isotropic elastic constants with the Young modulus E = 84 GPa and Poisson's ratio $\nu = 0.3$.
23. At 292 K, the voltage-current (V-I) curve above threshold was modeled by $U = U_0 + R \times I$, with U_0 = 5.34 V and R = 5.87 ohm.
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25. Computed with the formula used in (*11*), with the following parameters (at 300 K): period length L_p = 60 nm; dipole matrix element z = 3 nm; intersubband lifetimes τ_{32} = 1.45 ps, τ_3 = 0.52 ps, and an effective τ_2 = 0.5 ps; overlap factor Γ_p = 0.0183; broadening of the transition $2\gamma_{32}$ = 22 meV; and effective index n_{eff} = 3.2 and $n_{th} = 8 \times 10^8$ cm^{-2}.
26. We gratefully acknowledge M. Ebnöther for technical assistance with the lateral InP regrowth. Financially supported by the Swiss National Science Foundation and the Science Foundation of the European Community under IST project SUPERSMILE.

20 September 2001; accepted 20 November 2001
Published online 20 December 2001;
10.1126/science.1066408
Include this information when citing this paper.

Remarkably Selective Iridium Catalysts for the Elaboration of Aromatic C–H Bonds

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Arylboron compounds have intriguing properties and are important building blocks for chemical synthesis. A family of Ir catalysts now enables the direct synthesis of arylboron compounds from aromatic hydrocarbons and boranes under "solventless" conditions. The Ir catalysts are highly selective for C–H activation and do not interfere with subsequent in situ transformations, including Pd-mediated cross-couplings with aryl halides. By virtue of their favorable activities and exceptional selectivities, these Ir catalysts impart the synthetic versatility of arylboron reagents to C–H bonds in aromatic and heteroaromatic hydrocarbons.

Carbon-carbon bonds are the molecular "bricks and mortar" from which diverse architectures in living organisms and man-made materials are constructed. As the field of organic chemistry has evolved, numerous methods for carbon-carbon bond construction have been developed, ranging from classic examples, like the Diels-Alder reaction, to more recent metal-catalyzed processes, such as olefin polymerizations and metatheses.

Biaryl subunits and their heteroaromatic analogs are abundant in natural and synthetic materials, and controlled methods for linking aromatic rings via C–C sigma bonds have long been pursued by organic chemists. Activity in this regard intensified in the late 1970s, during which Pd-catalyzed methods for C–C bond construction emerged (*1*). First disclosed by Miyaura and Suzuki, the Pd-catalyzed coupling of an arylboronic acid and an aryl halide (Y = OH, X = halide)

$$\mathrm{Ar^1{-}BY_2 + Ar^2{-}X \xrightarrow{[Pd]} Ar^1{-}Ar^2 + X{-}BY_2} \tag{1}$$

has become a method of choice for preparing biaryls because it is performed under mild conditions that are tolerant of diverse functionality (*2*). Subsequent developments in metal-catalyzed cross-couplings of organoboron compounds and organic halides have yielded practical C–C bond forming strategies that complement existing methodology (*3*). Today, the Miyaura-Suzuki reaction is routinely applied in high-throughput screening for drug discovery (*4*), in the final steps of convergent natural product syntheses (*5*), and in the synthesis of conjugated organic materials (*6*).

Arylboron reagents are typically synthesized in a multistep process such as that depicted in Fig. 1A. Shorter routes that avoid undesirable halogenated aromatic intermediates would be attractive. To this end, theoretical estimates of B–H and B–C bond enthalpies gave credence to organoborane synthesis via the thermal dehydrogenative coupling of B–H and C–H bonds (Fig. 1B) (*7*). Some key steps in putative catalytic cycles for this process had been established in reports by Hartwig and co-workers (*8*) and Marder and co-workers (*9*) of stoichiometric borylations of arenes, alkenes, and alkanes by metal boryl complexes (M–BR$_2$). Whereas Hartwig and co-workers developed elegant photochemical methods for hydrocarbon borylation using catalytic amounts of metal complexes (*10*), thermal, catalytic borylations of unactivated hydrocarbons were not documented before our report in 1999 (*11*).

Our initial work was inspired by Bergman's (*12*) and Jones's (*13*) fundamental studies of hydrocarbon (R–H, where R = alkyl or aryl) activation by Cp*(PMe$_3$)M$^{\mathrm{I}}$ intermediates (where M = Ir, Rh; Cp* = η^5-C$_5$Me$_5$), which produce Cp*(PMe$_3$)M$^{\mathrm{III}}$(H)(R) where M–H and M–R bonds result from R–H scission. While investigating stoichiometric B–C bond formation in reactions between Cp*(PMe$_3$)Ir(H)(Ph) and pinacolborane (HBPin), we noticed that substantial quantities of arylboron products were produced from catalytic solvent activation. The major metal-containing product in this reaction, Cp*(PMe$_3$)Ir(H)(BPin) (**1**), was a precatalyst for benzene borylation with an effective turnover number (TON) corresponding to the formation of three molecules of Ph-BPin per molecule of **1** (*11*). Subsequently, Hartwig and co-workers reported alkane and arene borylations with the use of much more active Rh precatalysts, such as Cp*Rh(η^4-C$_6$Me$_6$) (**2**) (*14*).

A comparison of precatalysts **1** and **2** in borylations of various substituted arenes revealed that the Ir system was more selective toward arene C–H activation (*15*). Given the importance of selectivity in chemical synthesis, these findings spurred a detailed investigation of the original Ir system.

Compound **1** was stable in benzene solutions after prolonged thermolysis, which eliminates several mechanistic possibilities, including PMe$_3$ dissociation to generate Cp*Ir(H)(BPin), an analog of proposed intermediates in the Rh system. However, added PMe$_3$ strongly inhibited catalysis where HBPin was present. This finding raised the possibility that small quantities of phosphine-free Ir$^{\mathrm{V}}$ species could be active. Because Cp*IrH$_{4-x}$(BPin)$_x$ species (where x = 1, 2) form in the thermolysis of Cp*IrH$_4$ and HBPin (*16*), anisole borylations with identical loadings of Cp*IrH$_4$ and **1** were compared. From this experiment, Cp*IrH$_{4-x}$(BPin)$_x$ intermediates could be eliminated because they are not kinetically competent for catalysis and because the borylation regioselectivities for Cp*IrH$_4$ and **1** differed substantially (*17*).

Exclusion of a simple phosphine dissociative pathway narrows the plausible catalysts to two choices: (i) Ir phosphine species arising from Cp* loss or (ii) species where both Cp* and PMe$_3$ have been lost. The latter possibility is

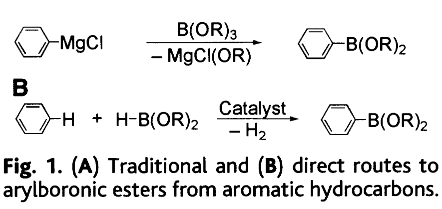

Fig. 1. (**A**) Traditional and (**B**) direct routes to arylboronic esters from aromatic hydrocarbons.

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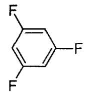
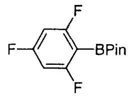
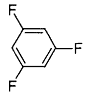
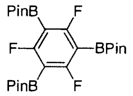
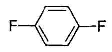
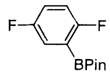
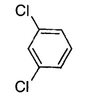
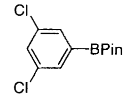
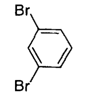
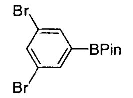
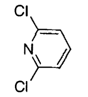
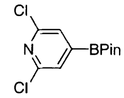
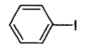
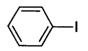
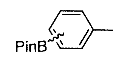
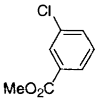
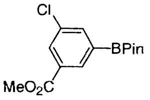
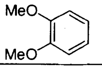
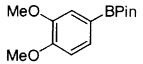
*To whom correspondence should be addressed. E-mail: smithmil@msu.edu intriguing in light of Marder's syntheses of (η^6-arene)Ir(BCat)$_3$ complexes (where Cat = *ortho*-catecholate) from (Ind) Ir(COD) (**3**, where Ind = η^5-C_9H_7, COD = 1,5-cyclooctadiene) and HBCat in arene solvents (*9*). Using an analogous route, we prepared (η^6-mesitylene)Ir(BPin)$_3$ (**4**) in 19% yield from (Ind)Ir(COD) and HBPin (*18*). Compound **4** reacts with benzene at 150°C to produce Ir metal and three equivalents (equiv.) of C_6H_5BPin, but does not catalyze C_6H_5BPin formation from benzene and HBPin. Thus, it appears that phosphines or related donor ligands are required for catalysis.

Using the lability of the mesitylene ligand in **4**, Ir phosphine species can be generated in situ from **4** and appropriate phosphines and can subsequently be screened for activity. Borylation with the use of 2 mol% **4** and 4 mol% PMe$_3$ is viable (Fig. 2, entry 1), and both catalytic activity and TONs for benzene borylation increase dramatically relative to precatalyst **1**. Borylation rates are appreciable when [P]:[Ir] $< 3:1$ but decrease dramatically when the [P]:[Ir] ratio equals or exceeds 3:1.

The low isolated yields of **4** hampered screening efforts and precluded practical applications despite the dramatic improvement in catalytic activity. Hence, we sought alternative means for generating active catalysts. Because nuclear magnetic resonance (NMR) spectra indicated virtually quantitative generation of **4** from **3**, in situ generation of active catalysts by phosphine addition to **3** were examined (*19*). This approach was successful, and results for benzene borylations are shown in Fig. 2 (entries 2 to 5). Chelating phosphines substantially increase activity and TONs as highlighted for 1,2-bis(dimethylphosphino)ethane (dmpe), where the effective TON of 4500 (entry 5) represents an improvement of more than 1000-fold over precatalyst **1**. In addition, active catalysts can be generated from commercially available sources such as [IrCl(COD)]$_2$ (entry 6).

If the primary active species generated by PMe$_3$ addition to **3** and **4** are identical to those generated from **1**, borylations of substituted benzenes should exhibit similar regio- and chemoselectivities. Anisole is a useful substrate for probing regioselectivity, and the meta:para ratios determined from borylations by active species generated by PMe$_3$ addition to **3** and **4** are similar to those for **1** (*20*). To assess chemoselectivities, the ratios of arene to benzylic activation in *m*-xylene were examined. The selectivities of catalysts generated from **3** (13:1) and **4** (12:1) are diminished relative to the selectivity of precatalyst **1** (35:1). Nevertheless, the Ir catalysts are more selective for arene activation than the Rh catalyst, **2**, where the selectivity is 7:1 (*15*, *21*), and the addition of one equiv. of the chelating phosphine, 1,2-bis(diphenylphosphino)ethane (dppe) per equivalent of **3** or **4** generates catalysts where the arene to benzylic selectivities exceed 142:1.

Entry	Substrate	Arene:HBPin	Product	Catalyst	Ligand	Temp. (°C)	Time (h)	Yield (%)
1	C_6H_6	16:1	PhBPin	(MesH)Ir(BPin)$_3$ (**4**)	PMe$_3$	150	15	98*
2	C_6H_6	16:1	PhBPin	(Ind)Ir(COD) (**3**)	PMe$_3$	150	18	88*
3	C_6H_6	16:1	PhBPin	**3**	dppe	150	2	95*
4	C_6H_6	16:1	PhBPin	**3**	dmpe	150	2	84
5	C_6H_6	16:1	PhBPin	0.02 mol% **3**	dmpe	150	61	90*
6	C_6H_6	16:1	PhBPin	[IrCl(COD)]$_2$	dmpe	150	8	74*
7		4:1		**3**	dmpe	150	1	63
8		1:5		**3**	dmpe	150	62	76
9		4:1		**3**	dppe	100	3	81
10		1:1.5		**3**	dppe	100	14	89
11		1:1.5		**3**	dppe	100	17	92
12†		1:2		**3**	dppe	100	4	69
13		10:1	--	**3**	dppe	100	60	--
14		10:1	 *m*:*p* = 79:21	**4**	dppe	100	57	77
15†		1:2		**3**	dppe	100	25	95
16†		1:3		**3**	dmpe	150	95	62

* GC yield based on HBPin.

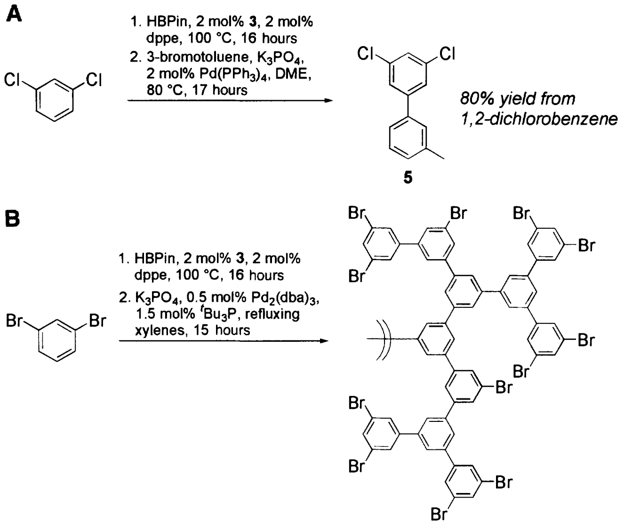
† Reactions run in cyclohexane.

Fig. 2. Ir-catalyzed aromatic borylations. Reactions run in neat arene, [Ir] = 2 mol%, [P]:[Ir] = 2:1, and yields are reported for isolated materials unless otherwise noted.

Dramatic differences in chemoselectivities between Ir and Rh catalysts were found for halogenated substrates, where the Ir catalysts preferentially activate C–H bonds (*22*). Thus, good yields of mono- or triborylated products of 1,3,5-trifluorobenzene are obtained by adjusting the arene:HBPin ratio (Fig. 2, entries 7 and 8). In contrast, previous attempts to effect multiple borylations of 1,3,5-trifluorobenzene with the use of the Rh catalyst **2** led to increased defluorination (*15*). Borylations of arenes with heavier halogen substituents provide an even starker contrast between Ir and Rh catalysts. For example, Ir-catalyzed borylations of 1,3-dichlorobenzene and 1,3-dibromobenzene generate meta-functionalized products in high yields (entries 10 and 11), whereas dehalogenation is the dominant pathway in Rh-catalyzed reactions (*23*). The finding that aromatic C–Br bonds survive in the Ir-catalyzed reactions contrasts Pd-catalyzed reactions of boranes and aryl bromides, where the C–Br bonds are converted to C–B or C–H bonds (*24*). Entry 12 illustrates an extension of meta-selective borylation to a halogenated heterocycle.

Because aryl iodides have the weakest carbon-halogen bonds, they are most susceptible to reductive cleavage by transition metals. Hence, it is not surprising that the Ir catalysts generated from **3** are ineffective in aromatic borylation of iodobenzene (Fig. 2, entry 13). However, iodobenzene and HBPin reacted smoothly to yield a mixture of C_6H_4I(BPin) isomers when active catalysts are generated from the Ir^{III} source, **4**, and dppe (entry 14). Thus, Ir catalysts are compatible with the entire range of aryl halides. In addition, functional group tolerance that was previously found in Rh-catalyzed borylations extends to Ir-catalyzed reactions (namely, ester compatibility in entry 15), and Ir catalysts selectively borylate symmetrical 1,2-substituted

Fig. 3. Examples of one-pot C–H activation and cross-coupling reactions as applied to (**A**) biaryl and (**B**) polyphenylene syntheses.



arenes at the 4-position (entry 16) (*25*). Lastly, as we recently demonstrated for Rh-catalyzed borylations, cyclohexane can function as an inert solvent (entries 12, 15, and 16), which is useful in borylations of more valuable substrates (*25*).

The remarkable selectivity of Ir borylation catalysts for aromatic C–H bonds suggested that Ir byproducts might not interfere in subsequent reactions of the arylboron products. Thus, we envisaged one-pot elaborations of arene C–H bonds, where catalytic borylations are followed by other metal-catalyzed events in a catalytic cascade (*26*). To assess this possibility, the union of catalytic borylations and Miyaura-Suzuki cross-couplings for one-pot biaryl synthesis from C–H and C–X precursors was attempted. As shown in Fig. 3A, the biaryl product **5** was prepared in good yield from the in situ Pd-catalyzed cross-coupling of 3-bromotoluene with 1,3,5-$C_6H_3Cl_2(BPin)$, generated by Ir-catalyzed borylation of 1,3-dichlorobenzene with HBPin. An interesting extension of Ir-Pd tandem catalysis that highlights Ir compatibility with halogenated aromatics is shown in Fig. 3B. The specific target was a hyperbranched polyphenylene that Kim and Webster prepared via Pd-catalyzed coupling of the bromo-boronic acid monomer, 1,3,5-$C_6H_3Br_2(B(OH)_2)$ (*27*). Using Ir-Pd tandem catalysis, material with virtually identical NMR (^{13}C, ^{1}H) and gel permeation chromatography (GPC) data was obtained from HBPin and 1,3-dibromobenzene in a one-pot reaction (*28*).

From a mechanistic standpoint, catalytic cycles involving oxidative addition or reductive elimination from $Ir^{I/III}$ and/or $Ir^{III/V}$ intermediates are potentially consistent with the present results. Within this context, we considered Ir^{I} and Ir^{III} boryl intermediates to be the most likely C–H activating species in the $Ir^{I/III}$ and $Ir^{III/V}$ cycles, respectively. Hence, the Ir^{I} and Ir^{III} boryl complexes, $[Ir(BPin)(PMe_3)_4]$ (**6**) and *fac*-$[Ir(BPin)_3(PMe_3)_3]$ (**7**), were prepared in order to evaluate their stoichiometric reactions with arenes (*29*). Indeed, compounds **6** and **7** both reacted cleanly with benzene to produce PhBPin and the corresponding hydride complexes shown in Eqs. 2 and 3, consistent with the notion that Ir^{I} or Ir^{III} species can effect arene borylation. However, the arene products from stoichiometric reactions of **6** and **7** with iodobenzene differ substantially. Specifically, compound **6** reacted rapidly with iodobenzene at room temperature, but isomers of $C_6H_4I(BPin)$ were not detected, even after prolonged thermolysis. Conversely, thermolysis of **7** in iodobenzene produced *m*- and *p*-$C_6H_4I(BPin)$ in 54% yield, in addition to a 45% yield of PhBPin.

$$\underset{\mathbf{6}}{[Ir(BPin)(PMe_3)_4]} + C_6H_6 \rightarrow [Ir(H)(PMe_3)_4] + C_6H_5BPin \quad (2)$$

$$\underset{\mathbf{7}}{fac\text{-}[Ir(BPin)_3(PMe_3)_3]} + C_6H_6 \rightarrow fac\text{-}[Ir(BPin)_2(H)(PMe_3)_3] + C_6H_5BPin \quad (3)$$

Because conversion rates in catalytic reactions plummeted when [P]:[Ir] ratios equaled or exceeded 3:1, the observation that **6** and **7** were not kinetically competent for catalysis was expected. This finding does not prove that the intermediates involved in the stoichiometric and catalytic reactions are different, because the generation of the respective intermediates under catalytic conditions could simply be more efficient. Nevertheless, the stoichiometric transformations lend credence to either Ir^{I} or Ir^{III} species mediating C–H activation under catalytic conditions. Furthermore, the reactions of **6** and **7** with iodobenzene indicate that the reactive intermediates generated from the Ir^{I} and Ir^{III} sources can differ significantly.

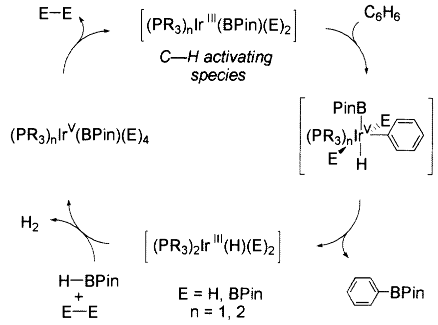


Fig. 4. A putative mechanism for aromatic borylations catalyzed by Ir boryl complexes.

Although the present data do not categorically eliminate a mechanism involving Ir^{I} intermediates, we presently favor the simplified scheme involving Ir^{III} and Ir^{V} intermediates (Fig. 4) for three reasons, as follows: (i) Borylation products of iodobenzene are not obtained when Ir^{I} sources are used under stoichiometric or catalytic conditions, whereas Ir^{III} complexes effect both stoichiometric and catalytic borylations. (ii) Improved catalytic activity is observed with chelating phosphines and inhibition is observed when [P]:[Ir] ratios equal or exceed 3:1, strongly supporting the viability of bisphosphine intermediates (Fig. 4, n = 2), which could be generated via E–E reductive elimination (E = H, BPin) from an 18-electron bisphosphine Ir^{V} resting state. (iii) The 18-electron bisphosphine compound, $Ir(PMe_3)_2H_5$, is an effective precatalyst for borylation. A more definitive characterization of the catalytic manifold is under way (*30*).

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17. At 150°C, the following isomer ratios were obtained for anisole borylation with 20 mol% precatalyst loadings: Cp^*IrH_4, *o*:*m*:*p* = 3:49:48; **1**, *o*:*m*:*p* = 2:79:19.
18. Compound **4** has been prepared as an analytically pure white solid. Relevant spectroscopic data include: ^1H NMR (C_6D_6) δ 1.33 (s, 36 H, $BO_2C_6H_{12}$), 2.23 (s, 9 H, $C_6H_3(CH_3)_3$), 5.62 (s, 3 H, $C_6H_3(CH_3)_3$); ^{11}B NMR (C_6D_6) δ 32.5; ^{13}C NMR (C_6D_6) δ 19.68, 25.73, 80.95, 96.97, 118.05.
19. Compound **3** is synthesized in 86% yield from indenyl lithium and $[IrCl(COD)]_2$ [J. S. Merola, R. T. Kacmarcik, *Organometallics* **8**, 778 (1989)].
20. For catalysts generated from 4 mol% PMe_3 and 2 mol% **3** or **4**, isomer ratios were obtained for anisole borylation at 150°C as follows: **3**, *o*:*m*:*p* = 9:74:17; **4**, o:*m*:*p* = 8:75:17. For **3** and **4**, ortho borylation increases slightly, which could signify a minor pathway that is not accessible from **1**.
21. A Rh catalyst that is highly selective for benzylic borylation has been recently reported [S. Shimada, A. S. Batsanov, J. A. K. Howard, T. B. Marder, *Angew. Chem. Int. Ed. Engl.* **40**, 2168 (2001)].
22. A representative procedure for borylation is given for entry 10 of Fig. 2. In a glove box under N_2, compound **3** (57 mg, 0.14 mmol) and dppe (54 mg, 0.14 mmol) were dissolved in HBPin (1.30 g, 10.2 mmol). The solution was transferred to a thick-walled air-free flask containing 1,3-dichlorobenzene (1.00 g, 6.80 mmol). The clear yellow solution was heated at 100°C under N_2 and monitored by GC-flame ionization detection (GC-FID). After 14 hours, the reaction mixture was pumped down to obtain a brown oil, which was vacuum distilled at 93° to 94°C (0.03 mm Hg). The resulting oil was then dissolved in Et_2O (10 ml) and washed with H_2O (5 × 100 ml). After drying over $MgSO_4$, ether was removed under high vacuum to give 1.65 g (89% yield) of colorless 1,3,5-$C_6H_3Cl_2$BPin (melting point, 36° to 38°C). NMR values are as follows: ^1H (500 MHz, $CDCl_3$) δ 1.32 (s, 12 H), 7.41 (t, *J* = 2.0 Hz, 1 H), 7.63 (d, *J* = 2.0 Hz, 2 H); ^{13}C (125 MHz, $CDCl_3$) δ 24.82, 84.49, 131.1, 133.7, 134.7; ^{11}B ($CDCl_3$) δ 30.
23. Dechlorination was observed during attempted silylations of 1,3-dichlorobenzene with the use of closely related Rh catalysts [K. Ezbiansky *et al.*, *Organometallics* **17**, 1455 (1998)].
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28. For the material in Fig. 3B, the weight-average molecular weight M_w = 6374 and the number-average molecular weight M_n = 3460, compared with the previously reported values of M_w = 5750 and M_n = 3820 (*27*).
29. Compounds **6** and **7** have been fully characterized, and details will be reported separately. The following spectroscopic data are included: **6**, ^1H NMR (C_6D_6, 25°C) δ 1.24 (s, 12H), 1.58 (b, 36H); ^{11}B NMR (C_6D_6) δ 38; $^{31}P\{^1H\}$ NMR (C_6D_6) δ −57.5. 7, ^1H NMR (C_6D_6) δ 1.34 (s, 36 H), 1.52 (m, 27 H); ^{11}B NMR (C_6D_6) δ 36.0; $^{31}P\{^1H\}$ NMR (C_6D_6) δ −64.
30. We thank A. Odom for stimulating discussions and C. Radano for assistance with polymer characterization. Supported by the NIH-NIGMS (grant R01 GM63188-01 to M.R.S.), the NSF (grant CHE-9817230 to M.R.S.), the Michigan Life Sciences Corridor Fund (to R.E.M. and M.R.S), and the Yamanouchi USA Foundation (to D.H. and R.E.M.).

12 October 2001; accepted 13 November 2001
Published online 22 November 2001;
10.1126/science.1067074
Include this information when citing this paper.

Synthesis and Structure of Formally Hexavalent Palladium Complexes

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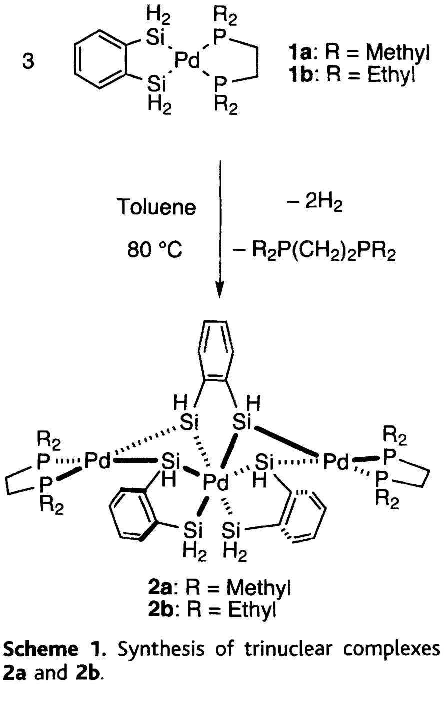
Formally hexavalent palladium complexes have been isolated and structurally characterized for the first time. Thermal condensation reaction of three molecules of 1,2-$C_6H_4(SiH_2)_2Pd^{II}(R_2PCH_2CH_2PR_2)$ (where R is defined as a methyl or ethyl) provided trinuclear palladium complexes. Single-crystal x-ray analysis revealed that each of the central palladium atoms of the complexes is ligated by six silicon atoms and is hexavalent, whereas the other palladium atoms are divalent.

The highest oxidation state theoretically attainable for an element is the total number of valence shell electrons. However, most transition metals of group 8 or later cannot attain their maximum oxidation states (*1*, *2*). For group 10 metals (platinum, palladium, and nickel), the highest oxidation state known in an isolable compound is metal(VI) and is attained only for platinum as $Pt^{VI}F_6$, which was first synthesized in 1957 (*3*) and has been the subject of many experimental and theoretical studies (*4*–*6*). High-oxidation-state compounds are generally less stable for the elements of the first and second transition series than those of the third transition series, and no structurally characterized metal(V) and metal(VI) complexes are known for palladium and nickel (*1*, *2*), although electrochemical formation of $Pd^{VI}O_3$ has been discussed (*7*, *8*).

Palladium is one of the most versatile transition metal catalysts for the transformation of organic and heteroatom compounds as well as for the treatment of vehicle exhaust gas. Although palladium generally prefers lower oxidation states (Pd^0 or Pd^{II}) (*9*), recent studies showed the importance of a higher oxidation state (Pd^{IV}) in catalytic processes (*10*, *11*). The highest-oxidation-state compounds of transition metals are often attained with highly electronegative ligands, such as fluorides or oxides, for example, PtF_6, IrF_6, RhF_6, OsO_4, and RuO_4 (*1*, *6*). Recently, several examples of high-oxidation-state complexes with silyl ligands, which are more electropositive than fluoride or oxide ligands, have been reported (*12*–*15*), although the oxidation states in these complexes are rather formal ones because M-Si (where M-metal) bond is much less ionic than M-F and M-O bonds. We also have found that a bidentate silyl ligand can stabilize silyl complexes of Pt^{IV}, Pd^{IV}, and Ni^{IV}, which are unusually thermally stable (*16*–*19*). On the basis of these results, we designed a new tridentate silyl ligand (*20*) to attain higher-oxidation-state silyl transition-metal complexes. Although the attempt to obtain a hexavalent silylplatinum complex by using the tridentate silyl ligand was not successful (*21*), we succeeded unexpectedly in isolating formally hexavalent palladium complexes as trinuclear ones by the trimerization reaction of Pd^{II} complexes bearing the bidentate silyl ligand.

The trinuclear palladium complex **2a** was obtained by the condensation reaction of three molecules of palladium complex, 1,2-$C_6H_4(SiH_2)_2Pd^{II}$(dmpe) **1a** [where dmpe = 1,2-bis(dimethylphosphino)ethane], in toluene at 80°C for 2 days (Scheme 1) (*22*). Complex **2a** was isolated as red crystals in 28% yield from the reaction mixture by keeping the mixture at room temperature. Com-



Scheme 1. Synthesis of trinuclear complexes **2a** and **2b**.

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