Si–H Bond Activation by Electrophilic Phosphinidene Complexes

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The terminal electrophilic phosphinidene complex [CpFe(CO)₂{PN-i-Pr₂}]AlCl₄ (2), generated via chloride abstraction from [CpFe(CO)₂{P(CN-i-Pr₂)}] (1), reacts with primary, secondary, and tertiary silanes to form the silyl phosphine complexes [CpFe(CO)₂{P(H)SiR₃N-i-Pr₂}]AlCl₄ (3, SiR₃ = SiPh₂H; 4, SiR₃ = SiPh₂H; 5, SiR₃ = SiEt₃), in which the phosphinidene has inserted into the Si–H bond. A computational study shows that the insertion is concerted and has a triangular transition state. The silyl phosphine complexes 3–5 are very susceptible to nucleophilic attack, which leads to P–Si bond cleavage and formation of the bridging phosphido complex [{CpFe-(CO)}₂(μ-CO){μ-P(H)N-i-Pr₂}]AlCl₄ (6).

Introduction

Transition metal terminal phosphinidene complexes can be considered analogous to transition metal carbene complexes, and like carbenes, their reactivity ranges between nucleophilic and electrophilic extremes. Stable nucleophilic phosphinidenes have been known since 1987, and characteristic reactivity of nucleophilic phosphinidenes includes [2+2] cycloaddition, nucleophilic attack by P, and protonation at P. The first electrophilic phosphinidenes were transient species generated in situ, and their reactivity has been well studied using trapping reactions with a wide variety of reagents. Characteristic reactions of electrophilic phosphinidenes include nucleophilic attack at P, [1+2] cycloadditions with unsaturated substrates, and bond insertions. In particular, insertion reactions of phosphinidenes into O–H and N–H bonds, strained C–N and C–O bonds, carbon–transition metal bonds, and carbon–halogen bonds have been described. A few isolated examples of C–H activation by terminal phosphinidene complexes have also been observed. Of these bond activation reactions, the one with the most potential synthetic utility is C–H activation. Carbene complexes, particularly transient carbene complexes generated by diazoalkane decomposition, undergo bond insertion reactions, and these reactions form the basis of a well-established synthetic methodology. More recently, stable electrophilic phosphinidenes have been isolated, however, their reactivity is not yet as well studied as that of the transient phosphinidenes. Here we discuss bond insertion reactions of the stable electrophilic terminal phosphinidene complex [CpFe(CO)₂{PN-i-Pr₂}]AlCl₄. It belongs to a class of cationic phosphinidene complexes generated by chloride abstraction from chloro-phosphido ligands. These complexes are thermally stable and isolable, being stabilized by a heteroatom substituent that acts as a π-donor to the electron-deficient phosphorus atom. In contrast to the transient phosphinidenes W(CO)₅PR, which are generated by thermal decomposition of precursor complexes, stable, isolable phosphinidene complexes allow us to carry out reactions at room temperature or lower. Lower temperature reactions allow us to take a more detailed look at the mechanism of bond insertion reactions and can also be expected to lead to different reactivity. However, the

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stability of these complexes also has the disadvantage of lowering the reactivity, and the stabilized phosphinidenes are not generally electrophilic enough to activate C−H bonds directly. As a result, we looked for analogous but weaker X−H bonds to activate and have focused here on Si−H bond activation reactions. Transition metal phosphido and phosphinidene complexes have been used in P−E bond forming reactions (E = P, C, Si, B, S), and the metal-mediated reactions often provide facile and safe routes to bond forming reactions (E=P, C, Si, B, S), and the metallo and phosphinidene complexes have been used in P−Si−H bonds directly. As a result, we looked for analogous but are not generally electrophilic enough to activate C−H, and the stablilized phosphinidenes lowering the reactivity, and the stablilized phosphinidenes.

### Results and Discussion

The cationic terminal aminophosphinidene complex [CpFe(CO)2{PN-i-Pr2}][AlCl4] (2) is readily formed by abstraction of chloride from the chloroaminophosphido complex [CpFe(CO)2{P(Ph)N-i-Pr2}] (1). Compound 2 reacts at room temperature with primary, secondary, and tertiary silanes, resulting in insertion of the phosphinidene phosphorus into the Si−H bonds and formation of secondary silyl amino phosphine complexes 3−5 (see Scheme 1). In solution, the additions are essentially quantitative. Isolated yields range from 53% to 69%. The reactions of 2 with silanes can be carried out using isolated samples of 2. Alternatively, solutions of 2 can be prepared in situ by dissolving 1 and AlCl3 in dichloromethane. Silanes are then added to the solution to form 3−5. However, optimal yields and purity are obtained by first dissolving 1 and the silane in CH2Cl2 and then adding this solution to solid AlCl3. Compound 1 does not react directly with the silane, but reacts with 2 as it is generated in situ. All three methods result in the formation of compounds 3−5 as the only significant product.

The resulting compounds have been characterized by 1H, 31P, and 29Si NMR spectroscopy and infrared spectroscopy. The spectral features of compound 3, which results from reaction of 2 with PhSiH3, will be used to illustrate the general spectral features. The 1H NMR spectrum of 3 shows a doublet of doublets of doublets at δ 7.82, which corresponds to the P−H. The large JPH coupling of 386.6 Hz indicates a direct P−H bond. Small couplings of 4.4 and 4.1 Hz are observed to two diastereotopic silicon-bound hydrogen atoms. The two Si−H resonances appear at δ 5.02 and 4.87 and are coupled to each other (5.9 Hz), to phosphorus (20.5 and 31.1 Hz, respectively), and to the P−H (4.4 and 4.1 Hz). The 1H NMR shows additional peaks for the phenyl group, the cyclopentadienyl ligand, and the isopropyl groups on the amine substituent. The 31P NMR of 3 shows a singlet at δ 13.0, while the 29Si spectrum shows a doublet at δ 34.1, with an Si−P coupling of 38 Hz. Silicon satellite peaks are also apparent in the 31P spectrum, and their coupling constant matches the 31P coupling constant observed in the 29Si spectrum. The Si−P, P−H, and H−H couplings clearly establish the formation of the new Si−P bond.

The infrared spectrum of 3 shows carbonyl stretching frequencies of 2064 and 2021 cm−1 and a band at 2146 cm−1 that is attributed to the Si−H stretch. The observed carbonyl stretching frequencies are comparable to those of known analogous CpFe(CO)2(PR3)4 complexes. For comparison, the carbonyl stretching frequencies of the phosphinidene complex 2 are 2074 and 2036 cm−1. The shift to lower frequency upon silane addition suggests that the silyl phosphine ligand in 3 is a stronger donor and weaker acceptor than the phosphinidene ligand in 2.

The compound [CpFe(CO)2{P(H)(SiHPh2)(N-i-Pr2)}][AlCl4] (4) has been structurally characterized. An ORTEP diagram of the X-ray crystal structure is shown in Figure 1. The cation consists of a CpFe(CO)2 fragment coordinated by an amino-silyl secondary phosphine. The P−Si bond length of 2.2927(6) Å is typical for P−Si single bonds, and the substituents on the tetrahedral P and Si centers are staggered, with the two H substituents in anti positions (H−P−Si−H dihedral angle = 178°). The P−N bond length of 1.669(2) Å is consistent with a nitrogen−phosphorus single bond. This distance is significantly longer than the typical P−N distance in analogous amino-phosphinidene complexes (1.629−1.634 Å). The lengthening of the P−N bond upon reaction with the silane results from the loss of the N-to-P π-donation that stabilizes the phosphinidene (see below). Similar lengthening of the P−N bond has been observed upon reaction of related amino-phosphinidene complexes with phosphines and alkynes.

![Image](https://example.com/image1.png)

**Figure 1.** ORTEP diagram showing the crystal structure of [CpFe(CO)2{P(H)(SiHPh2)(N-i-Pr2)}][AlCl4] (4). Thermal ellipsoids are shown at the 50% level. Hydrogen atoms, except those on P and Si, and the AlCl4− counterion have been omitted. Selected distances (Å) and angles (deg): Fe−P = 2.2522(6), Si−P = 2.2927(6), P−N = 1.669(2), N−P−Fe = 121.48(8), N−P−Si = 109.03(8), Fe−P−Si = 113.14(3), C20−Si−C14 = 113.2(1), C20−Si−P = 109.77(8), C14−Si−P = 107.99(7).

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The Si−H activation reaction has been examined computationally using SiH$_4$ addition to [CpFe(CO)$_2$(PNMe$_2$)$_2$] as a model system and Gaussian 03$^{25}$ with density functional theory B3LYP$^{26}$ and orbital basis sets LANL2DZ for the Fe atom and 6-31G(d) for other atoms.$^{25}$ The addition of SiH$_4$ to [CpFe(CO)$_2$(PNMe$_2$)$_2$] was found to be concerted, occurring via a triangular transition state. No intermediates were identified. Calculated reactant, transition state, and product geometries are shown in Figure 2. The overall reaction is exergonic by 7 kcal/mol. Two possible pathways and transition states were identified, with activation barriers of 25 and 32 kcal/mol. The transition states differ in the orientation of the silane relative to the phosphinidene (Figure 3). Mulliken partial charges for the key atoms in reactants, transition state, and product are shown in Table 1, and selected distances are given in Table 2.

The bonding in the electrophilic phosphinidene is viewed as being analogous to the bonding in a Fischer carbene. The phosphinidene ligand can be considered to be formally derived from free singlet phosphinidene, which donates one lone pair to the cationic iron center. This leaves on phosphorus a second lone pair and an empty p orbital perpendicular to the π-system. Thus, the p$_z$ orbital is stabilized by β-backdonation from the N lone pair and π-donation from an appropriate filled metal d orbital.$^{27}$ Thus, in the starting phosphinidene complex, the positive charge is stabilized by donation from an appropriate filled metal d orbital.27 Thus, in the starting phosphinidene complex, the positive charge is stabilized by donation from an appropriate filled metal d orbital.27

Figure 2. Calculated geometries for the addition of SiH$_4$ to [CpFe(CO)$_2$(PNMe$_2$)$_2$]. Selected distances (Å) and angles (deg) in transition state 1 (+25 kcal/mol): Si−P = 2.62, Si−H = 1.85, P−H = 1.50, P−Si−H = 33.9. Selected distances (Å) and angles (deg) in transition state 2 (+32 kcal/mol): Si−P = 2.47, Si−H = 1.75, P−H = 1.59, P−Si−H = 40.0, P−H = 45.0, P−H−Si = 95.0.

Table 1. Calculated Mulliken Partial Charges for Key Atoms in Si−H Activation Reaction

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$^a$Transition state values are those of the lower energy transition state.

Table 2. Selected Distances (Å) in Optimized Reactant, Transition State, and Product

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$^a$Transition state values are those of the lower energy transition state.

Figure 3. Schematic representation of silane orientation in two calculated transition states.


primarily localized on the P as a result of the P→Fe donor interaction, with some positive charge delocalized onto N as a result of N-to-P π-donation and some back onto the metal through π-back-donation.\(^{28}\) Nucleophilic attack is expected to occur at the empty phosphorus \(p_z\) orbital, and in the calculated transition states, the silane nucleophile approaches the phosphinidene from this direction (Figure 2). Of the two calculated transition states, the lower energy state is the one in which the Si is oriented toward the phosphorus lone pair and the H is oriented toward the \(p_z\) orbital (Figure 3). The preferred orientation thus aligns the partially positive silicon atom with the phosphorus lone pair, and the partially negative hydrogen atom with the empty \(p_z\) orbital.

In the transition state, approach of the silane nucleophile decreases the charge at P, as the empty \(p_z\) orbital overlaps with the incoming filled Si−H bonding orbital. The charge on N also decreases because N-to-P π-donation to the phosphorus \(p_z\) orbital is displaced by the incoming nucleophile. Upon formation of the final product, the charge at phosphorus again increases as the electropositive SiH\(_3\) fragment is added to P. However, the charge at N does not increase from transition state to product because the positive charge at P can no longer be delocalized onto N, as there is no longer an empty \(p_z\) orbital on P capable of accepting π-donation from N. For the same reasons, the calculated P−N distance (Table 2) increases from the reactant phosphinidene (1.650 Å) to the transition state (1.679 Å) to the product distance (1.706 Å) as the N-to-P π-donor interaction is displaced by the incoming nucleophile. This increase correlates well with the P−N bond distance increase observed experimentally upon Si−H addition to the phosphinidene (see above). Calculated Fe−P distances also increase from reactant to product as π-back-donation from iron to the phosphorus \(p_z\) orbital is eliminated.

A comparison of the iron partial charges suggests that the silyl phosphine in the product is a weaker donor/stronger acceptor than the phosphinidene in the starting material. However, this is not corroborated by IR spectroscopy, where the formation of the silyl phosphine results in a shift of the carbonyl stretching bands to lower frequency (2: 2074, 2036 cm\(^{-1}\); 4: 2064, 2021 cm\(^{-1}\)). The experimental infrared data support our bonding model because the loss of Fe-to-P back-donation upon reaction of the phosphinidene with silane will lead to an increase in Fe to carbonyl back-donation and a corresponding decrease in carbonyl stretching frequency.

For comparison, insertion of the phosphinidene into the C−H bond of methane and the H−H bond of dihydrogen was also studied. Like the Si−H insertion, both of these reactions are concerted and exergonic, with \(\Delta G\) values of −7 and −11 kcal/mol, respectively. However, the activation barriers of 52 and 40 kcal/mol are significantly higher than that of the Si−H insertion, suggesting that modification of the phosphinidene complex to increase electrophilicity will be necessary to achieve C−H or H−H activation.

Bond activation by electrophilic phosphinidene complexes is well established. Transient phosphinidenes have been shown to react with X−H bonds and have been trapped by water, alcohols, and amines. These reactions likely occur via initial coordination of the N or O lone pair to P, followed by proton transfer, although the mechanism has not been studied in detail.\(^{6}\) A similar mechanism has been described for C−Br activation by phosphinidenes, where the initial step is coordination of a Br lone pair to P, followed by bond insertion.\(^{12}\) Silanes, however, lack lone pairs so the initial Lewis acid/base coordination is not possible and the addition to the phosphinidene is concerted.

Attempts to explore the reaction chemistry of the silyl phosphine complexes were generally unsuccessful, as the silyl phosphine complexes are extremely sensitive to P−Si bond cleavage. Most reactions attempted led to loss of the silyl group and formation of the bridging phosphido complex [\(\text{[CpFe(CO)}_2(\mu-\text{CO})]\mu-P(H)\text{N}-i-\text{Pr}_2]\text{[AlCl}_4\text{]}\text{]} (6) (Scheme 2). Compound 6 was also observed during attempts to crystallize the silyl phosphine complexes, presumably as a result of reactions with trace water. It is structurally analogous to several known di-iron bridging phosphido complexes.\(^{29,30}\) Di-iron and iron-group VI heterobimetallic complexes containing bridging \(i\)-Pr\(_2\)NPH phosphido groups have also been described.\(^{31}\)

Compound 6 can be formed rationally and in good yield by reaction of any of the silyl phosphine complexes with phenol, allowing us to propose a mechanism for the decomposition.

of the silyl phosphines as shown in Scheme 3. Initial nucleophilic attack by phenol at Si breaks the P–Si bond. The leaving group is a neutral iron phosphido complex A, which is then protonated to form the primary aminophosphine complex B. In the reaction of 5 (SiR = SiEt3) with phenol, the side product PhOSiEt3 was identified by GC-MS (m/z = 208) and was the only significant volatile component of the reaction mixture. Support for the intermediacy of B comes from its observation as a fragment in electrospray mass spectra of metal complexes, where it likely forms through reaction of the silyl phosphine with adventitious water. Attempts to observe or isolate forms through reaction of the silyl phosphine with adventitious water. Attempts to observe or isolate B in solution were not successful. Direct experimental evidence for the final dimerization step of the mechanism could not be found, as the proposed side product, Ph2N-i-Pr2, was not observed in solution. This compound has been synthesized but is known to be unstable and likely decomposes under our reaction conditions. However, support for this step of the mechanism comes from related work, where hydrosilylation of P–Si bonds in silyl phosphine complexes has been used to form bridging phosphido complexes.

In summary, we have shown that terminal electrophilic phosphinidene complexes activate Si–H bonds, resulting in insertion of phosphorus in the Si–H bond and leading to secondary silyl phosphines. The addition occurs via a concerted mechanism and results in the formation of a new P–Si bond, as well as a P–H bond, which may serve as a site for further functionalization. This reaction represents a facile new method of P–Si bond formation.

Experimental Section

General Comments. All procedures were carried out under a nitrogen atmosphere using standard Schlenk techniques or in an inert atmosphere glovebox. THF was distilled from Na/benzophenone. Dichloromethane and hexane were purified using solvent purification columns containing alumina (dichloromethane) or alumina and copper catalyst (hexane). Deuterated chloroform was distilled from P2O5. The NMR spectra were recorded in CDCl3 or CD2Cl2 using a Varian Mercury 300 at 300.179 MHz (1H), 121.515 MHz (31P{1H}), or 59.637 MHz (29Si{1H}). Infrared spectra were recorded in CH2Cl2 solution. Compounds 3, 4, and 5 are extremely water sensitive, and crystalline samples rapidly revert to oils upon supernatant removal. As a result, satisfactory elemental analysis could not be obtained for these compounds. However, their formulations and purity are well supported by mass spectrometry and spectroscopy. Mass spectra of metal complexes were carried out using a Finnigan-Matt INCOS 50 connected to an HP-5890A gas chromatograph equipped with a J&W DB-5MS column. The MS was operated in positive ion mode with electron impact ionization.

a. Synthesis of [CpFe(CO)2{P(Ph)N-i-Pr2}] (1), This compound was synthesized using a modification of the published procedure. Excess sodium/potassium alloy (NaK 2.8, 2.0 mL, 1.14 g, 24 mmol K) was added to a vigorously stirred solution of [CpFe(CO)2]2 (1.0 g, 2.8 mmol) in THF (75 mL). The mixture was stirred for 3 h and then filtered via inverse filtration. The filtrate was added in small portions via canula to a solution of Cl2NP-i-Pr2 (1.06 mL, 1.44 g, 7.2 mmol) in THF (75 mL) at −78 °C. After the addition was complete, the solution was warmed to room temperature and stirred for 30 min. The solvent was removed in vacuo, and the residue was extracted into pentane (5 × 10 mL). The pentane extracts were filtered and cooled to −25 °C for 24 h, resulting in the formation of red-orange crystals. The supernatant was decanted and the solid was dried in vacuo. Yield: 0.90 g, 46%.

b. Synthesis of [CpFe(CO)2{PN-i-Pr2}][AlCl4] (2), This compound was synthesized using a modification of the published procedure. In a typical experiment, a solution of 2 was prepared by dissolving [CpFe(CO)2{P(Ph)N-i-Pr2}] (1) (30 mg, 0.087 mmol) and AlCl3 (17 mg, 0.13 mmol) in CH2Cl2 (0.5 mL) and then reacted in situ. Conversion of 1 to 2 is essentially quantitative by NMR spectroscopy. Compound 2 is not routinely isolated because it is extremely air and water sensitive, and isolated yields are poor.

c. Synthesis of [CpFe(CO)2{P(H)(SiH3Ph)(N-i-Pr2)}][AlCl4] (3), The compound [CpFe(CO)2{P(Ph)N-i-Pr2}] (50 mg, 0.146 mmol) was dissolved in CH2Cl2 (2 mL), and H2SiPh (36.0 μL, 0.292 mmol) was then added. The resulting solution was added to AlCl3 (29.2 mg, 0.219 mmol) and stirred for 30 min. Pentane (5 mL) was added slowly with mixing, and the resulting cloudy solution was cooled to −30 °C for 3 days, resulting in the formation of a red oil and yellow-orange crystals. The supernatant was decanted, and the oil was triturated with pentane (3 × 1 mL), resulting in the formation of a semicrystalline oily solid, which was dried under vacuum. Yield: 45 mg, 53%. IR (CH2Cl2 solution, cm−1): νSi–H = 2146; νCO = 2064, 2121. 1H NMR: δ 7.82 (dd, 1H, PhH, 3J(HP) = 386.6 Hz, 2J(HH) = 4.1, 4.4 Hz), 7.8–7.4 (m, Ph), 5.17 (s, 5H, C5H5), 5.02 (dd, 1H, SiH, 2J(HP) = 20.5 Hz, 2J(HH) = 5.9 Hz, 3J(HH) = 4.1 Hz), 4.87 (dd, 1H, SiH, 2J(HP) = 31.1 Hz, 2J(HH) = 5.9 Hz, 3J(HH) = 4.4 Hz), 3.28 (sept, 1H, CH(CH3)2, 2J(HH) = 6.6 Hz), 3.24 (sept, 1H, CH(CH3)2, 3J(HH) = 6.3 Hz), 1.19 (doublet, 6H, CH(CH3)2, 3J(HH) = 6.3 Hz), 1.09 (doublet, 6H, CH(CH3)2, 3J(HH) = 6.6 Hz). 31P NMR: δ 13.0 (s w satellites, 1J(Hp) = 38 Hz). 29Si NMR: 34.1 (d, 1J(Hp) = 38 Hz). MS (electrospray, CH2Cl2 solution): m/z = 416 (M+), 308 (M − SiH2Ph). Note: although compounds 3–5 are routinely synthesized by generating the phosphinidene complex 2 in the presence of the silane, they can also be formed by first synthesizing and isolating 2 and then reacting it with silane. The procedure described above gives better yields and purity.
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57%. IR (cast, cm\(^{-1}\))

δNMR: dark red precipitate. The supernatant was decanted, and the resulting cloudy solution was cooled at \(-30^\circ C\) for 4 days, resulting in the formation of a dark red precipitate.

The supernatant was decanted, and the oil was triturated with pentane (3 mL), resulting in the formation of dark red crystals, which were collected and dried under vacuum. Yield: 60 mg, 69%. IR (KBr, cm\(^{-1}\))

δ: 3024, 2923, 2858, 1610, 1509, 1452, 1370, 1341, 1294, 1186, 1085, 1005, 974, 937, 908, 843, 800. MS (ESI, CH\(_2\)Cl\(_2\) solution): m/z = 492 (M\(^+\)), 506 (M - H\(^+\)).

e. Synthesis of [CpFe(CO)\(_2\)]\([\langle\mu\rangle\text{CO}\rangle][\langle\mu\rangle\text{P(\text{SiEt}_3)N-i-Pr}\rangle] \cdot [\text{AlCl}_4] (5).

The compound [CpFe(CO)\(_2\)]\([\langle\mu\rangle\text{P(\text{SiEt}_3)N-i-Pr}\rangle] (50 mg, 0.146 mmol) dissolved in CH\(_2\)Cl\(_2\) (0.5 mL), and H\(_2\text{SiPh}_2\) (54.2 mL, 0.292 mmol) was then added. The resulting solution was added to AlCl\(_3\) (29.2 mg, 0.219 mmol) and stirred for 30 min. Pentane (5 mL) was added slowly with mixing, and the resulting cloudy solution was cooled at \(-30^\circ C\) for 4 days, resulting in the formation of a dark red oil. The supernatant was decanted, and the resulting cloudy solution was kept at \(-30^\circ C\) for 30 days. The resulting cloudy solution was filtered through a silica gel column, and the resulting dark red oil was then dried under vacuum. Yield: 60 mg, 69%. IR (KBr, cm\(^{-1}\))

δ: 3024, 2923, 2858, 1610, 1509, 1452, 1370, 1341, 1294, 1186, 1085, 1005, 974, 937, 908, 843, 800. MS (ESI, CH\(_2\)Cl\(_2\) solution): m/z = 492 (M\(^+\)), 506 (M - H\(^+\)).

f. Synthesis of [CpFe(CO)\(_2\)]\([\langle\mu\rangle\text{CO}\rangle][\langle\mu\rangle\text{P(\text{SiEt}_3)N-i-Pr}\rangle] \cdot [\text{AlCl}_4] (6).

A solution of [CpFe(CO)\(_2\)]\([\langle\mu\rangle\text{P(\text{SiEt}_3)N-i-Pr}\rangle] (50 mg, 0.146 mmol) was added, and the resulting solution was stirred for 15 min. The resulting solution was filtered through a silica gel column, and the resulting dark red oil was then dried under vacuum. Yield: 60 mg, 69%. IR (KBr, cm\(^{-1}\))

δ: 3024, 2923, 2858, 1610, 1509, 1452, 1370, 1341, 1294, 1186, 1085, 1005, 974, 937, 908, 843, 800. MS (ESI, CH\(_2\)Cl\(_2\) solution): m/z = 492 (M\(^+\)), 506 (M - H\(^+\)).

Table 3. Crystal Data and Structure Refinement for 4 and 6

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</tr>
<tr>
<td>absorb coeff (mm(^{-1}))</td>
<td></td>
<td>0.947</td>
<td>1.612</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>F(000)</td>
<td></td>
<td>1360</td>
<td>636</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>crystal size (mm(^3))</td>
<td></td>
<td>0.37 × 0.36 × 0.19</td>
<td>0.53 × 0.26 × 0.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>θ range (deg)</td>
<td></td>
<td>1.67 to 27.48</td>
<td>1.62 to 27.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>index ranges</td>
<td></td>
<td>-31 ≤ h ≤ 31</td>
<td>-13 ≤ k ≤ 13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>reffs collected</td>
<td></td>
<td>25971</td>
<td>11453</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>indep reffs</td>
<td></td>
<td>7253 ([\text{Rint} = 0.0317])</td>
<td>5979 ([\text{Rint} = 0.0160])</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>completeness</td>
<td></td>
<td>100.0%</td>
<td>99.3%</td>
<td></td>
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</tbody>
</table>

Crystallography. Suitable crystals of compounds 4 and 6 were mounted on glass fibers. Programs for diffractometer operation, data collection, cell indexing, data reduction, and absorption correction were those supplied by Bruker AXS Inc., Madison, WI. Diffraction measurements were made on a PLATFORM diffractometer/SMART 1000 CCD using graphite-monochromated Mo K\(_\alpha\) radiation at \(-100^\circ C\). The unit cell was determined from randomly selected reflections obtained using the SMART CCD automatic search, center, index, and least-squares routines. Integration was carried out using the program SAINT, and an absorption correction was performed using SADABS. Crystal data and collection parameters are according to a Mulliken population analysis.
parameters are listed in Table 3. Structure solution was carried out using the SHELX97\textsuperscript{33} suite of programs and the WinGX graphical interface.\textsuperscript{34} Initial solutions were obtained by direct methods and refined by successive least-squares cycles. All non-hydrogen atoms were refined anisotropically. During solution of 6, the PLATON\textsuperscript{35} routine TWINROTMat was used to identify a 2-fold twin axis about [1 0 1], which was accounted for with the twin law 0 0 1 0 −1 0 1 0 0. Racemic twinning was also identified, resulting in a total of four twin components.

**Acknowledgment.** This work was financially supported by NSERC (Discovery Grant to B.T.S.) and the University of Regina. Computations were performed on a supercomputer funded by the CFI (New Opportunities Grant to A.L.E.) and Parallel Quantum Solutions, Arkansas (in-kind contribution). We also thank Bob McDonald and Mike Ferguson (University of Alberta) for X-ray data collection, and Ron Treble (University of Regina) for GC-MS analysis.

**Supporting Information Available:** Tables giving full coordinates, energies, and Mulliken charges for calculated structures, CIF files giving full details of X-ray crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.