adducts at the amino group without interference from the adjacent carbonyl functionality.[7] Correspondingly the allylic bromide **8** opens the door to a wide range of oxyallyl cation chemistry.[8]

This new facet of truly kinetic carbonyl chemistry should reveal a broad spectrum of complementary synthetic transformations that can be anticipated to take place with exceptional stereoelectronic control. These possibilities are being studied.

Acknowledgment. Dr. Mugrage thanks the National Institutes of Health for the award of a postdoctoral fellowship. Dr. Vince Lynch is gratefully thanked for X-ray structural determinations.

Supplementary Material Available: General spectral details for compounds **3-8** and **17-22**, details of the X-ray structure determination of **7**, tables of fractional coordinates, isotropic thermal parameters, anisotropic thermal parameters, bond lengths, and bond angles for $C_{23}H_{39}NO_3SSi$, and atom labeling and unit packing diagrams for $C_{23}H_{39}NO_3SSi$ (14 pages). Ordering information is given on any current masthead page.

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[7] 2-Aminocyclohexanone readily self-condenses on treatment with acids or bases to give after oxidation octahydrophenazine. Smith, P. A. S. *J. Org. Chem.* **1960**, *25*, 2047.

[8] Giguere, R. J.; Hoffmann, H. M. R.; Hursthouse, M. B.; Trotter, J. *J. Org. Chem.* **1981**, *46*, 2868.

Coupling of a 2-Oxacyclopentylidene and a Phosphonium Ylide Ligand at Platinum. Migratory Insertion of a Fischer Carbene into a Metal Alkyl Bond

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Intramolecular migratory insertion reactions involving transition-metal carbene and σ-carbon ligands are intermediate in several interesting organometallic transformations in which new carbon-carbon bonds are formed.[2] These insertions typically involve highly reactive carbene-alkyl precursors generated in situ; in only one case has a complex which undergoes subsequent insertion chemistry been isolated.[2h] Here we report an isolable 2-oxacyclopentylidene bis(phosphonium ylide) complex of platinum that undergoes a facile migration of one phosphonium ylide ligand to the carbene. This process represents both unique reactivity for the platinum oxacyclopentylidene system[3] and, to our knowledge, the first observation of a migratory insertion process involving a phosphonium ylide ligand. In addition, the ultimate organic product of this reaction is a patented synthetic intermediate prepared in low yield by conventional organic methodology.

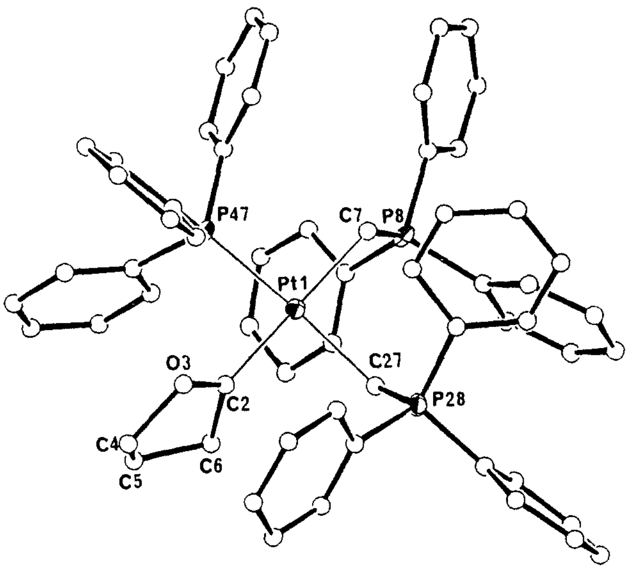
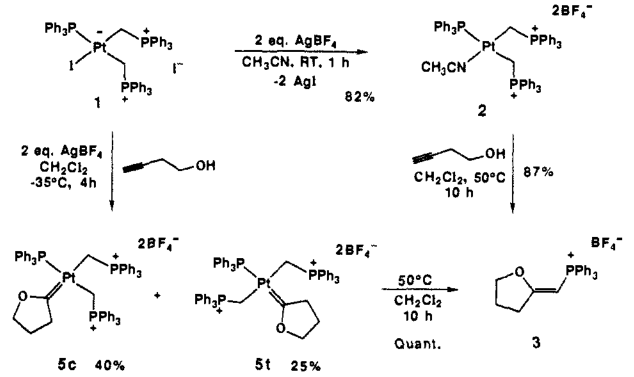


Figure 1. ORTEP drawing of **5c** (the hydrogen atoms have been omitted for clarity). Selected bond distances (Å): Pt(1)–C(2), 1.990 (22); Pt(1)–C(7), 2.122 (21); Pt(1)–C(27), 2.092 (22); Pt(1)–P(47), 2.299 (6); C(2)–O(3), 1.325 (27); C(7)–P(8), 1.772 (21); C(27)–P(28), 1.783 (22). Selected bond angles (deg): Pt(1)–C(2)–O(3), 123.2 (17); Pt(1)–C(2)–C(6), 123.2 (17); O(3)–C(2)–C(6), 113.5 (20); C(2)–Pt(1)–C(27), 90.2 (9); C(2)–Pt(1)–P(47), 87.5 (7); P(47)–Pt(1)–C(7), 91.1 (6); C(7)–Pt(1)–C(27), 91.1 (8); C(2)–Pt(1)–C(7), 174.9 (9); C(27)–Pt(1)–P(47), 177.4 (6). Least-squares acute plane angle (deg): ((Pt(1)–C(2)–O(3)–C(6))–((Pt(1)–C(7)–C(27)–P(47), 61.75. Final residuals: $R(F) = 0.068$ and $R_w(F) = 0.060$.

Scheme I



We considered the bis(phosphonium ylide) complex **1** (Scheme I), prepared by treatment of $(COD)Pt(CH_2I)_2$ (COD = 1,5-cyclooctadiene) with excess triphenylphosphine,[4] to be an ideal template on which to probe the nature and reactivity of the phosphonium ylide ligand. While the synthesis of ylide complexes has been extensively investigated,[5] substantially less is known about the reactivity of coordinated phosphonium ylides.[6,7] To provide an open coordination site for binding a potentially reactive ligand, abstraction of both iodide atoms was accomplished by using $AgBF_4$ in anhydrous acetonitrile, giving acetonitrile complex **2** in 82% yield after recrystallization from CH_2Cl_2/benzene.[8] The cis orientation of the ylide ligands follows from the observation of three signals in the ^{31}P NMR spectrum. The coordinated ace-

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[1] Du Pont Young Faculty Awardee, 1988-1989. Union Carbide Innovation Recognition Program Awardee, 1989.

[2] (a) Van Leeuwen, P. W. N. M.; Roobeek, C. F.; Huis, R. *J. Organomet. Chem.* **1977**, *142*, 243. (b) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984. (c) Thorn, D. L. *Organometallics* **1985**, *4*, 192. (d) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570. Jernakoff, P.; Cooper, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 3026. (e) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278. (f) Kletzin, H.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 46. (g) McCrindle, R.; Arsenault, G. J.; Farwaha, R.; Hampden-Smith, M. J.; McAlees, A. J. *J. Chem. Soc., Chem. Commun.* **1986**, 943. (h) Stenstrom, Y.; Koziol, A. E.; Palenik, G. J.; Jones, W. M. *Organometallics* **1987**, *6*, 2079, and references therein. Conti, N. T.; Jones, W. M. *Organometallics* **1988**, *7*, 1666. (i) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 4129.

[3] (a) Chisholm, M. H.; Clark, H. C. *J. Chem. Soc., Chem. Commun.* **1970**, 763. (b) Chisholm, M. H.; Clark, H. C. *Inorg. Chem.* **1971**, *10*, 1711. (c) Chisholm, M. H.; Clark, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 1532. (d) Chisholm, M. H.; Clark, H. C. *Acc. Chem. Res.* **1973**, *6*, 202.

[4] Hoover, J. F.; Stryker, J. M. *Organometallics* **1988**, *7*, 2082.

[5] An extensive listing of references is given in ref 4.

[6] (a) Reviews: Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907. Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1. (b) Recent investigations: Crocco, G. L.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1154. Alt, H. G.; Hayen, H. I. *J. Organomet. Chem.* **1986**, *316*, 301.

[7] Depending on metal, oxidation state, and ligand set, the phosphonium ylide ligand may be nucleophilic at carbon, reflecting polarization of the metal–carbon bond, or electrophilic at carbon, reflecting polarization of the carbon–phosphorus bond. In the former case, reactivity involving the intact ylide ligand is expected; in the latter, phosphine loss and reaction of the resultant methylene ligand should be observed.

[8] Complete spectroscopic and analytical data is provided as Supplementary Material.

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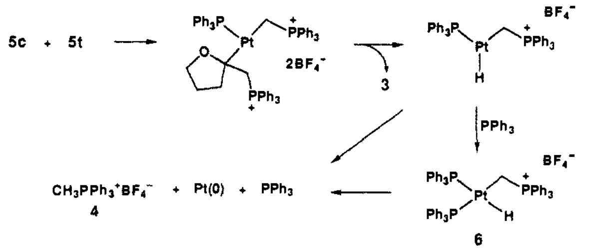
Scheme II



tonitrile undergoes exchange with CD_3CN at 45 °C without loss of stereochemical integrity.

Coordination of an oxacyclopentylidene moiety was anticipated by using classical alkynol cyclization methodology.[3] Reaction of acetonitrile complex **2** with 3-butyn-1-ol in CH_2Cl_2 solution required heating to 50 °C and gave instead the synthetically important dihydrofuranylidene phosphonium salt **3**[9] in 87% isolated yield, accompanied by free Ph_3P, $CH_3PPh_3^+BF_4^-$ (**4**), and a dark precipitate presumed to be Pt(0). Compound **3** was purified by fractional crystallization from THF/hexanes and its identity confirmed both by complete characterization[8] and independent synthesis.[9a]

To investigate the intermediacy of the expected alkoxy carbene complex in the formation of **3**, zwitterionic ylide complex **1** was treated with $AgBF_4$ at low temperature in the presence of 3-butyn-1-ol. Two isomeric oxacyclopentylidene bis(ylide) complexes, **5c**[8,10] and **5t**,[8,11] were formed in approximately equimolar ratio (by ^1H NMR analysis) and were separated and isolated in 40% and 25% yield, respectively, by a single fractional recrystallization from CH_2Cl_2/toluene. The structural and stereochemical formulations are fully consistent with the spectroscopic data: characteristic low field carbene carbon resonances and $^2J_{PC}$ values[3c] at δ 289.1 ($J_{PC} = 5.8$ Hz) for cis isomer **5c** and δ 292.8 ($J_{PC} = 137$ Hz) for trans isomer **5t**. Single crystals of **5c** were obtained from methanol/ether solution and structural assignment confirmed by X-ray crystallography (Figure 1). In the solid state, the carbene ligand is unusually distorted from its preferred perpendicular orientation with respect to the square plane of the complex:[12] the carbene plane intersects the square plane at an angle of 61.75°.

On warming, the isolated carbene complexes **5** independently or as a mixture convert quantitatively to phosphonium salt **3** and byproducts identical with those obtained starting with acetonitrile complex **2**.[13]

Our mechanistic rationale for the formation of **3** from carbene complexes **5c** and **5t** invokes the intramolecular migration of the intact phosphonium ylide ligand to the alkoxy carbene, followed by β-elimination and release of the organic product (Scheme II).[14] No competitive trapping of free methylenetriphenylphosphorane is observed on reaction of the carbene complex **5c** in the presence of excess benzaldehyde, supporting an intramolecular mechanism for the migratory insertion.[15] Decomposition of the 14-electron platinum fragment by reductive elimination accounts for the remainder of the observed reaction products. Evidence for the intermediacy of the hydride complex is obtained by warming the isomeric carbene complexes **5c** and **5t** in the presence of PPh_3; under these conditions an intermediate is observed spectroscopically by ^1H NMR. Although this intermediate is also unstable with respect to reductive elimination, it exhibits an upfield resonance at δ −5.80 (ddd, $J_{PH} = 125$, 18, 12 Hz), consistent with the hydride ligand in *cis*-bis(phosphine) complex **6**.

The reactivity of bis(phosphonium ylide) carbene complexes **5c** and **5t** toward migratory insertion undoubtedly results from a combination of features, including the cis disposition of the carbene and ylide ligand and the natural polarization of the electrophilic carbene carbon and the presumably nucleophilic alkyl ligand. The sterically congested coordination environment may also contribute both to the unusually twisted carbene orientation and to lowering the activation energy required for formation of the tricoordinate intermediate. Experiments designed to assess the relative importance of these factors are under investigation.

Acknowledgment. We thank Kirsten Folting for the X-ray crystal structure determination and Professor Malcolm H. Chisholm for helpful discussion. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supplementary Material Available: Full spectroscopic and analytical data for compounds **2**, **3**, **5c**, and **5t** and tables of data collection and structure solution for complex **5c**, atomic positional and thermal parameters, and complete bond distance and angles (19 pages); a listing of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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(9) (a) Mueller, R. A. Fr. Patent 2487357; *Chem. Abstr.* **1982**, *97*, P6526a. (b) See, also: Mueller, R. A. U.S. Patent 4297487; *Chem. Abstr.* **1982**, *96*, P20264z. Mueller, R. A. U.S. Patent 4347192; *Chem. Abstr.* **1983**, *98*, P34372m.

(10) Data for **5c**: mp 125–128 °C dec (sealed under vacuum); ^1H NMR (500 MHz, $CDCl_3$) δ 7.75–7.00 (m, 45 H), 3.71 (t, $J_{HH} = 7.8$ Hz, 2 H), 2.83 (t, $J_{HH} = 7.6$ Hz, 2 H), 2.42 (dd, $J_{PH} = 15.8$, 7.7 Hz, $J_{PtH} = 83.6$ Hz, 2 H), 1.46 (dd, $J_{PH} = 15.5$, 8.4 Hz, $J_{PtH} = 67.8$ Hz, 2 H), 1.10 (quint, $J_{HH} = 7.6$ Hz, 2 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 289.1 (d, $J_{PC} = 5.8$ Hz), 134.1–133.0 (overlapping resonances), 131.8 (s), 131.6 (s), 129.8 (m), 129.1 (m), 128.0 (d, $J_{PC} = 53.6$ Hz), 123.9 (d, $J_{PC} = 83.2$ Hz), 123.0 (d, $J_{PC} = 84.6$ Hz), 88.2 (s), 56.8 (s), 18.4 (s), −3.7 (d, $J_{PC} = 29.2$ Hz), −5.6 (dd, $J_{PC} = 85.7$, 36.0 Hz); $^{31}P\{^1H\}$ NMR (146 MHz, $CDCl_3$) δ 33.06 (s, $J_{PtP} = 39.3$ Hz), 30.95 (d, $J_{PP} = 5.6$ Hz, $J_{PtP} = 46.5$ Hz), 16.75 (d, $J_{PP} = 5.3$ Hz, $J_{PtP} = 2493$ Hz). Anal. Calcd for $C_{59}H_{55}B_2F_8OP_3Pt$: C, 57.07; H, 4.64. Found: C, 56.85; H, 4.59.

(11) A tungsten complex possessing both carbene and phosphonium ylide ligands has been reported: Huy, N. H. T.; Fischer E. O.; Alt, H. G.; Dötz, K. H. *J. Organomet. Chem.* **1985**, *284*, C9.

(12) Review: Schubert, U. *Coord. Chem. Rev.* **1984**, *55*, 261, and references therein.

(13) Qualitatively, conversion of **5t** proceeds at lower temperature than **5c**, giving **3** very slowly in CH_2Cl_2 even at room temperature.

(14) This mechanistic sequence is analogous to that reported for the migratory ring contraction in an iron alkoxy carbene complex: Stenstrom, Y.; Jones, W. M. *Organometallics* **1986**, *5*, 178. See also ref 2h.

(15) Rigorous exclusion of an intermolecular reaction pathway requires an appropriate crossover experiment. Intermolecular addition of a phosphonium ylide to an electrophilic carbene complex has been reported, although this reaction led to loss of triphenylphosphine and formation of an enol ether product: Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 6543.