities of D<sub>3</sub> and D<sub>4</sub> (the cyclic trimers and tetramers of 2) were formed. Comparative kinetic data were obtained from competitive experiments with pairs of reactions 1-3. When 1 was



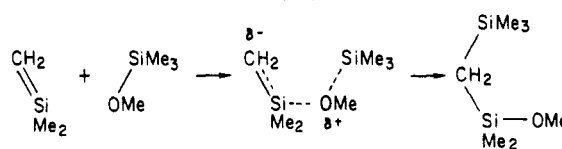
pyrolyzed between 400 and 475 °C in the presence of methanol and methoxytrimethylsilane, measurement of the yields of the products of reactions 1 and 2 gave

$$\log (A_2/A_1) = 1.8 \pm 0.5$$

$$(E_2 - E_1) = 32 \pm 7 \text{ kJ mol}^{-1}$$

- (1) Davidson, I. M. T.; Thompson, J. F. *J. Chem. Soc. D* **1971**, 251.  
 (2) Davidson, I. M. T.; Thompson, J. F. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 972.  
 (3) Davidson, I. M. T.; Thompson, J. F. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1088.  
 (4) Davidson, I. M. T.; Fenton, A.; Manuel, G.; Bertrand, G. *Organometallics* **1985**, *4*, 1324.  
 (5) Davidson, I. M. T.; Dean, C. E.; Lawrence, F. T. *J. Chem. Soc. D* **1981**, 52.  
 (6) Davidson, I. M. T.; Wood, I. T. *J. Chem. Soc. D* **1982**, 550.  
 (7) Gowenlock, B. G.; Groome, P.; John, P., reported at 7th International Symposium on Gas Kinetics, Gottingen, F.R.G., 1982.  
 (8) Kudo, T.; Nagase, S. *J. Phys. Chem.* **1984**, *88*, 2833.  
 (9) Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589.

Scheme I



Likewise,  $\log (A_3/A_2) = 0.2 \pm 0.2$  and  $(E_3 - E_2) = 22 \pm 3 \text{ kJ mol}^{-1}$ .

We have measured previously<sup>10</sup> the rate of reaction 2 relative to the formation of D<sub>3</sub>. As the mechanism of the latter reaction is unknown, the only meaningful parameter is the activation energy difference between reaction 2 and the formation of D<sub>3</sub>, viz.,  $31 \pm 5 \text{ kJ mol}^{-1}$ . The corresponding reaction of the silene 3 with methoxytrimethylsilane had an activation energy of only  $6.3 \pm 3 \text{ kJ mol}^{-1}$  relative to the dimerization of 3, which is believed to require no activation energy.<sup>6,11</sup>

Calculations on the parent silanone, H<sub>2</sub>Si=O, showed it to be unimolecularly stable. On the other hand, reaction with water was calculated to proceed by a four-center transition state with no overall energy barrier.<sup>8</sup> Formation of the cyclic dimer of H<sub>2</sub>Si=O was also calculated to require no energy barrier, but in this case the reaction was stepwise. The first step was head-to-tail addition of one highly polar silanone molecule to another, followed by ring closure. Potential energy steadily decreased along the reaction path, with no intermediate minima. The resulting ring was calculated to be highly strained, higher cyclic homologues being more stable, probably also with no barrier to cyclization.<sup>9</sup> In keeping with these calculations, the only cyclic dimer of a silanone yet reported is heavily substituted,<sup>12</sup> while cyclization of 2 leads to D<sub>3</sub> and D<sub>4</sub>, not D<sub>2</sub>.

We therefore offer the following tentative explanations for the results in Table I.

(i) The silene 3 may undergo (4 + 2) cycloaddition with dienes more readily than does the silanone 2 simply because the latter is so much more polar.<sup>8</sup>

(ii) By analogy with the reaction of H<sub>2</sub>Si=O with water,<sup>8</sup> the rapid reactions of 2 with water, hydrogen chloride, and methanol probably all proceed by a four-center process.

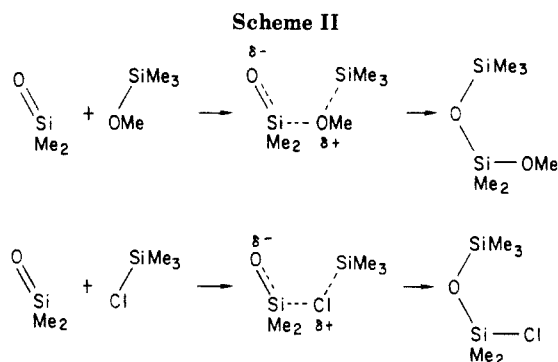
(iii) Reaction of 2 with methoxytrimethylsilane has an activation energy  $32 \pm 7 \text{ kJ mol}^{-1}$  higher than the activation energy for reaction of 2 with methanol and  $31 \pm 5 \text{ kJ mol}^{-1}$  higher than formation of D<sub>3</sub> from 2. Both of the last two reactions may therefore have zero activation energy, as might be expected theoretically.<sup>8,9</sup> If so,  $E_2 = 32$  and  $E_3 = 54 \text{ kJ mol}^{-1}$ .

(iv) The silanone 2, being considerably more polar than the silene 3, undergoes very rapid reactions with small polar molecules and with itself. It reacts with trimethylchlorosilane while 3 does not, but the latter only requires an activation energy of  $6.3 \text{ kJ mol}^{-1}$  to react with methoxytrimethylsilane, whereas  $E_2$  is at least  $32 \text{ kJ mol}^{-1}$ . This apparently paradoxical result may signal a change from a four-center to a stepwise mechanism,<sup>9</sup> with addition of a nucleophilic center to the silicon of the silene or silanone being followed by a 1,3-silyl shift to form the observed product. The reaction of 3 with methoxytrimethylsilane would then proceed as shown in Scheme I. In contrast to alkyl groups or hydrogen atoms, silyl groups undergo 1,3-shifts, generally by internal nucleophilic attack

(10) Recalculated from: Wood, I. T. Ph.D. Thesis, Leicester, 1983.

(11) Gusev, L. E.; Konobeyevski, K. S.; Vdovin, V. M.; Nametkin, N. S. *Dokl. Akad. Nauk SSSR* **1977**, *235*, 1086.

(12) Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 822.



at silicon.<sup>13</sup> Although a silyl shift from oxygen to carbon would be endothermic, it can occur if there is some suitable driving force, such as the concomitant formation of a carbon-oxygen  $\pi$ -bond at the expense of a weaker carbon-carbon  $\pi$ -bond.<sup>13</sup> In Scheme I, the necessary driving force would be provided by the initial addition, forming a "hot" intermediate that is chemically activated for the 1,3-shift.

(v) A similar stepwise mechanism would then account for the reaction of **2** with methoxytrimethylsilane and with trimethylchlorosilane, involving 1,3-silyl shifts from oxygen to oxygen and from chlorine to oxygen, respectively. As the "hot" intermediate formed initially would be "hotter" than in Scheme I because of the enhanced reactivity of **2** toward nucleophiles,<sup>9</sup> a wider range of silyl shifts would be expected than are observed in unactivated molecules.<sup>13</sup> While it is conceptually convenient to envisage these reactions as occurring in two distinct stages, there is probably no intermediate minimum along the reaction coordinate (cf. the dimerization of silanone<sup>9</sup>).

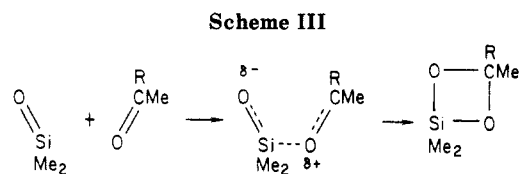
A further indicator of mechanistic dichotomy is provided by the measured *A* factor differences; reactions **2** and **3** have about the same *A* factor, while the *A* factor for reaction **1**, which presumably does occur via a tight four-center transition state, is almost two powers of 10 lower. These reactions are illustrated in Scheme II.

(vi) Of the reactions in Schemes I and II, reaction **3** requires the highest activation energy, probably because Cl is a poorer nucleophile than O and does not form a positive, two-coordinate intermediate as readily. These factors could account for the failure of **3** to react with trimethylchlorosilane.

(vii) According to the foregoing ideas, neither **2** nor **3** would be expected to react readily with Et<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, or Me<sub>3</sub>SiH because these molecules are too bulky for the four-center reaction and do not have labile groups which would undergo 1,3-shifts in the stepwise mechanism.

(viii) We can only speculate as to the structure of the 1:1 adducts of **2** with acetone and acetaldehyde because our evidence is based solely on mass spectra. The adducts were observed to decompose at 440 °C, accounting for earlier failures to observe them with sources of **2** that required higher temperatures. If they are cyclic adducts, they could have been formed by addition followed by ring closure, as in Scheme III.

In our earlier comments<sup>4</sup> on the mechanism of formation of D<sub>3</sub> from **2** we showed that D<sub>3</sub> formation could not result from self-reaction of **2**, forming successively "D<sub>2</sub>" and then D<sub>3</sub>, if the rate constant for dimerization of **2** was similar to that<sup>11</sup> for dimerization of **3**. As noted in (i) above, it now seems that **3** is sufficiently less polar than **2** to undergo cycloadditions more readily than **2**; if so, self-reaction of **2** to form "D<sub>2</sub>" then D<sub>3</sub> may occur by head-to-tail addition



with a rate constant sufficiently higher than that for the cyclodimerization of **3** for self-reaction of **2** to be a feasible route to D<sub>3</sub> [see comment on *A* factors in (v) above]. Nevertheless, we continue to think it more likely that D<sub>3</sub> is mainly formed in a cycle of reactions involving a molecular species with which **2** reacts rapidly, either homogeneously or heterogeneously, such as water.<sup>4</sup>

**Acknowledgment.** We thank the SERC and Dow Corning (Europe) Ltd. for support. We also thank Elsa Brackenbury and Richard Pocock for some of the kinetic measurements, undertaken during their undergraduate project work.

**Registry No.** 1, 65181-02-4; 2, 47956-45-6; 3, 61153-00-2.

### Reactions at the $\beta$ -Carbon of Anionic Tungsten Acetylide Complexes: Ion Pairing, Vinylidene Formation, and CO<sub>2</sub> Binding

K. R. Birdwhistell and J. L. Templeton\*

*W. R. Kenan, Jr. Laboratories  
Department of Chemistry, The University of North Carolina  
Chapel Hill, North Carolina 27514*

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**Summary:** Addition of CO<sub>2</sub> to the  $\beta$ -carbon of Li[*fac*-(OC)<sub>3</sub>(dppe)WC≡CR] (R = Me, *n*-Bu) followed by methylation yields vinylidene products, *mer*-(OC)<sub>3</sub>(dppe)W=C=C(R)CO<sub>2</sub>Me. Ion-pair formation at the  $\beta$ -carbon may act as a kinetic mediator in this system. We also report syntheses of *mer*-(OC)<sub>3</sub>(dppe)W=C=CRR' complexes, including the parent C=CH<sub>2</sub> derivative.

Coordination of acetylide anions to tungsten(0) effectively transfers the nucleophilicity of the C<sub>2</sub> fragment from C<sub>α</sub> to C<sub>β</sub>. Anionic complexes **1-4** (Scheme I) were prepared as alkali-metal salts by addition of the appropriate acetylide reagent to a THF solution of (acetone).<sup>1</sup> Table I contains  $\nu_{\text{CO}}$  and  $\nu_{\text{C=C}}$  infrared data for the lithium, sodium, and PPN salts of [*fac*-(OC)<sub>3</sub>(dppe)WC≡CR]<sup>-</sup> (R = H, **1**; Me, **2**). Changing the cation from PPN<sup>+</sup> to Na<sup>+</sup> to Li<sup>+</sup> results in an increase in the carbonyl CO frequencies. The simultaneous decrease observed for  $\nu_{\text{C=C}}$  in **2** is evidence of site selective ion pairing between the  $\beta$ -carbon and the alkali cations (Scheme I). This site selectivity is

(1) Yellow M[*fac*-(OC)<sub>3</sub>(dppe)WC≡CR] salts (M = Li, Na; dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) were isolated in good yields (60-95%). PPN salts (PPN = bis(triphenylphosphine)nitrogen(1+)) were prepared by ion exchange in CH<sub>2</sub>Cl<sub>2</sub>. IR data for **1-4** are presented in Table I. See ref 18 for preparation of (OC)<sub>3</sub>(dppe)W(acetone). [PPN][*fac*-(OC)<sub>3</sub>(dppe)WC≡CH], **1**: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.97-7.10 (m, Ph), 2.75 (m, PCHHCHHP), 2.45 (m, PCHHCHHP), 1.39 (t, <sup>4</sup>J<sub>HP</sub> = 3.5 Hz, W-CCH); <sup>13</sup>C NMR (<sup>1</sup>H coupled, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  201.9 (m, CO), 200.2 (m, CO) 140.0-126.4 (m, Ph), 99.5 (d, <sup>1</sup>J<sub>CH</sub> = 213 Hz, W-CCH), 28.6 (tm, <sup>1</sup>J<sub>CH</sub> = 126 Hz, PCH<sub>2</sub>CH<sub>2</sub>P), ( $\alpha$ -carbon of acetylide not observed).

(13) Brook, A. G.; Bassindale, A. R. *Org. Chem. (N.Y.)* **1980**, *42*, 149.