synthesis and to Dr. F. J. Hollander, Chexray facility, University of California at Berkeley, for carrying out the X-ray structural determination of **10**.

Supplementary Material Available: ^{1}H NMR, ^{13}C NMR, IR, HRMS, and combustion analysis data for **4–12** and intermediates and ORTEP rendition, X-ray parameters, and tables of atomic coordinates, thermal parameters, bond angles, and bond distances of **10** (13 pages). Ordering information is given on any current masthead page.

Coupling of a Vinyl Ligand and a Vinylidene Ligand at an Iridium Center: Generation of an Unusual Iridium(III) Butadienyl Complex Stabilized by a δ-Agostic C–H–Ir Interaction

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The formation of carbon–carbon bonds at transition-metal centers via migratory insertion reactions of metal alkylidene species has received a great deal of attention in the recent past. Much of the driving force for this work came from the desire to determine the validity of the various proposals for the chain-growth step in the Fischer–Tropsch reaction,[1] with a new proposal suggesting the intermediacy of surface vinyl species appearing quite recently.[1a] In addition, the desire to develop new methods for carbon–carbon bond formation of use in organic synthesis has spurred many such investigations.[2] From these studies, several examples of alkyl migration to a metal alkylidene group have been reported for a variety of metal systems.[3] In this communication, we report on what we believe to be the first example of the migratory insertion of a vinylidene group into a metal–vinyl bond and the implications that such a reaction may have for alkyne oligomerization catalysis.

In 1989, we showed that *mer*-$(C_6H_5)Ir(H)(Cl)(PMe_3)_3$ (**1**) reacted with 2-butyne (following chloride removal) to form a methallyliridium compound. A necessary step in the 2-butyne reaction is a β-hydride elimination step which allows the σ-butenyl group to rearrange to a π-methyl allyl fragment. When the alkyne has no hydrogens on carbon α to the triple bond, the reaction is forced to follow quite a different course. Reaction between **1** and an excess of *tert*-butylacetylene following chloride removal by $Tl[PF_6]$ leads to the production of a new complex, **2**, whose spectroscopy and elemental analysis indicate that *2 equiv* of *tert*-butylacetylene has been incorporated (eq 1).[5] Our original supposition was that, following the initial insertion to yield a vinyl compound, a second insertion occurred to form a σ,π-butadienyl complex. Double insertions of this type had been reported previously by both Bruce[6a,b] and Nixon.[6c] Resonances due to the vinylic protons in **2** clearly indicate that there are two protons that couple to each other with constants consistent with a trans disposition. The third vinylic proton is not coupled to the other two, but is strongly coupled to a phosphine. The ^{13}C NMR data indicate that the carbon directly bonded to the iridium is a quaternary carbon. These data are not in keeping with any form of a σ,π-butadienyl group.

$$\underset{\mathbf{1}}{(C_6H_5)Ir(H)(Cl)(PMe_3)_3} + \text{excess } {}^tBuC{\equiv}CH \xrightarrow[-TlCl]{Tl[PF_6]} \underset{\mathbf{2}}{[(C_6H_5)(Me_3P)_3Ir({}^tBuC{\equiv}CH)_2][PF_6]} \quad (1)$$

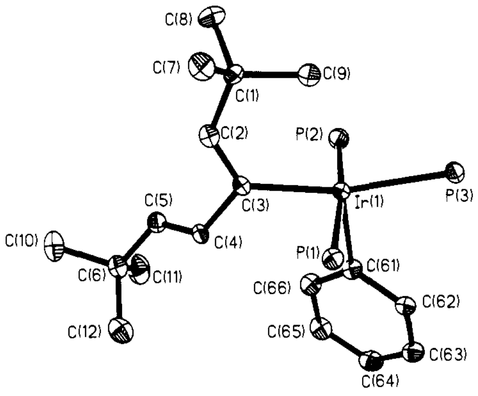
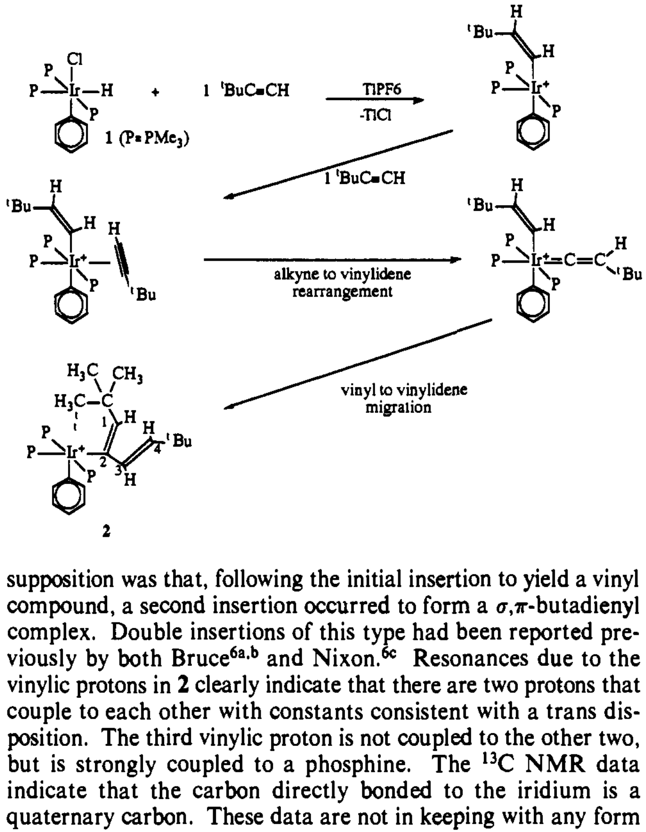


Figure 1. ORTEP plot of **2** (phosphine methyl groups removed for clarity). Some important bond distances (Å): Ir(1)–P(1), 2.363 (3); Ir(1)–P(2), 2.366 (3); Ir(1)–P(3), 2.398 (3); Ir(1)–C(61), 2.053 (9); Ir(1)–C(3), 2.109 (10); C(1)–C(2), 1.523 (13); C(2)–C(3), 1.352 (13); C(3)–C(4), 1.485 (12); C(4)–C(5), 1.314 (13); C(5)–C(6), 1.503 (13).

Scheme I



A single-crystal X-ray structure determination of **2** was carried out, and the resulting ORTEP plot of the cation is shown in Figure 1.[7] Overall, the structure consists of a distorted octahedral iridium

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(1) (a) Maitlis, P. M. *Pure Appl. Chem.* **1989**, *61*, 1747. (b) Ma, F.; Sunley, G. J.; Saez, I. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1990**, 1279. (c) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds.; Pergamon Press: New York, 1983; Vol. 8, p 19. (d) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181.

(2) For select examples of utilizing migratory insertion reactions of carbenes, see: (a) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 6232. (b) Hoover, J. F.; Stryker, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 464. (c) Liebeskind, L. S.; Chidambaram, R. *J. Am. Chem. Soc.* **1987**, *109*, 5025.

(3) In addition to refs 2a–c, see also: (a) Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580. (b) Thorn, D. L. *Organometallics* **1985**, *4*, 192. (c) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984.

(4) Merola, J. S. *Organometallics* **1989**, *8*, 2975.

(5) Data for **2**: ^{1}H NMR (200 MHz, CD_2Cl_2) δ 0.53 (br s, 9 H, $C(CH_3)_3$), 1.06 (s, 9 H, $C(CH_3)_3$), 1.49 (t, J_{P-H} = 3.5 Hz, 18 H, mutually trans PMe_3), 1.68 (d, J_{P-H} = 7.6 Hz, cis PMe_3), 5.57 (d, J_{H-H} = 15.5 Hz, 1 H), 5.88 (br d, J_{H-H} = 15.5 Hz, 1 H), 6.20 (br d, J_{P-H} = 14.6 Hz, 1 H, 6.75–7.15 ppm (m, 5 H, phenyl). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 15.55 (t, J_{P-C} = 18 Hz, mutually trans PMe_3), 18.8 (d, J_{P-C} = 27 Hz, PMe_3), 26.6 (br s, $C(CH_3)_3$), 29.1 (s, $C(CH_3)_3$), 33.0 (s, $C(CH_3)_3$), 36.5 (br s, $C(CH_3)_3$), 111.2 (q, J_{P-C} = 4.5 Hz, Ir–C of phenyl), 123.8, 126.7 (vinylic C), 141.8 (d of t, $J_{P(trans)-C}$ = 93 Hz, $J_{P(cis)-C}$ = 12 Hz, Ir–C of vinyl), 136.3, 138.3, 145.2 (phenyl C). ^{31}P NMR (81 MHz, CD_2Cl_2) δ −34.0 (d, J_{P-P} = 18 Hz, mutually trans PMe_3), −46.0 (t, J_{P-P} = 18 Hz, cis PMe_3). Anal. C, H.

(6) (a) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 106. (b) Bruce, M. I.; Gardner, R. C. F.; Howard, J. A. K.; Stone, F. G. A.; Welling, M.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 621. (c) Eshtiagh-Hosseini, H.; Nixon, J. F.; Poland, J. S. *J. Organomet. Chem.* **1979**, *164*, 107.

0002-7863/91/1513-4008$02.50/0

center with three meridionally situated PMe$_3$ ligands, a phenyl ligand, and what can best be described as a substituted σ-butadienyl ligand. While there appears to be no group in the sixth coordination site, one of the methyl groups from a *tert*-butyl fragment on the butadienyl chain sits over that sixth site at a distance of 2.782 Å, suggesting that there is an agostic Ir–H–C interaction occurring at that site.[8] While hydrogen atoms were not located in this structure, further support for an agostic interaction was obtained from low-temperature ^{1}H NMR.[9]

We propose that **2** is formed by the sequence of reactions shown in Scheme I. Following chloride removal to generate a coordinatively unsaturated iridium center, the *tert*-butylacetylene "inserts" into the Ir–H bond to form an iridium–vinyl intermediate. A second equivalent of *tert*-butylacetylene adds to this still coordinatively unsaturated complex.[10] The second *tert*-butylacetylene then rearranges to a *tert*-butylvinylidene group.[11] The final product is formed by migration of the vinyl group to the α-carbon of the vinylidene moiety with the agostic interaction between the iridium and one of the *tert*-butyl methyl hydrogens stabilizing the final product. Several deuterium labeling experiments fully support this mechanism. If **1** with hydride replaced by deuteride is allowed to react with 2 equiv of $^t\mathrm{BuC{\equiv}CH}$, the deuterium is found exclusively at postion 4 (refer to the numbering used for **2** in Scheme I). Reaction between hydrido **1** and 2 equiv of $^t\mathrm{BuC{\equiv}CD}$ gave complementary results, i.e., D located at positions 1 and 3. When hydride **1** is allowed to react sequentially with 1 equiv of $^t\mathrm{BuC{\equiv}CH}$ followed by 1 equivalent of $^t\mathrm{BuC{\equiv}CD}$ after a short time delay, the deuterium is predominantly incorporated at position 1.

The mechanism shown in Scheme I suggests that this iridium system may allow for further additions leading to the oligomerization of alkynes. Following the vinyl to vinylidene migration, the complex is still formally a coordinatively unsaturated metal vinyl complex in the absence of the stabilizing agostic interaction. A third equivalent of alkyne could then add and rearrange to a vinylidene, and the sequence could continue building up oligomers of alkynes with a branched structure. Preliminary information suggests that this may indeed be possible.[12]

In this work we have demonstrated an unusual reaction involving the coupling of two alkynes on iridiun via a vinyl to vinylidene migration pathway. The iridium complex isolated from the reaction of *tert*-butylacetylene is an unusual butadienyl compound stabilized by a δ-agostic interaction. We believe this work lays the foundation for future investigations into developing the vinyl to vinylidene migration into a synthetically useful reaction with an eye toward the synthesis and characterization of novel branched acetylene oligomers and polymers.

Acknowledgment. We are grateful to the Thomas F. Jeffress and Kate Miller Jeffress Memorial Trust and to the Exxon Education Foundation for financial support of this work and to Johnson-Matthey and Engelhard for iridium salts. We are also grateful to the reviewers for calling some important references to our attention.

Supplementary Material Available: Tables 1–5 including a structure determination summary, atomic coordinates, bond lengths and angles, and anisotropic displacement coefficients for **2** (5 pages). Ordering information is given on any current masthead page.

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[7] X-ray data for **2**: orthorhombic space group $Pbac$, $a = 11.658$ (4) Å, $b = 18.041$ (4) Å, $c = 33.731$ (8) Å with $Z = 8$. A total of 7449 independent reflections were collected (3.5–55° in 2θ) with 4878 observed ($F > 3.0\sigma(F)$); 344 variables refined to yield $R = 6.2\%$ and $R_w = 6.28\%$ with goodness-of-fit = 1.77. Full details are available in the supplementary material.

[8] Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

[9] On cooling, the broad *tert*-butyl singlet found at δ 0.53 in the ^{1}H NMR spectrum broadens further and collapses into the base line at –20 °C. On further cooling (–90 °C is the lowest we measured), two new resonances grow at δ –0.7 and 1.1 ppm. This indicates that we are freezing out the process that averages the three *tert*-butyl methyl groups, but rotation of the methyl coordinated to the iridium is still a fast process at –90 °C.

[10] Examples of iridium with both vinyl and η^2-alkyne ligands have been observed: (a) Baddley, W. H.; Fraser, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 3661. (b) McClure, G. L.; Baddley, W. H. *J. Organomet. Chem.* **1971**, *27*, 155. (c) Baddley, W. H.; Tupper, G. B. *J. Organomet. Chem.* **1974**, *67*, C16.

[11] The rearrangement of a coordinated alkyne to a vinylidene is a well-documented process: Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59 and references therein.

[12] Treatment of **1** with Tl[PF$_6$] in the presence of acetylene leads to a rapid reaction to produce a dark, purple oily material which has yet to be fully characterized but appears to be a branched acetylene oligomer.

Deuterium Isotope Effects in Gas-Phase Reactions of Alkyl Halides: Distinguishing E2 and S$_N$2 Pathways

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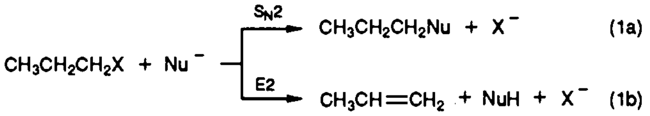
While E2 and S$_N$2 reactions of alkyl halides are among the most studied of all chemical processes in solution, investigations of their gas-phase ion–molecule counterparts have been greatly hindered by the difficulty of distinguishing between the two pathways.[1] This is the case because in most gas-phase experiments only the ions are detected, and halide is the exclusive ionic product of both reactions (eq 1).



$$\mathrm{CH_3CH_2CH_2X + Nu^-} \xrightarrow{S_N2} \mathrm{CH_3CH_2CH_2Nu + X^-} \quad (1a)$$

$$\mathrm{CH_3CH_2CH_2X + Nu^-} \xrightarrow{E2} \mathrm{CH_3CH{=}CH_2 + NuH + X^-} \quad (1b)$$

We report that with the proper choice of nucleophiles S$_N$2 and E2 reactions of halides can be distinguished in the gas phase, as in solution, by their differing deuterium kinetic isotope effects,[2] the former showing an inverse secondary k_H/k_D as small as 0.76 and the latter a normal primary k_H/k_D as large as 4.7.

What little information is available in the literature about this competition is conflicting. By using very difficult neutral detection techniques two groups of workers have come to rather different conclusions in what seem to be similar systems. Lieder and Brauman[3] observed substitution products in the reaction of fluoride ion with ethyl chloride in an ion cyclotron resonance spectrometer, whereas Jones and Ellison[4] detected only the elimination product, propylene, in the reaction of methoxide ion with *n*-propyl bromide in a flowing afterglow apparatus. When the leaving group is not a halide ion, the different paths can sometimes be distinguished by the formation of different product ions. For example, ethers,[5] formates,[6] nitrites,[7] and cyclic sulfides[8] have been shown to undergo elimination rather than substitution, even when the leaving group is primary, while sulfites[9] lead to nearly equal amounts of substitution and elimination.

Only a few kinetic isotope effects have heretofore been detected in gas-phase ion–molecule chemistry,[5c,10] primarily because these reactions are so rapid, with measurable rate constants in the range 10^{-9}–10^{-13} cm^3 molecule^{-1} s^{-1} (10^8–10^{12} L mol^{-1} s^{-1}). Most alkyl halides react with nucleophiles at or near the collision rate, making

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[1] Riveros, J. M.; Jose, S. M.; Takashima, I. *Adv. Phys. Org. Chem.* **1985**, *21*, 197.

[2] Melander, L.; Saunders, J. H., Jr. *Reaction Rates of Isotopic Molecules*; John Wiley and Sons: New York, 1980.

[3] Lieder, C. A.; Brauman, J. I. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *16*, 307.

[4] Jones, M. E.; Ellison, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 1645.

[5] (a) DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 5034. (b) DePuy, C. H.; Beedle, E. C.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1982**, *104*, 6483. (c) de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1987**, *109*, 1715.

[6] Faigle, J. F. G.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 2049.

[7] (a) King, G. K.; Maricq, M. M.; Bierbaum, V. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1981**, *103*, 7133. (b) Noest, A. J.; Nibbering, N. M. M. *Adv. Mass Spectrom.* **1980**, *8*, 227.

[8] Bartmess, J. E.; Hays, R. L.; Khatri, H. N.; Misra, R. N.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 4746.

[9] Lum, R. C.; Grabowski, J. J. *J. Am. Chem. Soc.* **1988**, *110*, 8568.

[10] Bierbaum, V. M.; Filley, J.; DePuy, C. H.; Jarrold, M. F.; Bowers, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 2818.

0002-7863/91/1513-4009$02.50/0