Articles

Synthesis and Reactivity of Phosphirane Ligands and the Structural Characterization of Cp^*IrCl_2(*tert*-butylphosphirane)

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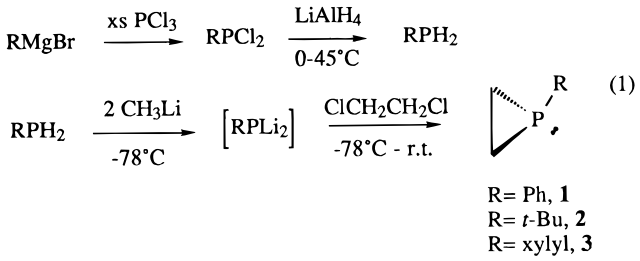
New and stable phosphiranes, *tert*-butylphosphirane and xylylphosphirane, were prepared. *tert*-Butylphosphirane is stable to polymerization in the presence of electrophiles. It was reacted with bis((μ-chloro)chloro(pentamethylcyclopentadienyl)iridium) to prepare (*tert*-butylphosphirane)dichloro(pentamethylcyclopentadienyl)iridium, which was characterized by X-ray diffraction. *tert*-Butylphosphirane was also reacted with pentacarbonyl(tetrahydrofuran)tungsten and borane to form (*tert*-butylphosphirane)pentacarbonyltungsten and the first phosphirane−borane adduct, respectively.

Phosphiranes are three-membered phosphorus heterocycles, first reported by Wagner *et al.* in 1967.[1] Chan *et al.* reported that unsubstituted phosphiranes were unstable toward polymerization or decomposition.[2] Because of their intrinsic instability, phosphiranes were not studied in detail until Mathey *et al.* developed a method to synthesize phosphiranes in the coordination sphere of group 6 transition metal complexes.[3−5] This approach provides an understanding of the structure of these heterocycles, but it does not give insight into their reactivity. Attempts have been made to synthesize stable free phosphiranes. The stability of these highly strained systems depends on two factors: the steric and electronic properties of the substituent at the phosphorus atom and the degree of substitution of the ring. For example, in 1991, Le Floch and Mathey were able to synthesize 1-chlorophosphirane. This compound, stable in solution, forms an insoluble and pyrophoric white powder when concentrated.[6] Baudler *et al.* prepared 2-methyl-1-*tert*-butylphosphirane, but in low (14%) yield and as a mixture of diastereomers.[7] By placing bulky groups on the phosphorus atom, (2,4,6-trimethylphenyl)-phosphirane and (2,4,6-tri-*tert*-butylphenyl)phosphirane were prepared.[8,9] We now describe an improved synthesis of phosphiranes together with preliminary studies of their unusual properties as phosphine donor ligands. The syntheses of phenylphosphirane (**1**), *tert*-butylphosphirane (**2**), and xylylphosphirane (**3**) are described. Phosphiranes **2** and **3** are found to be quite stable, and the reactivity of **2** and its use as a ligand are reported together with the X-ray crystal and molecular structure of Cp^*IrCl_2(*tert*-butylphosphirane) (**4**) ($Cp^* = C_5(CH_3)_5$).

Results and Discussion

The synthesis developed in our laboratories provides a general method to alkyl- and arylphosphiranes (eq 1).



The method is analogous to the one reported recently by Wild *et al.*[10] The most general version of our phosphirane synthesis is as follows. Treatment of a large excess of phosphorus trichloride at 0 °C with a Grignard reagent yields a mixture of dichloro- and monochloroalkyl(or aryl)phosphines. After the removal of excess PCl_3, the mixture is reduced with $LiAlH_4$ to the corresponding phosphines. The resulting primary and secondary phosphines are separated by distillation. Two equivalents of methyllithium are added to the desired primary phosphine. Then, 1 equiv of 1,2-dichloroethane is added. The resulting phosphirane can be purified by distillation. This synthesis is versatile. It allows one to start with either PCl_3, $RPCl_2$, or RPH_2, depending on their commercial availability. Starting from commercially available phenylphosphine, phenyl-

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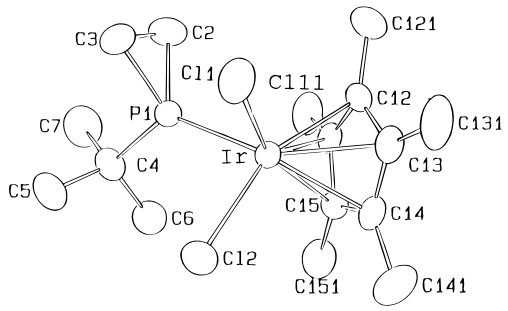
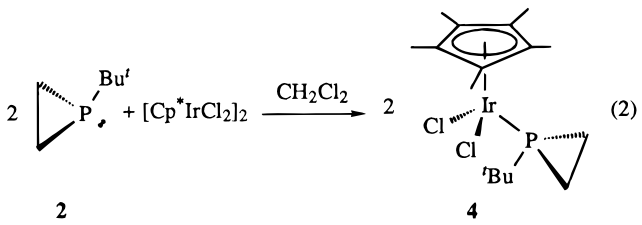


Figure 1. ORTEP view of Cp*$IrCl_2$(*tert*-butylphosphirane), **4**.

phosphirane (**1**) is produced in 65% yield as a colorless liquid. As reported earlier, this compound readily decomposes[2] to form a polymeric material. Because of its lower boiling point, *tert*-butylphosphirane (**2**) is typically codistilled with THF and used in this form after NMR titration. Phosphirane **2** can also be isolated as a pure colorless liquid. The neat liquid is stable at −20 °C under nitrogen for several weeks, after which time the $^{31}P\{^1H\}$ NMR spectrum shows some decomposition products, but even after 2 months, 30% of the starting material is still present. Xylylphosphirane (**3**) is obtained in 30% yield starting from xylylmagnesium bromide and PCl_3. Phosphirane **3** is stable as a neat liquid at −20 °C for extended periods of time. The $^{31}P\{^1H\}$ NMR signals of phosphiranes **1**−**3** occur at very high field ($\delta = -206$ to -239 ppm), but still downfield of the parent phosphirane PC_2H_5 ($\delta = -341$ ppm).[1] The $^{31}P\{^1H\}$ NMR resonance for *tert*-butylphosphirane (**2**) occurs considerably downfield of the arylphosphiranes **1** and **3**.

Phosphirane **2** was also characterized by its reaction with $[Cp^*IrCl_2]_2$ to afford Cp*$IrCl_2$(*tert*-butylphosphirane) (**4**, eq 2). The $^{13}C\{^1H\}$ NMR spectrum of **4**



2 **4**

shows a doublet, $^3J(P-C) = 4$ Hz, for the five equivalent methyl groups of the Cp* ring, indicating the presence of a phosphine ligand. Complex **4** was also characterized by a single-crystal diffraction study. The ORTEP of complex **4** is shown Figure 1, and data collection and refinement parameters are found in Table 1. Selected bond distances and angles are given in Table 2. Complex **4** possesses the expected "piano stool" structure. The Ir−Cl and the Ir−Cp* distances are normal. The Ir−P distance of 2.296(1) Å falls near the average length for Cp*$IrCl_2(PR_3)$ complexes. This is an apparent consequence of the low steric demand of the piano stool structure, which allows the phosphirane *tert*-butyl group to rotate away from the Cp* ring, enabling the phosphorus atom to more closely approach the Ir center. This is clearly seen in the ORTEP drawing of the complex, Figure 1. The P−C bond distances within the phosphirane ring, 1.808(8) and 1.799(8) Å, are shorter than the P−C bond distance to the *tert*-butyl group, 1.873(6) Å. The phosphirane ring C−C distance is in the range

Table 1. Summary of Crystallographic Data for 4

formula	$IrCl_2PC_{16}H_{28}$
fw	514.48
cryst size, mm	0.45 × 0.42 × 0.25
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	15.909(2)
b, Å	7.6358(9)
c, Å	17.259(2)
β, deg	115.309(9)
V, Å^3	1895.4(8)
Z	4
D_{calcd}, g cm^{-3}	1.803
μ, cm^{-1}	73.77
radiation (λ, Å)	Mo Kα (0.710 73 Å)
no. reflns measured	4287
no. reflns used	4150
no. variables	197
R^a	0.027
$R_w{}^b$	0.033

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$.

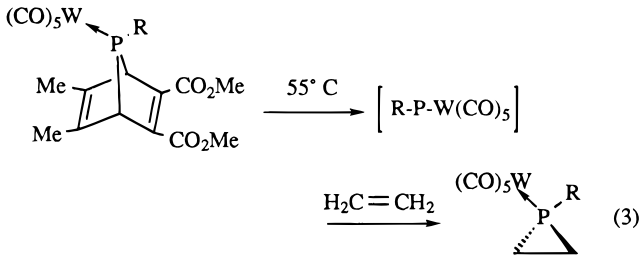
Table 2. Selected Bond Distances (Å) and Angles (deg) for 4

Bond Distances			
Ir−Cl(1)	2.415(2)	Ir−C(15)	2.165(6)
Ir−Cl(2)	2.408(2)	P(1)−C(2)	1.808(8)
Ir−P(1)	2.296(1)	P(1)−C(3)	1.799(8)
Ir−C(11)	2.152(6)	P(1)−C(4)	1.873(6)
Ir−C(12)	2.159(6)	C(2)−C(3)	1.51(1)
Ir−C(13)	2.229(6)	C(4)−C(5)	1.53(1)
Ir−C(14)	2.221(6)	C(4)−C(6)	1.51(1)
		C(4)−C(7)	1.535(9)

Bond Angles			
Cl(1)−Ir−Cl(2)	88.96(7)	C(3)−P(1)−C(4)	106.8(3)
Cl(1)−Ir−P(1)	88.44(5)	P(1)−C(2)−C(3)	65.0(4)
Cl(2)−Ir−P(1)	90.83(5)	P(1)−C(3)−C(2)	65.6(4)
Ir−P(1)−C(2)	119.4(3)	P(1)−C(4)−C(5)	107.9(4)
Ir−P(1)−C(3)	122.6(3)	P(1)−C(4)−C(6)	108.3(4)
Ir−P(1)−C(4)	125.1(2)	P(1)−C(4)−C(7)	112.8(5)
C(2)−P(1)−C(3)	49.5(4)	C(5)−C(4)−C(6)	109.3(6)
C(2)−P(1)−C(4)	110.1(4)	C(5)−C(4)−C(7)	108.8(6)

for C(sp^3)−C(sp^3) bonds (1.51(1) Å) and is in fact similar to those found in the *tert*-butyl group. The C−C−P angles, 65.0(4)° and 65.6(4)°, together with the C−P−C angle of 49.5(4)° attest to the high degree of strain in the phosphirane ring and the unusual chemical bonding required in such a structure.[11,12]

In order to better understand the properties of the new, stable phosphiranes prepared here, a systematic comparison to other phosphiranes is warranted. There is now a large body of physical data on $(CO)_5W$-(phosphirane) complexes prepared by Mathey's method[3] (eq 3). In order to compare the properties of our new



phosphiranes, we synthesized analogous tungsten−phosphirane complexes according to eq 4. The reactions are quantitative by IR, and isolated yields are in the

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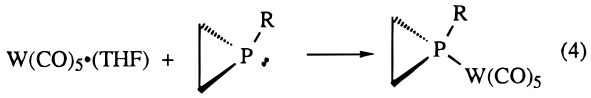


(4)

R= *t*-Bu, **5**
R= 2,6-dimethylphenyl, **6**

range of 80−90%. A comparison of the spectroscopic data for previously reported $(CO)_5W$(phosphirane) complexes and **5** and **6** appear in Table 3. The ν(CO) region of the IR spectrum for these complexes is not significantly affected by the different substituents on the phosphirane phosphorus atom. In fact, no significant difference is apparent in the ν(CO) bands of the alkylphosphirane **5** compared to the arylphosphirane **6**. This suggests that phosphiranes are intrisically weak σ-donor ligands. The ^1J(P−W) coupling constant is usually taken as a measure of the relative σ-donor ability within a series of compounds.[13] Indeed, ^1J(P−W) is directly related to the s character of the P−W bond, which can be related to the s character of the lone pair of the ligand. It appears likely that σ and π effects contribute in different ways to the magnitude of ^1J(P−W) in the $(CO)_5W$(phosphirane) complexes. Table 3 summarizes the ^1J(P−W) values for $(CO)_5WP(R)CH_2CH_2$ (R = xylyl, Ph, *t*-Bu, NHPh, NEt_2, Cl, OEt) complexes.

Phosphiranes with electron withdrawing substituents (*e.g.*, Cl or OEt) have significantly higher coupling constants (^1J(P−W) = 303 Hz) compared to the phosphiranes with electron-donating substituents, such as *tert*-butyl (^1J(P−W) = 244 Hz). This trend runs opposite to that expected for simple σ inductive effects. It is known that, in general, the magnitude of ^1J(P−W) in $W(CO)_5(PL_3)$ depends linearly on the electronegativity of the atom α to phosphorus.[13] Therefore, it appears that the W-P s-orbital *overlap* as well as the P lone pair *s character* are important. The phosphiranes with electron-withdrawing groups are stronger π-acceptor ligands. These will then have shorter W-P bond distances due to W(dπ)−P(σ*) back-bonding and, for that reason, greater s-orbital overlap. For example, the $(CO)_5WP(R)CH_2CH_2$ complex with R = Cl was found to have a relatively short W-P bond distance of 2.455(2) Å and high ^1J(P−W) = 303 Hz, while the complex with R = Ph was found to have a relatively long W-P bond distance of 2.504(2) Å and low ^1J(P−W) = 258 Hz. The complex with R = piperidine shows both an intermediate W-P bond distance and an intermediate value of ^1J(P−W) relative to the chloro- and aryl-subsituted systems. These data suggest that phosphiranes possess a high degree of s-character in their nonbonded electron pairs,[17,18] which contribute to weak σ-donating properties. Electron-withdrawing substituents at the phosphorus atom increase the phosphirane π-acceptor ability, decreasing W-P bond distances. Coupling constants

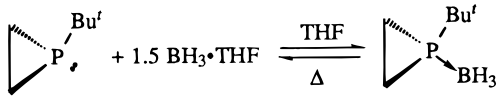
Table 3. Comparison of $^{31}P\{^1H\}$ NMR and IR Data for $(CO)_5W(P(R)CH_2CH_2)$ Complexes

R	$^{31}P\{^1H\}$ NMR, ppm (CD_2Cl_2)	J(P−W), Hz	IR $\nu_{(CO)}$, cm^{-1} (THF)	ref
xylyl (**6**)	−202	c	2073(m), 1945(vs), 1920(sh)	14
Ph	−187.6[a]	258		15
tert-butyl (**5**)	−163.5	244	2073(m), 1944(vs), 1914(m)	this work
NHPh	−132	288		15
NEt_2	−111[b]	278	2070(m), 1940(vs)[d]	16
Cl	−98	303		15
OEt	−46	303		15

[a] C_6D_6. [b] $CDCl_3$. [c] Not resolved. [d] Decalin.

^1J(P−W), thus, increase with the electron-acceptor ability of the substituents at the phosphirane phosphorus atom as the σ-orbital overlap between tungsten and phosphorus improves with bond distance contraction.

The unusual ligand donor/acceptor character of phosphiranes evident in their $^{31}P\{^1H\}$ NMR spectra was the basis for further study of their reactivity. In sharp contrast to previous reports concerning phenylphosphirane (**1**), *tert*-butylphosphirane (**2**) is remarkably robust. Mathey[19] has reported that phosphiranes are readily polymerized by electrophiles. However, treatment of **2** with triethyloxonium tetrafluoroborate does not result in *any* noticable reaction. Reaction of **2** with BH_3•THF resulted in the quantitative formation of the first phosphirane−borane adduct, **7** (eq 5). Phosphirane−



(5)

2 **7**

borane **7** was characterized by $^{31}P\{^1H\}$ NMR, which indicates a $J(^{31}P-^{11}B)$ coupling constant of 30 Hz. In this reaction, the phosphirane acts similarly to phosphines in forming borane adducts. However, unlike phosphines, which require the presence of an excess amount of a nucleophilic amine to be decomplexed,[20−22] gently heating complex **7** reforms **2**. No reaction is observed between **2** and BF_3•Et_2O, which is a somewhat weaker Lewis acid than BH_3. This reinforces our view that **2** is an exceedingly weak σ-donor. Reaction of **2** with 9-BBN also did not produce the phosphirane−borane adduct, likely for steric reasons. Phosphiranes are also reported to be susceptible to nucleophilic ring opening.[19] However, neither **2** nor **1** react with a strong nucleophiles, such as methyllithium.

In summary, a rational, apparently general synthesis of phosphiranes is reported. This provides the opportunity for substantial further development of the chemistry of these ligands with transition metals. To illustrate the possibilities, we have synthesized phosphirane complexes $(CO)_5WP(R)CH_2CH_2$ (R = *t*-Bu (**5**), xylyl (**6**)) to compare their spectroscopic properties to the known complexes (R = Ph, NHPh, NEt_2, Cl, OEt). We have shown that these ligands are weak σ-donors

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because of the high s-character of the phosphorus atom lone pair. We also find that π-acceptor properties, which increase with the electronegativity of the subsitutent at phosphorus, are important in the binding of phosphiranes to transition metal complexes. Our studies suggest that the often reported instability of phosphiranes can be avoided by increasing the bulk of the substituents at the phosphorus atom.

Experimental Section

General Procedures. All manipulations were carried out under nitrogen using standard Schlenk line and drybox techniques. Solvents were degassed and purified by distillation under nitrogen from the appropriate drying agents (sodium/benzophenone for THF, CaH_2 for CH_2Cl_2). Methyllithium (1.4 M in diethyl ether), 2-bromo-*m*-xylene,1, 2-dichloroethane, and tungsten hexacarbonyl were purchased from Aldrich Chemical Co. Tungsten hexacarbonyl was purified by sublimation under vacuum prior to use. Anhydrous diethyl ether was purchased from Mallinckrodt. The phosphines *tert*-butyldichlorophosphine, phosphorus trichloride, and phenylphosphine were purchased from Strem Chemical, Inc. $Cp^*_2Cl_2(\mu\text{-}Cl)_2Ir_2$[23] was prepared according to published procedures. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a General Electric QE-300 spectrometer at 300.6 and 75.2 MHz, respectively, with chemical shifts reported in ppm referenced to internal $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra were recorded on a QE-300 spectrometer at 121.4 MHz, with chemical shifts reported in ppm referenced to external H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrophotometer.

Synthesis of Phenylphosphirane (1). Phenylphosphirane was prepared by a modification of the literature procedure.[2] Phenylphosphine (2.75 mL, 25 mmol) in THF is cooled to −78 °C using a dry ice/isopropyl alcohol bath. Two equivalents of methyllithium (50 mmol) is added dropwise, and after complete addition, the mixture is stirred for 1 h. Degassed 1,2-dichloroethane (2.48 g, 25 mmol) is added slowly via syringe. The mixture is allowed to warm slowly to room temperature (*ca.* 12 h). The cream-colored suspension is then hydrolyzed with degassed water, and diethyl ether is added. The organic layer is separated and dried over magnesium sulfate. After filtration, the etheral layer is distilled under vacuum. Phosphirane **1** distills at 90 °C (3.5 mmHg) to yield a colorless oil. Yield: 65%. $^{31}P\{^1H\}$ NMR: δ −236. ^1H NMR: δ 0.9 (d, 2H), 0.95 (s, 2H), 7.0 (m, 5H). $^{13}C\{^1H\}$ NMR: δ 10.1 (d, CH_2, $^1J(C-P) = 42.3$ Hz), 127.9 (s), 127.9 (d, $^3J(C-P) = 2.7$ Hz), 132.3 (d, $^2J(C-P) = 9.4$Hz), 139.9 (d, $^1J(C-P) = 41.7$Hz).

Synthesis of *tert*-Butylphosphirane (2). A THF solution of $LiAlH_4$ (3.14 mmol) is added dropwise to a THF solution of dichloro-*tert*-butylphosphine (2.00 g, 12.6 mmol) at 0 °C. After addition, the solution is stirred at 45 °C for 2 h. The resulting *tert*-butylphosphine is distilled at 55 °C under atmospheric pressure. To a THF solution of the distilled phosphine, 2 equiv of methyllithium (25.2 mmol) is added dropwise at −78 °C. After 30 min of stirring, 1 equiv of 1,2-dichloroethane (1.25 g, 12.6 mmol) is added. The solution is allowed to warm back to room temperature. A water/ether extraction is performed, and the etheral phase is dried over magnesium sulfate. After filtration, the ether and a small amount of THF are removed by atmospheric distillation. The phosphirane **2** is codistilled with THF, using a bulb to bulb distillation apparatus. The concentration of **2** in the THF solution is determined by ^1H NMR. The phosphirane **2** can be kept in THF solution at −20 °C indefinitely. As a neat colorless liquid, obtained by atmospheric distillation of THF, $^{31}P\{^1H\}$ and ^1H NMR do not reveal any measurable decomposition over several weeks. Yield: 90%. $^{31}P\{^1H\}$ NMR: δ −206. ^1H NMR: δ 0.45 (m, 2H), 0.6 (m, 2H), 0.72 (d, $C(CH_3)_3$, $^3J(H-P) = 12$ Hz). $^{13}C\{^1H\}$ NMR: δ 2.7 (d, CH_2, $^1J(C-P) = 43.3$ Hz), 24.6 (d, $C(CH_3)_3$, $^1J(C-P) = 32.3$ Hz), 28.7 (d, $C(CH_3)_3$, $^3J(C-P) = 16.1$ Hz). EI MS (*m*/*e*): 116.

Synthesis of (2,6-Dimethylphenyl)phosphirane (xylylphosphirane, 3). The Grignard of 1-bromo-2,6-dimethylbenzene is obtained in 95% yield following a reported procedure.[24] $C_6H_3(CH_3)_2MgBr$ is added dropwise at 0 °C to a stirred solution of 3 equiv of trichlorophosphine in diethyl ether over the course of several hours. The reaction yields a mixture of dichloroxylylphosphine (Cl_2P(xylyl)) and chlorodixylylphosphine (ClP(xylyl)$_2$). The ratio of the two compounds depends on the addition rate. Phosphorus trichloride is removed, along with THF, via vacuum distillation. The remaining residue is transferred to a drybox, where magnesium salts are filtered and washed with diethyl ether. The corresponding phosphines, xylylphosphine (H_2P(xylyl)) and dixylylphosphine (HP(xylyl)$_2$) are then prepared by the addition of an excess amount of $LiAlH_4$, using a method similar to the formation of *tert*-butylphosphirane (**2**). After hydrolysis and ether extraction, the organic layer is dried with magnesium sulfate, and the phosphines are separated by vacuum distillation. Two equivalents of methyllithium are added dropwise at −78 °C to a THF solution of xylylphosphine. After 30 min, 1 equiv of 1,2-dichloroethane is syringed in the reaction mixture. The solution is allowed to warm back to room temperature. A water/ether extraction is performed, and the etheral phase is dried over magnesium sulfate. After filtration, xylylphosphirane is distilled under vacuum to yield a colorless oil. Yield: 30%. $^{31}P\{^1H\}$ NMR: δ −239. ^1H NMR: δ 0.9 (m, 2H), 1.05 (m, 2H), 2.4 (s, 6H, $(CH_3)_2$) 6.8 (m, 3H). $^{13}C\{^1H\}$ NMR: δ 12.4 (d, CH_2, $^1J(C-P) = 39.8$ Hz), 22.6 (d, $C(CH_3)_2$, $^2J(C-P) = 8.9$ Hz), 127.9 (s), 127.9 (d, $^3J(C-P) = 2.7$ Hz), 139.9 (d, $^1J(C-P) = 41.7$ Hz), 142.3 (d, $^2J(C-P) = 9.4$ Hz). EI MS (*m*/*e*): 164. Anal. Calcd for $C_{10}H_{13}P$: C, 73.16; H, 7.98. Found: C, 73.40; H, 8.09.

Synthesis of (*tert*-Butylphosphirane)dichloro(pentamethylcyclopentadienyl)iridium (4). Three equivalents of *tert*-butylphosphirane (**2**) (per equivalent of iridium) are syringed into a CH_2Cl_2 solution of $[Cp^*IrCl_2]_2$ (Cp^*=$C_5(CH_3)_3$) at −78 °C. Upon warming, the solution mixture turns from orange to yellow in color. The reaction is then stirred at room temperature overnight. The solution volume is reduced, and hexane is added. An orange solid precipitates and is removed by filtration. Yield: 95%. $^{31}P\{^1H\}$ (CD_2Cl_2): δ −143.2. ^1H NMR (CD_2Cl_2): δ 1.2 (d, $C(CH_3)_3$, $^3J(H-P) = 17.25$ Hz), 1.45 (m, 4H), 1.65 (d, 15H, $^4J(H-P) = 3.0$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 4.1 (d, CH_2, $^1J(C-P) = 8.9$ Hz), 8.7 (s, $C_5(CH_3)_5$), 28.7 (d, $C(CH_3)_3$, $^1J(C-P) = 39.2$ Hz), 29.0 (d, $C(CH_3)_3$, $^3J(C-P) = 4.0$ Hz), 92.2 (s, $C_5(CH_3)_5$). PDMS ($M + H$): 515. Anal. Calcd for $C_{16}H_{28}PIrCl_2$: C, 37.35; H, 5.49. Found: C, 37.00; H, 5.73.

Synthesis of (*tert*-Butylphosphirane)pentacarbonyltungsten (5). A Schlenk flask is charged with tungsten hexacarbonyl (100 mg, 0.28 mmol) dissolved in 100 mL of THF. The solution is purged with nitrogen during a 1 h photolysis (λ = 330 nm, 1000 W). The formation of $W(CO)_5$·(THF) is followed by IR spectroscopy. *t*-Butylphosphirane (0.28 mmol) is added (in a mixture of Et_2O and THF) to the deep yellow solution of $W(CO)_5$·THF. The reaction is then stirred at room temperature overnight. The THF is removed in *vacuo*, and the residue is taken up with hexanes. The solution is filtered, and the yellow-orange filtrate is cooled to −20 °C. Yellow crystals of (*tert*-butylphosphirane)pentacarbonyltungsten were collected by filtration. Yield: 90%. $^{31}P\{^1H\}$ (CD_2Cl_2): δ −163

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ppm (^1J(W-P) = 244 Hz). ^{1}H NMR (CD_2Cl_2): δ 1.25 (d, C(CH_3)$_3$, ^3J(H−P) = Hz), 1.35 (m, 2H), 1.60 (m, 2H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 6.0 (t, CH_2, ^1J(C−W) = 8.0 Hz), 29.1 (s, C(CH_3)$_3$), 31.2 (s, C(CH_3)$_3$). IR (THF) ν_{CO} (cm^{-1})): 2073 (m), 1944 (vs), 1914 (m). Anal. Calcd for $C_{11}H_{13}PWO_5$: C, 30.02; H, 2.98. Found: C, 29.78; H, 3.11.

Synthesis of (Xylylphosphirane)pentacarbonyltungsten (6). Prepared according to the same procedure as above. Yield: 90%. ^{31}P{^{1}H} (CD_2Cl_2): δ −202. IR (THF) ν_{CO} (cm^{-1})): 2073 (m), 1945 (vs), 1914 (sh). Anal. Calcd for $C_{15}H_{13}PWO_5$: C, 36.91; H, 2.68. Found: C, 36.76; H, 2.86.

Synthesis of the *tert*-Butylmethylphosphirane−Borane Adduct (7). To a solution of **2** in THF is added 1.5 equiv of a solution of borane−THF (1 M). The reaction is followed by ^{31}P NMR, and after 12 h, the reaction is complete. Attempts to remove the solvent under vacuum at low temperatures led only to the quantitative reformation of **2**. ^{31}P{^{1}H} (CD_2Cl_2): δ −114.5 ppm (^1J(P−B) = 30.0 Hz).

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Supporting Information Available: Description of experimental procedures and tables of crystal data and collection parameters, positional parameters, general temperature factors, bond distances, bond angles, and torsion angles for complex **4** (21 pages). Ordering information is given on any current masthead page.

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