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Synthesis and Characterization of $IrH_2\{Si(OTf)Ph_2\}(TFB)(PR_3)$ ($PR_3 = P^iPr_3$, PCy_3): First Base-Stabilized Silylene Complexes of Iridium

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Summary: The reactions of H_2SiPh_2 with the triflato complexes $Ir(OTf)(TFB)(PR_3)$ afford the base-stabilized silylene complexes $IrH_2\{Si(OTf)Ph_2\}(TFB)(PR_3)$ (TFB = tetrafluorobenzobarrelene; $PR_3 = P^iPr_3$, PCy_3). The single-crystal X-ray structural analysis of $IrH_2\{Si(OTf)Ph_2\}(TFB)(P^iPr_3)$ has been performed. The distances Ir−Si (2.337(2) Å) and Si−O (1.790(5) Å) as well as the summation of angles at silicon, ignoring the Si−OTf bond (343.5°), are in agreement with the partial unsaturated character of the base-stabilized silylene ligand.

Introduction

The development of transition-metal base-stabilized silylene chemistry reached a significant milestone in 1987, when Tilley[1] and Zybill[2] reported the synthesis and crystal structures of the base-stabilized silylene derivatives $[Ru(\eta^5\text{-}C_5Me_5)\{Si(NCCH_3)Ph_2\}(PMe_3)_2]BPh_4$ and $Fe\{Si(HMPA)(O^tBu)_2\}(CO)_4$ (HMPA = hexamethylphosphoric triamide), respectively. Over the past few years well-characterized silylene complexes of Cr,[3] Mo,[3g] W,[3c] Mn,[3egh,4] Re,[5] Fe,[2,3acegh,4b,6] Ru,[1,7] Os,[8] and Co[3] have been reported. However, no iridium−silylene derivatives are known.

For several years, we have been exploring the reactivity of square-planar iridium(I) complexes toward silanes.[9] Thus, recently, we have observed that the reactions of the π-alkyne complexes $Ir(acac)(\eta^2\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)(PR_3)$ with H_2SiPh_2 lead to $Ir(acac)\{C[CH(OCH_3)OSiPh_2]{=}CHCO_2CH_3\}(PR_3)$ ($PR_3 = P^iPr_3$, PCy_3), which are a net result of a transformation involving addition of one Si−H bond across the C═O bond and a second across the alkyne triple bond. In these compounds the bonding situation in the Ir−Si−O sequence could be described as a intermediate state between metal−silylene stabilized by an oxygen base and a tetrahedral silicon.[10]

As a continuation of our work in this field, we have now carried out the reactions of square-planar iridium(I) complexes $Ir(OTf)(TFB)(PR_3)$ (TFB = tetrafluorobenzobarrelene; $PR_3 = P^iPr_3$, PCy_3) with H_2SiPh_2. During this study, we have isolated the derivatives $IrH_2\{Si(OTf)Ph_2\}(TFB)(PR_3)$, which are the first base-stabilized iridium−silylene complexes. In this note, we report their syntheses and structural characterization.

Results and Discussion

The base-stabilized silylene complexes $IrH_2\{Si(OTf)Ph_2\}(TFB)(PR_3)$ ($PR_3 = P^iPr_3$ (**6**), PCy_3 (**7**)) can be prepared via the reaction sequence shown in Scheme 1. On treatment with P^iPr_3 and PCy_3, the bis(tetrafluorobenzobarrelene)iridium(I) compound **1** affords the square-planar derivatives **2** and **3**. The reactions of these compounds with AgOTf lead to complexes **4** and **5**, which react with the stoichiometric amount of diphenylsilane, in toluene at room temperature, to give yellow solutions, from which the base-stabilized silylene derivatives **6** and **7** are separated as white solids in 39% (**6**), and 68% (**7**) yield, respectively, by addition of hexane.

Complexes **6** and **7** were characterized by elemental analysis and IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. Complex **6** was further characterized by an X-ray crystallographic study. The molecular structure of **6** is presented in Figure 1. Selected bond distances and angles are listed in Table 1.

The coordination geometry around the iridium atom could be rationalized as derived from a highly distorted

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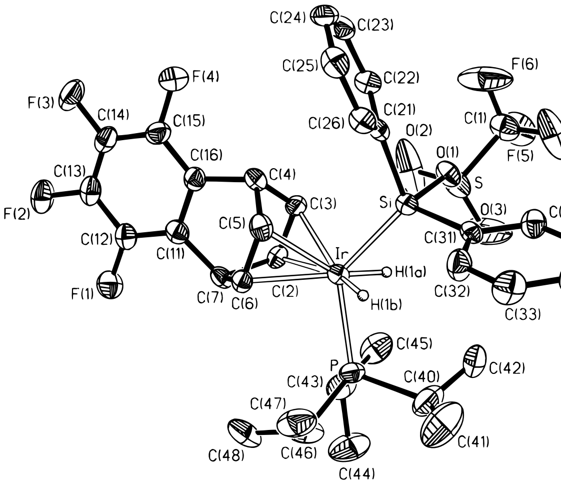
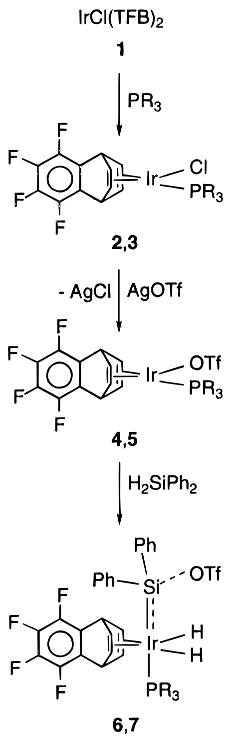


Figure 1. Molecular structure of IrH$_2${Si(OTf)Ph$_2$}(TFB)(P^{i}Pr$_3$) (**6**).

Scheme 1



PR$_3$	complex		
P^{i}Pr$_3$	**2**	**4**	**6**
PCy$_3$	**3**	**5**	**7**

octahedron with the triisopropylphosphine and the silylene ligands occupying pseudo-trans positions (P−Ir−Si = 129.51(7)°), at opposite sites of an ideal coordination plane defined by the two *cis*-hydrido ligands (H(1a)−Ir−H(1b) = 97(4)°) and the chelate diolefinic molecule.

The most conspicuous features of the structure are the structural parameters related to the silicon atom, which suggest the presence of partial unsaturated character, and the small Si−Ir−P angle.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex IrH$_2${Si(OTf)Ph$_2$}(TFB)(P^{i}Pr$_3$) (6)

Ir−P	2.355(2)	Ir−Si	2.337(2)
Ir−C(2)	2.239(7)	Ir−C(3)	2.229(7)
Ir−C(5)	2.227(7)	Ir−C(6)	2.214(7)
C(2)−C(3)	1.37(1)	C(5)−C(6)	1.38(1)
Si−O(1)	1.790(5)	Si−C(21)	1.877(7)
Si−C(31)	1.870(7)		
P−Ir−Si	129.51(7)	O(1)−Si−Ir	114.8(2)
C(21)−Si−Ir	119.0(2)	C(31)−Si−Ir	115.9(2)
O(1)−Si−C(21)	95.8(3)	O(1)−Si−C(31)	99.3(3)
C(31)−Si−C(21)	108.6(3)		

As expected for a base-stabilized silylene−iridium(III) complex, the Ir−Si distance of 2.337(2) Å is significantly shorter than those determined previously for the six-coordinate silyliridium(III) compounds IrH$_2$(SiEt$_3$)(COD)(AsPh$_3$) (COD = 1,5-cyclooctadiene, 2.414(2) Å),[11] IrH$_2$(SiMe$_2$Ph)(CO){P(p-tol)$_3$}$_2$ (2.414(2) Å),[12] IrH(Ph$_2$SiC$_6$H$_4$)(PMe$_3$)$_3$ (2.404(3) Å),[13] IrH(SiMe$_2$Cl)$_2$(CO)(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane, 2.396(2) Å), and IrH(SiEtF$_2$)$_2$(CO)(dppe) (2.360(10) Å).[14] The silylene character of **6** is also supported by the relatively long Si−O(1) bond length of 1.790(5) Å. Typical Si−O single bonds in silyl compounds normally fall in the range 1.63−1.66 Å,[15] whereas metal−silylene complexes stabilized by oxygen bases have Si−O distances between 1.68 and 1.85 Å. The Si−O(1) distance in **6** is longer than the related bond length reported for the complexes Fe{Si(HMPA)Cl$_2$}(CO)$_4$ (1.683(3) Å),[3c] Cr{Si(HMPA)Cl$_2$}(CO)$_5$ (1.690(2) Å),[3c] Fe{Si(HMPA)Me$_2$}(CO)$_4$ (1.735(3) Å),[6c] Cr{Si(HMPA)Me$_2$}(CO)$_5$ (1.743(2) Å),[3c] Fe{Si(HMPA)(S^{t}Bu)$_2$}(CO)$_4$ (1.734(2) Å),[6e] Fe{Si(HMPA)(O^{t}Bu)$_2$}(CO)$_4$ (1.730(3) Å),[2] and Ru(η^5-C$_5$Me$_5$){Si[S(Tol-p)](OTf)$_2$}(PMe$_3$)$_2$ (1.765(8) Å)[7d] but shorter than those found in Os(TTP){Si(THF)Et$_2$} (TTP = *meso*-tetra-*p*-tolylporphyrin, 1.82(2) Å),[8] Ru(η^5-C$_5$Me$_5$){Si(OTf)Ph$_2$}(PMe$_3$)$_2$ (1.853(5) Å),[7a] and Ru(η^5-C$_5$Me$_5$){Si[S(Tol-p)]$_2$(OTf)}(PMe$_3$)$_2$ (1.856(5) Å).[7d]

The bond angles at silicon fall into four distinct groups: the C(21)−Si−Ir angle (119.0(2)°) is close to the standard sp^2 angle (120°), while the C(31)−Si−C(21) (108.6(3)°) is close to a tetrahedral angle of 109°, and the O(1)−Si−Ir (114.8(2)°) and C(31)−Si−Ir (115.9(2)°) angles lie in between, while O(1)−Si−C(21) (95.8(3)°) and O(1)−Si−C(31) (99.3(3)°) are noticeably smaller. It has previously been proposed that for a base-stabilized silylene compound the summation of angles at silicon, ignoring the Si−base bond, should be between 329 and 360°.[3,7] For complex **6** the summation of the angles C(21)−Si−Ir, C(13)−Si−Ir, and C(21)−Si−C(31) gives a value of 343.5°, which is very close to the arithmetic mean between the tetrahedral and trigonal values (344.5°) and agrees well with those reported for [Ru(η^5-C$_5$Me$_5$){Si(NCCH$_3$)Me$_2$}(PMe$_3$)$_2$]BPh$_4$ (344°)[7d] but is greater than those reported for M{Si(HMPA)R$_2$}(CO)$_n$ (M = Fe, n = 4; M = Cr, n = 5; 337−342°)[3c] and Ru(η^5-C$_5$Me$_5$){Si(OTf)R$_2$}(PMe$_3$)$_2$ (R = S(p-Tol) (334°), Ph (341°))[7d] and smaller than that calculated for [Ru(η^5-C$_5$Me$_5$){Si(NCCH$_3$)Ph$_2$}(PMe$_3$)$_2$]BPh$_4$ (352°).[7d]

The small Si−Ir−P angle (129.51(7)°) may be due to different steric requirements, relatively small for the

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hydridos and comparatively large for the diene, P^iPr_3, and silylene ligands. Angular distortions in hydrido complexes are not unusual. We note that in the complex $IrH_2(SnPh_3)(TFB)(PCy_3)$ the angle between the stannyl and phosphine ligands is 129.46(3)°.[16] A similar observation has been reported for the silyl compound $IrH_2(SiEt_3)(COD)(AsPh_3)$, in which the major deviation from the ideal octahedron geometry arises from the Si−Ir−As angle (133.40(4)°).[11] For the complex $IrH_2(SnCl_3)(PPh_3)_3$ the angle P−Ir−P involving two chemically equivalent phosphine groups, which are pseudo-trans to each other, is 145.95(9)°.[17] Values of about 150° have been also reported for the related angle in the complexes *mer*-$IrH_3(PPh_3)_3$,[8] $[(PPh_3)Au(\mu\text{-}H)IrH_2(PPh_3)_3]^+$,[19] *mer*-$[IrH_2(CO)(PPh_3)_3]^+$,[20] and $[IrH_2(PPh_3)_2(C_4H_8S)_2]^+$.[21]

In agreement with the structure shown in Figure 1 the IR spectra of **6** and **7** in Nujol contain one absorption at 2155 (**6**) and 2145 cm^{-1} (**7**), attributable to ν(Ir−H). In the ^1H NMR spectra in toluene-d_8 the hydrido resonances appear as a doublet at −15.16 (**6**) and −14.85 ppm (**7**) with P−H coupling constants of 18.9 and 18.3 Hz, respectively. At room temperature, the spectra contain two resonances from the diolefin, one due to the aliphatic protons at approximately 4.8 ppm and the other, due to the olefinic protons, at about 3.2 ppm. At −55 °C, the spectra show two aliphatic and two olefinic resonances, in agreement with the arrangement of ligands around the iridium atom (Figure 1). This behavior suggests that, in solution, the complexes **6** and **7** possess rigid structures only at low temperature. At room temperature an intramolecular exchange process takes place, which involves the relative positions of the atoms of the diolefin, similarly to that observed for the dihydrido−silyl and dihydrido−stannyl complexes $IrH_2(SiPh_3)(TFB)(PCy_3)$ and $IrH_2(SnPh_3)(TFB)(PCy_3)$. The fluxional process could proceed via five-coordinate intermediates, resulting from the dissociation of the phosphine ligand or of one arm of the chelating tetrafluorobenzobarrelene diolefin.[16] The $^{31}P\{^1H\}$ NMR spectra show singlets at 23.0 (**6**) and 7.1 ppm (**7**), along with the satellites due to the ^{29}Si isotope. In accordance with the pseudo-trans positions of the silylene and phosphine ligands, the values of the P−^{29}Si coupling constants are 83.5 (**6**) and 82.4 Hz (**7**). Under off-resonance conditions, both singlets are split into triplets due to the P−H coupling.

The formation of **6** and **7** probably involves the initial oxidative addition of H_2SiPh_2 to **4** and **5** to give hydrido−silyl intermediates of the type $IrH(OTf)(SiHPh_2)(TFB)(PR_3)$.[22] According to general trend shown for these compounds to release phosphine, the dissociation of the phosphine ligands from the hydrido-silyl intermediates could lead to the unsaturated species $IrH(SiHPh_2)(OTf)(TFB)$, which by an α-elimination reaction should give the silylene derivative $IrH_2({=}SiPh_2)(OTf)(TFB)$. Following this is attack of the silylene group by the $[OTf]^-$ anion to form the unsaturated dihydrido $IrH_2\{Si(OTf)Ph_2\}(TFB)$, which by coordination of the phosphine ligand should give **6** and **7**. A similar mechanism has previously been proposed for the formation of $IrH_2\{Si[OC(O)CH_3]Ph_2\}(TFB)(PR_3)$[9b] and $IrH_2\{Si(OR)Ph_2\}(CO)_2(PCy_3)$.[9c]

In conclusion, the reactions of $Ir(OTf)(TFB)(PR_3)$ with H_2SiPh_2 afford $IrH_2\{Si(OTf)Ph_2\}(TFB)(PR_3)$ ($PR_3 = P^iPr_3$, PCy_3). The single-crystal X-ray structural analysis of $IrH_2\{Si(OTf)Ph_2\}(TFB)(P^iPr_3)$ indicates that the structural parameters at the silicon atom agree well with those previously reported for types of silyl compounds generally known as base-stabilized silylene complexes.

Experimental Section

All reactions were carried out under argon atmosphere using standard Schlenk techniques. Solvents were dried using appropiate drying agents and freshly distilled under argon before use. Complex $IrCl(TFB)_2$ (**1**) was prepared by a published method.[23]

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on either a Varian UNITY 300 or on a Bruker 300 AXR spectrophotometer. Chemical shifts are expressed in ppm upfield from Me_4Si (^1H) and 85% H_3PO_4 ($^{31}P\{^1H\}$). Coupling constants are given in hertz. IR data were recorded on a Perkin-Elmer 783 or on a Nicolet 550 spectrophotometer. Elemental analyses were carried out with a Perkin-Elmer 2400 CHNS/O microanalyzer.

Preparation of $IrCl(TFB)(P^iPr_3)$ (2). A suspension of **1** (100 mg, 0.147 mmol) in acetone (10 mL) was treated with P^iPr_3 (28 μL, 0.147 mmol). The resulting solution was stirred for 15 min at room temperature. After concentration of the solution to dryness, hexane was added to afford an orange solid. The solution was decanted, and the solid was washed with hexane and dried in vacuo; yield 73 mg (81.5%). Anal. Calcd for $C_{21}H_{27}ClF_4IrP$: C, 41.07; H, 4.43. Found: C, 40.73; H, 4.13. IR (Nujol, cm^{-1}): ν(Ir−Cl) 320 (m). ^1H NMR (300 MHz, C_6D_6, 20 °C): δ 5.50 (br, 2H, −CH), 4.18 (br, 2H, =CH), 2.27 (m, 5H, =CH and PC*H*CH$_3$), 1.31 (dd, $J_{H-H} = 7.3$, $J_{P-H} =$ 13.7, 18H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 28.8 (s).

Preparation of $IrCl(TFB)(PCy_3)$ (3). This compound was prepared analogously to **2**, starting from $IrCl(TFB)_2$ (100 mg, 0.147 mmol) and PCy_3 (41.2 mg, 0.147 mmmol). Compound **2** was isolated as an orange solid: yield 101 mg (93%). Anal. Calcd for $C_{30}H_{39}ClF_4IrP$: C, 49.07; H, 5.35. Found: C, 49.28; H, 5.74. IR (Nujol, cm^{-1}): ν(Ir−Cl) 325 (m). ^1H NMR (300 MHz, C_6D_6, 20 °C): δ 5.16 (br, 2H, −CH), 4.05 (br, 2H, =CH), 2.00 (br, 2H, =CH), 1.98−1.09 (m, 33H, PCy_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 17.7 (s).

Preparation of $Ir(OTf)(TFB)(P^iPr_3)$ (4). A solution of **2** (100 mg, 0.163 mmol) in acetone (10 mL) was treated with AgOTf (42 mg, 0.163 mmol). After stirring for 1 h in the dark, the suspension was filtered, and the solution was concentrated to ca. 0.5 mL. Hexane was added to afford a yellow solid. The

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solution was decanted, and the solid was washed with hexane and dried in vacuo; yield 90.2 mg (76%). Anal. Calcd for $C_{22}H_{27}F_7IrO_3PS$: C, 36.31; H, 3.74; S, 4.41. Found: C, 36.52; H, 4.33; S, 4.13. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 4.92 (br, 2H, $-$CH), 4.53 (br, 2H, $=$CH), 1.60 (m, 5H, $=$CH and PC*H*CH$_3$), 0.91 (dd, $J_{H-H} = 7.0$, $J_{P-H} = 14.0$, 18H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 31.1 (s).

Preparation of Ir(OTf)(TFB)(PCy$_3$) (5). This compound was prepared analogously to **4**, starting from **3** (100 mg, 0.135 mmol) and AgOTf (35 mg, 0.135 mmol). Compound **5** was isolated as a deep yellow solid; yield 89 mg (77%). Anal. Calcd for $C_{31}H_{39}F_7IrO_3PS$: C, 43.91; H, 4.64; S, 3.78. Found: C, 43.73; H, 5.53; S, 3.85. IR (Nujol, cm^{-1}): ν_{asym}(SO) 1346 (s). ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 4.99 (br, 2H, $-$CH), 4.54 (br, 2H, $=$CH), 1.88 (br, 2H, $=$CH), 1.75$-$1.10 (m, 33H, PCy$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 19.2 (s).

Preparation of IrH$_2${Si(OTf)Ph$_2$}(TFB)(P^{i}Pr$_3$) (6). A solution of **4** (100 mg, 0.137 mmol) in toluene (10 mL) was treated with H_2SiPh_2 (27 μL, 0.137 mmol). The orange solution became pale yellow immediately. This solution was concentrated to ca. 0.5 mL, and addition of hexane caused the precipitation of a white solid. The solution was decanted, and the solid was washed with hexane and dried in vacuo; yield 49 mg (39%). Anal. Calcd for $C_{34}H_{39}F_7IrO_3PSSi$: C, 44.78; H, 4.31; S, 3.52. Found: C, 44.33; H, 4.37; S, 3.71. IR (Nujol, cm^{-1}): ν(Ir$-$H) 2155 (m), ν_{asym}(SO) 1366 (s). ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 7.95$-$7.15 (m, 10H, Ph), 4.77 (br, 2H, $-$CH), 3.20 (s, 4H, $=$CH), 1.89 (m, 3H, PC*H*CH$_3$), 0.79 (dd, $J_{H-H} = 7.0$, $J_{P-H} = 13.9$, 18H, PCHC*H*$_3$), $-$15.16 (d, $J_{P-H} = 18.9$, 2H, Ir$-$H). ^{1}H NMR (300 MHz, C_7D_8, $-$55 °C): δ 4.88 (br, 1H, $-$CH), 4.34 (br, 1H, $-$CH), 3.36 (br, 2H, $=$CH), 2.56 (br, 2H, $=$CH). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 23.0 (s with ^{29}Si satellites, $J_{P-Si} = 83.5$).

Preparation of IrH$_2${Si(OTf)Ph$_2$}(TFB)(PCy$_3$) (7). This compound was prepared analogously to **6**, starting from **5** (100 mg, 0.118 mmol) and H_2SiPh_2 (23 μL, 0.118 mmmol). Compound **7** was isolated as a white solid; yield 83 mg (68%). Anal. Calcd for $C_{43}H_{52}F_7IrO_3PSSi$: C, 49.99; H, 5.07; S, 3.10. Found: C, 50.27; H, 4.94; S, 2.85. IR (Nujol, cm^{-1}): ν(Ir$-$H) 2145 (m), ν_{asym}(SO) 1375 (s). ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 7.97$-$7.12 (m, 10H, Ph), 4.84 (br, 2H, $-$CH), 3.28 (br, 4H, $=$CH), 2.06$-$1.15 (m, 33H, PCy$_3$), $-$14.85 (d, $J_{P-H} = 18.3$, 2H, Ir$-$H). ^{1}H NMR (300 MHz, C_7D_8, $-$55 °C): δ 4.94 (br, 1H, $-$CH), 4.53 (br, 1H, $-$CH), 3.46 (br, 2H, $=$CH), 2.78 (br, 2H, $=$CH). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 7.1 (s with ^{29}Si satellites, $J_{P-Si} = 82.4$; triplet in off-resonance).

X-ray Structure Analysis of IrH$_2${Si(OTf)Ph$_2$}(TFB)(P^{i}Pr$_3$) (6). Crystals suitable for the X-ray diffraction study were obtained from a toluene/pentane solution. An oil-coated rapidly cooled colorless crystalline rectangular block was mounted directly from solution.[24] Crystal and collection data: orthorhombic space group *Pbca* (No. 61); $a = 15.798(4)$, $b = 13.527(1)$, $c = 32.403(2)$ Å; $V = 6925(2)$ Å^3 (from 50 reflections $10 \le 2\theta \le 25°$); $Z = 8$, $d_{calcd} = 1.750$ g cm^{-3}; (Mo Kα) = 4.07 mm^{-1}; crystal dimensions 0.45 × 0.44 × 0.31 mm; 4-circle Stöe AED diffractometer, Mo Kα radiation (0.71073 Å), graphite-oriented monochromator; $T = 153$ K; $2\theta/\omega$ scan method, max $2\theta = 50°$; 6088 reflections measured, 6070 independent reflections. Intensity data were corrected for Lorentz and Polarization effects, and a semiempirical absorption correction (ψ scan method[25]) was applied. The structure was solved by direct methods and conventional Fourier techniques.[26] All non-hydrogen atoms were refined anisotropic by full-matrix least squares. The hydrides and the hydrogens of the TFB ligand were located and freely refined isotropically. Remaining hydrogens were fixed in idealized positions (distance C$-$H = 0.96 Å). *R* values: R_1 ($F_o > 4\sigma(F_o)$, for 4657 reflections) = 0.0388; R_2 (all data) = 0.1068; $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_2(F^2) = \sqrt{\{\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4\}}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3]$ (where $x = 0.03$ and $y = 63.55$). Largest peak and hole in the final difference map: 1.129 and $-$1.534 e Å^{-3}.

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Supporting Information Available: Tables of atomic coordinates and thermal parameters, anisotropic thermal parameters, experimental details of the X-ray study, and complete bond distances and angles (7 pages). Ordering information is given on any current masthead page.

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