3904 *Organometallics* **2007,** *26,* 3904−3907

Synthesis, Structure, and Spectroscopy of Silaallyl− and Silapentadienyl−Iridium−Phosphine Complexes[1]

John R. Bleeke,*,† Todsapon Thananatthanachon,† and Nigam P. Rath‡

Department of Chemistry, Washington University, One Brookings Drive, St. Louis, Missouri 63130, and Department of Chemistry and Biochemistry, University of Missouri−St. Louis, One University Boulevard, St. Louis, Missouri 63121

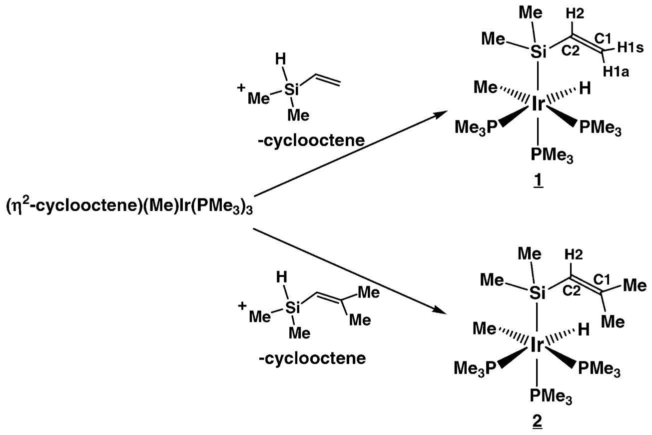
Received May 16, 2007

Summary: Silaallyl− and silapentadienyl−iridium−phosphine complexes have been synthesized via the reaction of "(Me)Ir(PMe_3)$_3$" with vinyl- and butadienyldimethylsilanes. Upon heating, these complexes lose methane and undergo a variety of reactions, including C−H bond activation to produce a five-membered iridasilacycle, C═C bond coordination to generate an η^1,η^2-silapentadienyl ligand, and decomposition.

Allyl−metal[2] and pentadienyl−metal[3] complexes have been extensively investigated, and heteroatom-containing analogues such as oxaallyl−metal[4] and thiapentadienyl−metal[5] complexes have recently received increased attention. In contrast, surprisingly few examples of the closely related silicon-containing systems have been reported. In fact, the first example of an η^3-silaallyl−metal complex, (η^5-cyclopentadienyl)W(CO)$_3$(η^3-1,1,3,3-tetramethyl-1-silaallyl), was only recently synthesized,[6] and no examples of silapentadienyl−metal complexes have to date appeared in the literature.

Metal complexes containing allyl ligands, pentadienyl ligands, or their heteroatom analogues often exhibit interesting reactivity due to the accessibility of a range of η^1-, η^3-, and η^5-bonding modes. There is even the intriguing possibility of catalysis based on facile interconversions between these modes.[5a] With this in mind, we set out to synthesize a series of silaallyl− and silapentadienyl−iridium−phosphine complexes and to explore their reactivity. In this communication, we report a successful synthetic strategy for producing the desired complexes, as well as structural and spectroscopic data on several key members of this compound class.

Scheme 1



As shown in Scheme 1, treatment of (η^2-cyclooctene)(Me)-Ir(PMe)$_3$[7] with vinyldimethylsilane[8] or with (dimethylvinyl)-dimethylsilane[6] produces Si−H bond activation[9] products, **1** and **2**, respectively, in which the methyl, hydrido, and η^1-silyl ligands reside in a mutually *cis* arrangement. This geometry is evident from the ^{31}P{^{1}H} NMR spectra of **1** and **2**, where all three phosphines are inequivalent and appear as separate phosphorus-coupled doublet-of-doublet (dd) patterns.

In the ^{1}H NMR spectrum of **1**, the three vinyl protons—H2, H1$_s$, and H1$_a$—appear downfield at δ 6.57, 5.53, and 5.35, respectively. The silyl methyl groups are diastereotopic and appear at δ 0.20 and 0.18. The iridium-methyl group is highly coupled, appearing as a complex multiplet at δ 0.13, while the iridium-hydride resonates at δ −12.53 and exhibits a doublet-of-doublets-of-doublets (ddd) pattern with one very large coupling (J_{H-P} = 132.0 Hz) due to the *trans* phosphine and two smaller couplings ($J_{H-P} \approx$ 18.5 Hz) due to the *cis* phosphines. In the ^{13}C{^{1}H} NMR spectrum, vinyl carbons C2 and C1 appear far downfield (δ 155.6 and 122.6, respectively), while the iridium-methyl resonates at δ −31.3 and is a ddd pattern with strong coupling to the *trans* phosphine (J_{C-P} = 64.2 Hz) and weak coupling to the two *cis* phosphines (J_{C-P} = 8.2 and 6.6 Hz).

The NMR spectra of compound **2**, reported in the Supporting Information, are similar to those of **1** and fully consistent with

---

* To whom correspondence should be addressed. E-mail: bleeke@wustl.edu.

† Washington University.

‡ University of Missouri−St. Louis.

(1) Pentadienyl−Metal−Phosphine Chemistry. 34. Part 33: Bleeke, J. R.; Shokeen, M.; Wise, E. S.; Rath, N. P. *Organometallics* **2006**, *25*, 2486−2500.

(2) See, for example: *Comprehensive Organometallic Chemistry*: Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, 1995; Vol. 9, Sections 3.3, 6.4, and 9.4.

(3) (a) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15−29. (b) Powell, P. *Adv. Organomet. Chem.* **1986**, *26*, 125−164. (c) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255−1291.

(4) (a) Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 3724−3726. (b) Burkhardt, E. R.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022−2039. (c) Kündig, E. P.; Bernardinelli, G.; Kondratenko, F.; Romanens, P. *Helv. Chim. Acta* **2003**, *86*, 4169−4183.

(5) For recent reviews of heteropentadienyl−metal chemistry, see: (a) Bleeke, J. R. *Organometallics* **2005**, *24*, 5190−5207. (b) Paz-Sandoval, M. A.; Rangel-Salas, I. I. *Coord. Chem. Rev.* **2006**, *250*, 1071−1106.

(6) Sakaba, H.; Watanabe, S.; Kabuto, C.; Kabuto, K. *J. Am. Chem. Soc.* **2003**, *125*, 2842−2843. See also: Dysard, J. M.; Tilley, T. D.; Woo, T. K. *Organometallics* **2001**, *20*, 1195−1203.

(7) This previously unreported compound is produced by treating (η^2-cyclooctene)(Cl)Ir(PMe$_3$)$_3$ (ref 13) with MeLi. Cyclooctene dissociates in solution, producing reactive "(Me)Ir(PMe$_3$)$_3$".

(8) Vinyldimethylsilane was synthesized by reacting chlorodimethylsilane with vinylmagnesium bromide in tetrahydrofuran. Its ^{1}H NMR spectrum matched the spectrum previously reported for this compound: Barton, T. J.; Wulff, W. D. *J. Organomet. Chem.* **1979**, *168*, 23−31.

(9) Milstein has used a similar Si−H bond activation strategy to produce silyl−iridium complexes. Milstein's starting material is (Me)Ir(PMe$_3$)$_4$, which loses PMe$_3$ to produce "(Me)Ir(PMe$_3$)$_3$". See: (a) Aizenberg, M.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 317−319. (b) Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 6456−6464.

10.1021/om700487n CCC: $37.00 © 2007 American Chemical Society
Publication on Web 06/30/2007

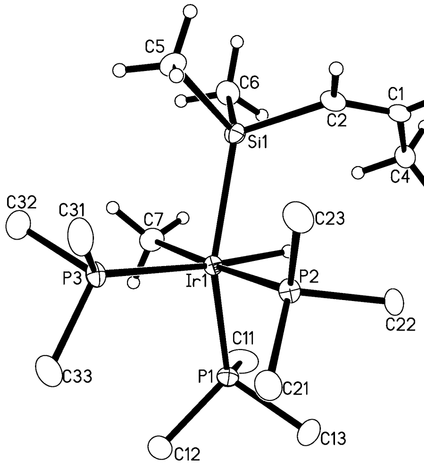
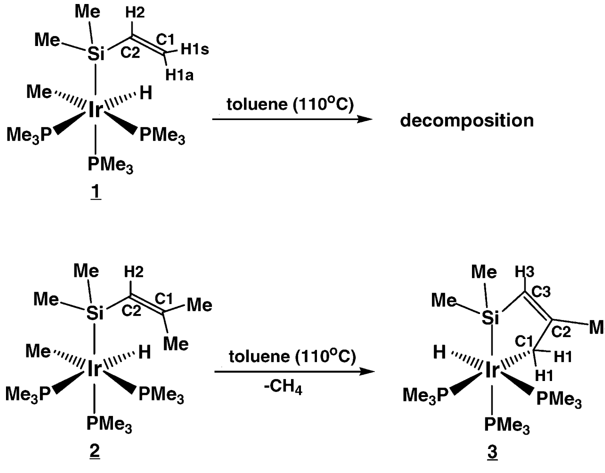


Figure 1. ORTEP drawing of **2**, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown. Selected bond distances (Å): Ir1−P1, 2.3466(10); Ir1−P2, 2.3018(10); Ir1−P3, 2.3216(11); Ir1−C7, 2.191(4); Ir1−H1, 1.71(4); Ir1−Si1, 2.4061(11); Si1−C2, 1.905(4); Si1−C5, 1.907(4); Si1−C6, 1.899(4); C1−C2, 1.343(5); C1−C3, 1.511(6); C1−C4, 1.511(6).

Scheme 2



the proposed structure. As shown in Figure 1, this structure has been confirmed by single-crystal X-ray diffraction. The coordination geometry about iridium is a distorted octahedron. The *trans*-diaxial silyl and phosphine ligands are noticeably tilted (angle Si1−Ir1−P1 = 151.33(4)°), apparently to avoid steric contacts. The facial arrangement of the phosphines allows for a direct comparison of the *trans* influence of the three opposing ligands. On the basis of the iridium−phosphorus bond distances (see caption to Figure 1), the opposing ligands exert a *trans* influence in the following order: Me < H < silyl.[10] Bonding within the η^1-silaallyl ligand is fully localized, as expected, and the Ir1−Si1−C2−C1 torsional angle is 65.3(4)°.

Given the *cis* relationship of the methyl and hydrido groups in the coordination geometry of **1** and **2**, we anticipated that heating these compounds might lead to release of methane, followed by coordination of the silaallyl π bond to produce an η^3-silaallyl ligand. However, as shown in Scheme 2, this was not the observed result. Heating of **1** in toluene led only to decomposition, while similar treatment of **2** produced the iridasilacyclopentene complex **3** in high yield. The mechanism of formation for **3** involves reductive elimination of methane from **2**, followed by oxidative addition across a methyl C−H bond of the dimethylvinyl group.[11] In the case of **1**, similar C−H bond activation (of C1−H1) would lead to a four-membered ring, but ring strain makes this a far less desirable outcome.

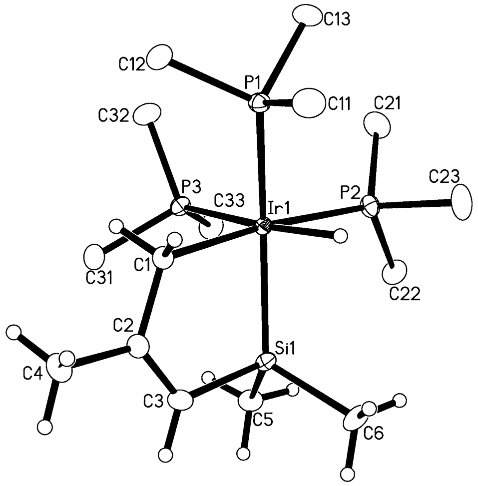
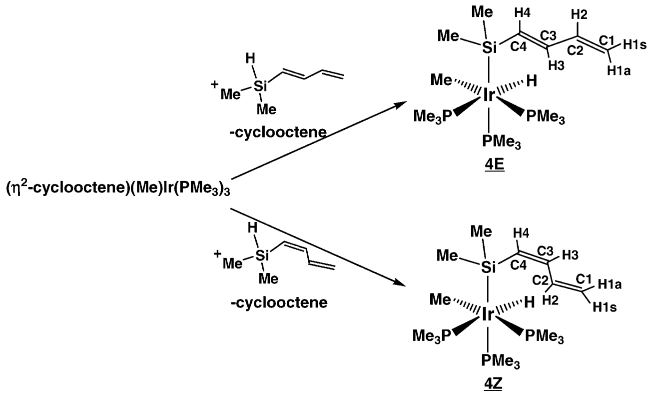


Figure 2. ORTEP drawing of **3**, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown. Selected bond distances (Å): Ir1−P1, 2.3473(6); Ir1−P2, 2.2931(6); Ir1−P3, 2.3107(6); Ir1−Si1, 2.3767(6); Ir1−C1, 2.176(2); C1−C2, 1.503(3); C2−C3, 1.333(4); C2−C4, 1.510(4); Si1−C3, 1.865(3); Si1−C5, 1.909(3); Si1−C6, 1.899(3).

Scheme 3



The $^{31}P\{^1H\}$ NMR spectrum of **3** consists of three separate dd patterns, indicative of a *fac*-octahedral geometry. In the ^1H NMR spectrum, olefinic H3 resonates at δ 6.06, the aliphatic H1's resonate at δ 2.5 and 1.8, and the metal-hydride appears as a characteristic ddd pattern at δ −11.90. In the $^{13}C\{^1H\}$ NMR spectrum, carbons C2 and C3 resonate at δ 164.8 and 137.0, respectively, while C1 appears at δ 11.6 and is strongly coupled to the *trans* phosphine (J_{C-P} = 65.6 Hz).

The X-ray crystal structure of **3** has been obtained and is shown in Figure 2. As with **2**, the coordination geometry around iridium is distorted octahedral with severe tilting of the Si1−Ir1−P1 axis (angle = 157.30(2)°). A comparison of the Ir−P bond distances (see Figure 2 caption) confirms that the alkyl group (C1) exerts the weakest *trans* influence, while the silyl group (Si1) exerts the strongest. The metallacycle is essentially planar (mean deviation = 0.018 Å) with the sum of the five internal angles totaling 539.9°.

As shown in Scheme 3, we were able to generate the first examples of silapentadienyl−metal complexes, **4E** and **4Z**, by

---

[10] A similar trend has been observed by Aizenberg and Milstein: see ref 9b.

[11] For other examples of cyclometalations to form iridasilacycles, see ref 9 and (a) Mitchell, G. P.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 5472−5474. (b) Aizenberg, M.; Milstein, D. *Organometallics* **1996**, *15*, 3317−3322.

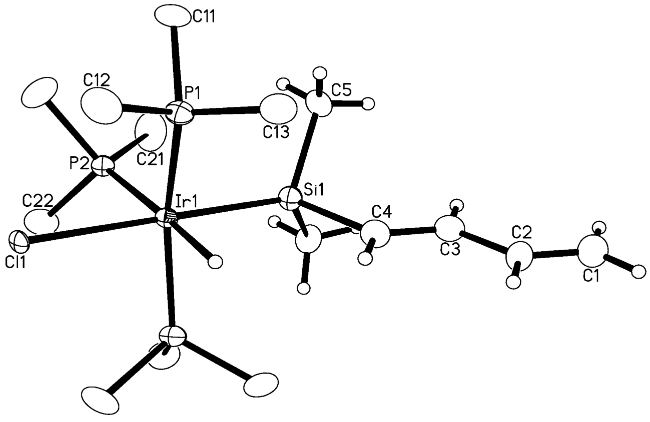
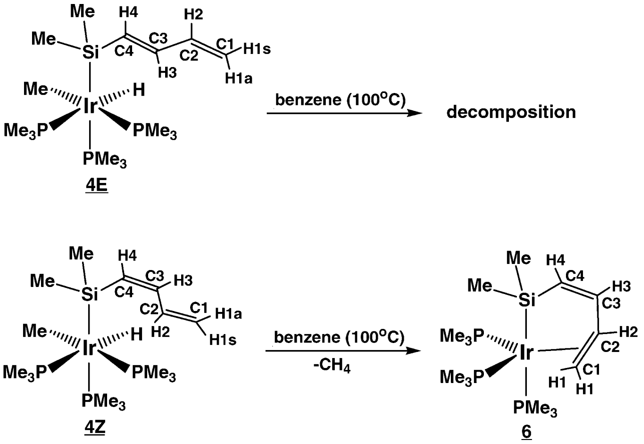


Figure 3. ORTEP drawing of **5E**, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown. Selected bond distances (Å): Ir1−P1, 2.3134(13); Ir1−P2, 2.3627(17); Ir1−Cl1, 2.5991(14); Ir1−H1, 1.77(10); Ir1−Si1, 2.343(2); Si1−C4, 1.910(8); Si1−C5, 1.901(5); C1−C2, 1.338(11); C2−C3, 1.443(10); C3−C4, 1.346(11).

Scheme 4



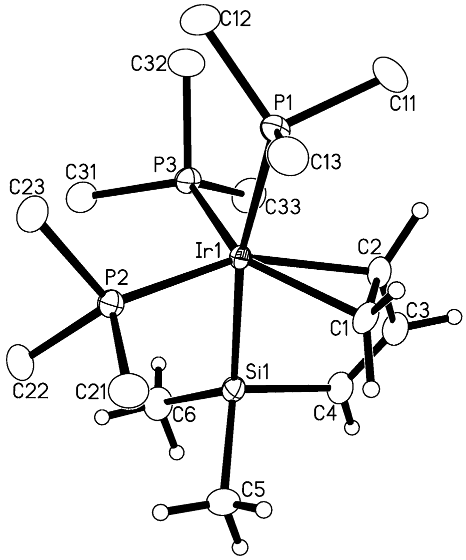


Figure 4. ORTEP drawing of **6**, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown. Selected bond distances (Å): Ir1−P1, 2.3593(7); Ir1−P2, 2.2830(5); Ir1−P3, 2.2884(6); Ir1−Si1, 2.4006(8); Ir1−C1, 2.145(2); Ir1−C2, 2.167(2); C1−C2, 1.464(3); C2−C3, 1.482(3); C3−C4, 1.341(3); Si1−C4, 1.870(2); Si1−C5, 1.896(2); Si1−C6, 1.897(3).

treating (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$ with *E*- or *Z*-butadienyldimethylsilane. These previously unknown silanes were synthesized by treating *E*- or *Z*-bromobutadiene[12] with *tert*-butyllithium and then with chlorodimethylsilane. The $^{31}P\{^1H\}$ NMR spectrum of **4E** displays the three dd patterns that characterize a *fac*-octahedral coordination geometry. In the ^1H NMR spectrum, all five chain hydrogens appear downfield at δ 6.80 (H3), 6.73 (H4), 6.61 (H2), 5.20 ($H1_a$), and 4.99 ($H1_s$), as expected for an η^1-silapentadienyl ligand. The large coupling between H3 and H4 ($J = 18.0$ Hz) is consistent with the *E*-stereochemistry of the C3−C4 double bond. The iridium-methyl group resonates at δ 0.30 and is a complex multiplet due to ^{31}P coupling, while the hydride appears at δ −12.18 as the familiar ddd pattern, again due to phosphorus coupling. In the $^{13}C\{^1H\}$ NMR spectrum, the chain carbons all resonate in the downfield region (δ 113.0−151.7), while the iridium-methyl resonates far upfield (δ −30.8) and exhibits strong coupling to the *trans* phosphine ($J_{C-P} = 62.2$ Hz). The NMR spectra of **4Z** bear a strong resemblance to those of **4E**, the key difference being the coupling between H3 and H4 on the silapentadienyl chain. In **4Z**, $J_{H3-H4} = 14.1$ Hz (as compared to 18.0 Hz in **4E**), indicating a *cis* relationship between H3 and H4.

Compounds **4E** and **4Z** proved difficult to crystallize, but we were able to obtain crystals of the chloro analogue, (η^1-dimethylsilapentadienyl)(H)(Cl)Ir(PMe_3)$_3$ (**5E**), by treating (η^2-cyclooctene)(Cl)Ir(PMe_3)$_3$[13] with *E*-butadienyldimethylsilane. As is evident from the ORTEP drawing in Figure 3, compound **5E** crystallizes as the *mer* isomer with the chloro ligand oriented *trans* to the silyl ligand and the hydride ligand *trans* to a phosphine (P2). The molecule resides on a crystallographically imposed mirror plane that includes Cl, P2, Ir1, and the entire silapentadienyl chain. All of the bonds along the chain are oriented in a *transoid* fashion, so the torsional angles are all 180°. Bonding within the chain is localized, giving rise to the expected long−short−long−short pattern (see Figure 3 caption).

Upon heating in benzene at 100 °C (under pressure), compound **4E** decomposed. In contrast, under exactly the same conditions, compound **4Z** cleanly converted to (η^1,η^2-dimethylsilapentadienyl)Ir(PMe_3)$_3$ (**6**, Scheme 4) by loss of methane and coordination of the terminal double bond of the silapentadienyl ligand. The decomposition of **4E** can be readily understood by noting that the *E*-stereochemistry about C3═C4 prevents C1═C2 from coordinating to iridium. In addition, **4E** possesses no attractive targets for C−H bond activation; the only bond that presents itself to the iridium center is C3−H3, which, if activated, would lead to a highly strained four-membered ring.

In the ^1H NMR spectrum of **6**, H3 and H4 remain downfield (at δ 7.65 and 5.88, respectively), while H2 and the two H1's move significantly upfield from their positions in precursor **4Z** (to δ 2.52, 1.76, and 1.63, respectively). These upfield chemical shifts indicate aliphatic character, which in turn implies substantial back-bonding from the electron-rich iridium center into the C1═C2 π^* orbital. These same trends are mirrored in the ^{13}C NMR spectrum, where C3 and C4 resonate at δ 159.0 and 133.1, respectively, while C2 and C1 are shifted upfield to δ 39.0 and 24.1, respectively. Both C1 and C2 show sizable coupling to phosphorus.

The X-ray crystal structure of **6** has been obtained and is shown in Figure 4. The coordination geometry around iridium

---

(12) Keegstra, M. A.; Verkruijsse, H. D.; Andringa, H.; Brandsma, L. *Synth. Commun.* **1991**, *21*, 721−726.

(13) Herskovitz, T.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 1615−1616. Cyclooctene dissociates in solution, producing the reactive "(Cl)Ir(PMe_3)$_3$".

is intermediate between octahedral and trigonal bipyramidal; the key P2−Ir−P3 angle is 105.56(2)°. The silicon atom occupies an axial position, while C1 and C2 lie in the molecule's equatorial plane. As predicted from the NMR data, bond C1−C2 has lengthened significantly to a value of 1.464(3) Å as a result of π back-bonding, while C3−C4 retains its double-bond character (1.341(3) Å). Atoms Ir1, Si1, C4, C3, and C2 form a roughly planar iridasilacyclopentene ring (mean deviation = 0.10 Å) with C1 lying 1.44 Å out of this plane.

Previously, we reported the isolation and characterization of the pentadienyl,[14] oxapentadienyl,[15] and thiapentadienyl[16] analogues of **6**. While (η^1,η^2-pentadienyl)Ir(PMe_3)$_3$ is stable upon heating, the oxapentadienyl and thiapentadienyl compounds both undergo C−H bond activation processes, leading ultimately to five-membered metallacycles. Like the pentadienyl compound, **6** shows no tendency to undergo C−H bond activation, even upon heating in toluene at reflux for extended periods. The thermal stability of **6** is probably a consequence of the very strong interaction between C1═C2 and the iridium center.

In conclusion, we have reacted (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$ with vinyl- and butadienylsilanes to produce the first examples of silaallyl− and silapentadienyl−iridium complexes. Because these molecules possess *cis* methyl and hydrido groups (in addition to the silyl ligands), heating causes release of methane and the production of reactive 16e$^-$ silyl intermediates. These species undergo a variety of reactions, including C−H bond activation to produce a five-membered iridasilacycle, C═C bond coordination to generate the η^1,η^2-silapentadienyl ligand, and decomposition. A complete reactivity study of these and related molecules is now underway.

Acknowledgment. Support from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Washington University's High-Resolution NMR Service Facility was funded in part by NIH Support Instrument Grants (RR-02004, RR-05018, and RR-07155). The regional X-ray Facility at the University of Missouri−St. Louis was funded in part by the National Science Foundation's MRI Program (CHE-0420497). Mass spectrometry was provided by the Washington University Mass Spectrometry Resource with support from the NIH National Center for Research Resources (Grant No. P41RR0954).

Supporting Information Available: Detailed synthetic procedures for compounds **1** through **6**, including spectroscopic data; structure determination summaries and listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, and torsional angles for compounds **2**, **3**, **5E**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700487N

---

[14] Bleeke, J. R.; Boorsma, D.; Chiang, M. Y.; Clayton, T. W., Jr.; Haile, T.; Beatty, A. M.; Xie, Y.-F. *Organometallics* **1991**, *10*, 2391−2398.

[15] (a) Bleeke, J. R.; Haile, T.; Chiang, M. Y. *Organometallics* **1991**, *10*, 19−21. (b) Bleeke, J. R.; Haile, T.; New, P. R.; Chiang, M. Y. *Organometallics* **1993**, *12*, 517−528.

[16] (a) Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1992**, *11*, 2740−2743. (b) Bleeke, J. R.; Ortwerth, M. F.; Rohde, A. M. *Organometallics* **1995**, *14*, 2813−2826.