Notes

Synthesis, X-ray Structure, and Catalytic Activity of the Unusual Complex [Ir(TFB)(P*i*Pr$_3$)$_2$]BF$_4$ (TFB = Tetrafluorobenzobarrelene)

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*Summary: Complex IrCl(TFB)(PiPr$_3$) (**1**) reacts with AgBF$_4$ in the presence of triisopropylphosphine to afford [Ir(TFB)(PiPr$_3$)$_2$]BF$_4$ (**2**). The structure of **2** was determined by an X-ray diffraction study. The coordination geometry around the iridium center is distorted square-planar with a P−Ir−P angle of 102.7(1)°. Complex **2** reacts with molecular hydrogen to give cis-trans-[IrH$_2$(TFB)(PiPr$_3$)$_2$]BF$_4$ (**3**), and with phenylacetylene to afford Ir(C$_2$Ph)(TFB)(PiPr$_3$) (**4**). Complex **2** is found to be a very active catalyst for the hydrogenation of olefins and phenylacetylene. In dichloromethane as solvent at 25 °C and atmospheric pressure, selectivities close to 80% are achieved for the hydrogenation of the alkyne to alkene.*

Introduction

The dimeric complex [Ir(μ-Cl)(COD)]$_2$ exhibits a particulary rich and interesting chemistry, which has formed one of the cornerstones in the development of organometallic chemistry. In particular, it is the key starting material for the preparation of the well known catalysts [Ir(COD)(PR$_3$)$_n$]$^+$.[1]

The value of *n* in these systems depends upon the cone angle of the phosphine ligand. Thus, the five-coordinate complexes [Ir(COD)(PR$_3$)$_3$]$^+$ are stabilized by phosphine ligands with cone angles smaller than 130°, while the four-coordinate derivatives [Ir(COD)(PR$_3$)$_2$]$^+$ are obtained when the cone angle of the phosphorus donor ligand is between 130° and 145°. Very bulky phosphine ligands, as for example P*i*Pr$_3$, do not form cations of this type.[2]

We have previously reported that treatment of IrCl$_3$·*x*H$_2$O with tetrafluorobenzobarrelene (TFB) in refluxing ethanol/water leads to the complex IrCl(TFB)$_2$ in nearly quantitative yield.[3] The accessibility of this compound has promoted the development of an extensive chemistry of neutral and cationic complexes containing the iridium−tetrafluorobenzobarrelene moiety, which shows significant differences with respect to the chemistry of the typical iridium−1,5-cyclooctadiene moiety.[4]

As a continuation of our work on the chemical properties of iridium−tetrafluorobenzobarrelene unit, we now prove that this diolefin allows to stabilize the four-coordinate cation [Ir(TFB)(P*i*Pr$_3$)$_2$]$^+$. In this note, we report the synthesis, X-ray structure, and some reactivity and catalytic activity of this unusual complex.

Results and Discussion

Complex [Ir(TFB)(P*i*Pr$_3$)$_2$]BF$_4$ (**2**) was prepared in high yield (93%) by reaction of IrCl(TFB)(P*i*Pr$_3$) (**1**) with AgBF$_4$ in the presence of triisopropylphosphine (Scheme 1). The reaction was carried out at room temperature in a dichloromethane−acetone mixture as solvent and was isolated as a violet solid.

A view of the molecular geometry of **2** is shown in Figure 1. The coordination geometry around the iridium center is distorted square-planar (minimum displacement for the best square-plane coordination 0.136(11) Å for M(2)), with a P(1)−Ir−P(2) angle of 102.7(1)°, which is similar to the P−Rh−P angles found in the complexes Rh(η^2-O$_2$CCH$_3$)(P*i*Pr$_3$)$_2$ (106.00(4)°)[5] and Rh(acac)(PCy$_3$)$_2$ (105.63(4)°).[6] The relative large value of

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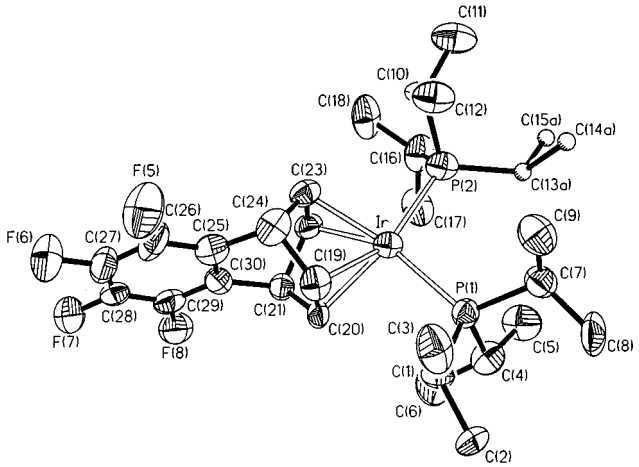
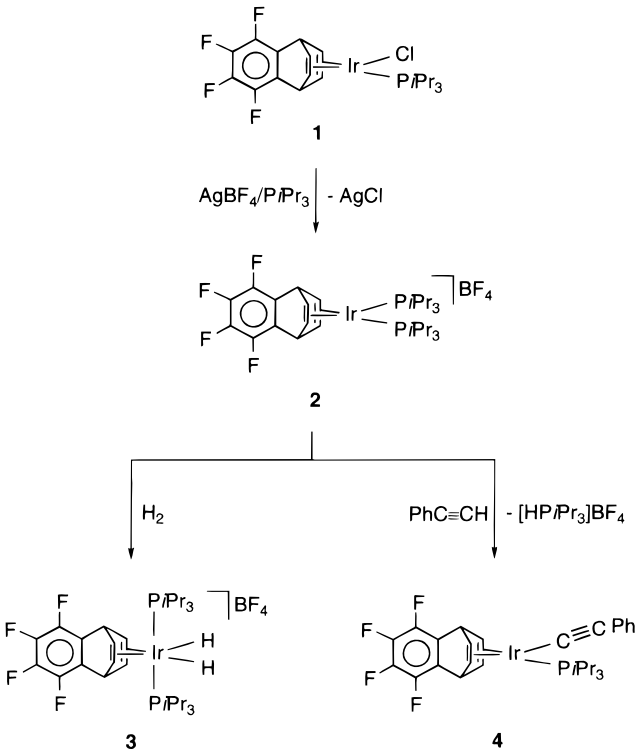


Figure 1. Molecular diagram of complex [Ir(TFB)(P*i*Pr$_3$)$_2$]-BF$_4$ (**2**). Selected bond distances (Å) and angles (deg): Ir−P(1) 2.383(3), Ir−P(2) 2.400(3), Ir−C(19) 2.19(1), Ir−C(20) 2.21(1), Ir−C(22) 2.21(1), Ir−C(23) 2.22(1), C(19)−C(20) 1.39(2), C(22)−C(23) 1.38(2), P(1)−Ir−P(2) 102.7(1), P(1)−Ir−M(1)[a] 94.8(3), P(2)−Ir−M(2)[a] 94.9(3), M(1)[a]−Ir−M(2)[a] 67.9(4) [[a]M(1) and M(2) are the midpoints of the olefinic double bonds C(19)−C(20) and C(22)−C(23), respectively]. C(13a)−C(15a) represents a set of distorted C atoms refined isotropically.

Scheme 1



this angle can be explained by the fact that the two phosphine ligands, *cis* disposed, experience a large steric hindrance, as a result of the large cone angle of the triisopropylphosphine group (160°).[7]

The tetrafluorobenzobarrelene bite angle of 67.9(5)° is similar to values found in other iridium−tetrafluorobenzobarrelene compounds.[4] In this context, it should be mentioned that the 1,5-cyclooctadiene bite angle in Ir(η^4-1,5-cyclooctadiene) complexes is 86(3)°.[8] Thus, the higher space required by the 1,5-cyclooctadiene diolefin in comparison with the tetrafluorobenzobarrelene could explain why with 1,5-cyclooctadiene it has not been possible to stabilize a related compound to **2**.

Table 1. Initial Rate of Hydrogenation (r_i) of Various Olefins Catalyzed by [Ir(TFB)(P*i*Pr$_3$)$_2$]BF$_4$ (2) in Dichloromethane at 25 °C (1 atm of H$_2$; 0.27 M olefin; 1 × 10^{-3} M [Ir]$^+$)

substrate	H$_2$ uptake (mL min^{-1})	r_i, 10^5 (M s^{-1})
styrene	4.7	40
1-hexene	4.2	35
cyclohexene	0.6	5.1
2,3-dimethyl-2-butene	0.1	0.5

In dichloromethane as solvent, complex **2** and the previously reported 1,5-cyclooctadiene cations [Ir(COD)-(PR$_3$)$_2$]$^+$ show a different behavior toward molecular hydrogen. While complex **2** reacts with molecular hydrogen to give the dihydrido derivative *cis-trans*-[IrH$_2$(TFB)(P*i*Pr$_3$)$_2$]BF$_4$ (**3**, in Scheme 1), the reactions of the cations [Ir(COD)(PR$_3$)$_2$]$^+$ with hydrogen afford *cis-cis*-[IrH$_2$(COD)(PR$_3$)$_2$]$^+$.[9,10] Complexes [Ir(DCT)(PR$_3$)$_2$]$^+$ (DCT = dibenzo[*a*,*e*]cyclooctatetraene) show a similar behavior to that of [Ir(COD)(PR$_3$)$_2$]$^+$.[11]

Complex **3**, which in contrast to *cis-cis*-[IrH$_2$(COD)-(PR$_3$)$_2$]$^+$ is stable at room temperature in solution, was isolated as a white microcrystalline solid in 87% yield. The IR spectrum in Nujol shows a strong absorption at 2249 cm^{-1} attributable to ν(Ir−H), in agreement with a *cis* arrangement of these ligands. The ^{1}H NMR spectrum shows the hydrido resonances at −16.79 ppm, as a triplet with a H−P coupling constant of 17.0. In the low field region of the spectrum, the diene give rise to two resonances at 5.11 (CH) and 4.26 (CH=) ppm. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 20.8 ppm, which is split into a triplet under off-resonance conditions, as a result from the coupling with two hydrido ligands.

As expected from the reactivity of **2** and the 1,5-cyclooctadiene cations [Ir(COD)(PR$_3$)$_2$]$^+$ toward molecular hydrogen, both systems are active catalysts for the reduction of unsaturated organic substrates. However, between them, there is a significant difference in versatility. Cations [Ir(COD)(PR$_3$)$_2$]$^+$ are excellent catalysts for the reduction of olefins,[12] but substrates such as styrene, stylbene, and α-methylstyrene cannot be reduced, due to the formation of arene derivatives.[13] In contrast to [Ir(COD)(PR$_3$)$_2$]$^+$, complex **2** is an active catalyst for the hydrogenation of styrene to ethylbenzene. The reduction rate of this olefin is even faster than those observed for the reduction of 1-hexene, cyclohexene, and 2,3-dimethyl-2-butene (Table 1). Al-

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(9) Complexes *cis, trans*-[IrH$_2$(COD)(PR$_3$)$_2$]$^+$ can be prepared by reaction of [Ir(COD)(PR$_3$)$_2$]$^+$ with molecular hydrogen in the presence of 1,5-cyclooctadiene or alternatively by treatment of the solvated compounds [IrH$_2$(acetone)$_2$(PR$_3$)$_2$]$^+$ with 1,5-cyclooctadiene. See reference 9.

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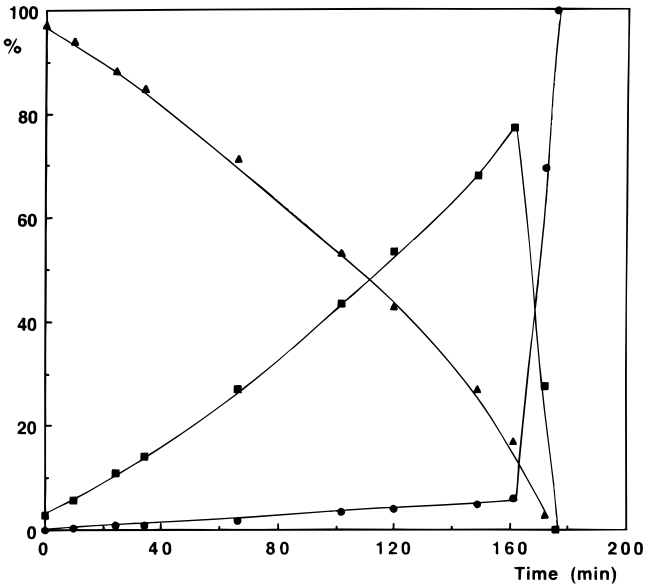

Figure 2. Hydrogenation of phenylacetylene catalyzed by $[Ir(TFB)(P\textit{i}Pr_3)_2]BF_4$ (**2**) in dichloromethane at 25 °C [1 atm of H_2; 0.12 M PhC_2H; 3.3×10^{-3} M $[Ir]^+$. (▲) Phenylacetylene, (■) styrene, (●) ethylbenzene].

though the reduction of 2,3-dimethyl-2-butene is slower than those of unhindered olefins, deactivation of **2** is not observed. This is the other significant difference with regard to the $[Ir(COD)(PR_3)_2]^+$ cations, which in the presence of hindered olefins undergo an irreversible deactivation, as a result of the formation of the $[(PR_3)_2HIr(\mu\text{-}H)_3IrH(PR_3)_2]^+$ dimers.[13] So, complex **2** is not only a more versatile catalyst than $[Ir(COD)(PR_3)_2]^+$ but also more stable.

The hydrogenation of terminal alkynes catalyzed by $[M(COD)(PR_3)_2]^+$ (M = Rh, Ir) systems is not easy.[4i,12c,14] In this sense, it has been proposed that the terminal alkynes, which are fairly acidic, destroy the active species by formation of metal−alkynyl derivatives.[14a] Complex **2** reacts with phenylacetylene to give the square-planar alkynyl complex $Ir(C_2Ph)(TFB)(P\textit{i}Pr_3)$ (**4**, in Scheme 1). In spite of this, complex **2** is a very active and highly selective catalyst for the reduction of phenylacetylene in dichloromethane and acetone as solvents. In dichloromethane solution at 25 °C and atmospheric pressure, selectivities close to 80% are achieved for the hydrogenation of the alkyne to the alkene, as illustrated in Figure 2.

The presence of an alkynyl ligand in **4** is supported by its IR spectrum in pentane, which contains a ν(C≡C) band at 2085 cm^{-1}. In agreement with the square-planar structure proposed for this compound in Scheme 1, the ^1H NMR spectrum shows two resonances corresponding to the vinylic protons of the diene at 4.10 and 2.40 ppm.

In conclusion, bulky phosphines do not form cations of type $[Ir(diolefin)(PR_3)_2]^+$ when the diolefin is 1,5-cyclooctadiene. However, the tetrafluorobenzobarrelene allows stabilization of the complex $[Ir(TFB)(P\textit{i}Pr_3)_2]BF_4$, as a result from its space requirement for coordination. This derivative is a more versatile and stable catalyst for the reduction of olefins and alkynes than the previously reported $[Ir(COD)(PR_3)_2]^+$ complexes.

Experimental Section

All reactions were carried out under an atmosphere of argon by using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material $IrCl(TFB)(P\textit{i}Pr_3)$ (**1**) was prepared by a published method.[4m] IR spectra were recorded on a Nicolet 550 spectrometer, and the NMR spectra on Varian UNITY 300 and Bruker ARX 300 instruments (vt = virtual triplet; $N = {}^3J(PH) + {}^5J(PH)$). C and H analyses were carried out with a Perkin Elmer 2400 CHNS/O microanalyzer.

Preparation of $[Ir(TFB)(P\textit{i}Pr_3)_2]BF_4$ (2). A solution of $IrCl(TFB)(P\textit{i}Pr_3)$ (**1**) (500.0 mg, 0.81 mmol) in dichloromethane−acetone (2:1, 30 mL) was treated with $AgBF_4$ (158.5 mg, 0.81 mmol). After stirring for 90 min in the dark the AgCl was filtered off through Kieselgur. The orange solution was treated with $P\textit{i}Pr_3$ (158 μL, 0.81 mmol), and a change from orange to violet occurred almost instantaneously. The solvent was removed and the residue washed with ether to give a violet mycrocrystalline solid. Yield: 625 mg (93%). Anal. Calcd for $C_{30}H_{48}BF_8IrP_2$: C, 43.64; H, 5.86%. Found: C, 43.09; H, 6.11. IR (Nujol, cm^{-1}): $\nu(BF_4)$ 1062. ^1H NMR (300 MHz, $CDCl_3$): δ 5.67 (br, 2H, C*H* of TFB), 3.93 (m, 4H, =C*H* of TFB), 2.48 (m, 6H, PC*H*CH_3), 1.40 (dd, 36H, $J(PH) = 14.3$ Hz, $J(HH) = 7.2$ Hz, PCHC*H*$_3$). ^{19}F NMR (282 MHz, CD_2Cl_2): δ −146.34 (second order spin system, 2F, TFB), −152.98 (m, 4F, BF_4^-), −158.67 (second order spin system, 2F, TFB). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 26.9 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2): δ 57.7 (second order spin system, =*C*H of TFB), 41.4 (second order spin system, *C*H of TFB), 27.6 (second order spin system, P*C*H), 20.9 (s, PCH*C*H_3).

Preparation of $[IrH_2(TFB)(P\textit{i}Pr_3)_2]BF_4$ (3). A stream of H_2 was passed through a solution of compound **2** (200 mg, 0.24 mmol) in 20 mL of dichloromethane at 0 °C, and the violet solution turned to pale yellow. The solvent was removed *in vacuo*, and the oil residue was washed with ether to give a pale yellow solid. Recrystallization in dichloromethane−ether gives a white microcrystalline solid. Yield: 156 mg (87%). Anal. Calcd for $C_{30}H_{50}BF_8IrP_2$: C, 43.53; H, 6.09%. Found: C, 43.16; H, 6.13. IR (Nujol, cm^{-1}): ν(IrH) 2249, $\nu(BF_4)$ 1045. ^1H NMR (300 MHz, $CDCl_3$): δ 5.11 (m, 2H, CH of TFB), 4.26 (m, 4H, =CH of TFB), 2.65 (m, 6H, PC*H*CH_3), 1.34 (dvt, 36H, $N = 13.9$ Hz, $J(HH) = 6.9$ Hz, PCHC*H*$_3$), −16.79 (t, 1H, $J(PH) = 17.0$ Hz, IrH). ^{19}F NMR (282 MHz, CD_2Cl_2): δ −144.21 (second order spin system, 2F, TFB), −152.87 (m, 4F, BF_4^-), −159.35 (second order spin system, 2F, TFB). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 20.8 (s; t in off resonance). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2): δ 53.9 (s, =CH of TFB), 36.8 (s, *C*H of TFB), 30.6 (vt, $N = 29.8$ Hz, P*C*H), 19.6 (s, PCH*C*H_3).

Preparation of $Ir(C_2Ph)(TFB)(P\textit{i}Pr_3)$ (4). To a solution of complex **2** (200 mg, 0.24 mmol) in 10 mL of dichloromethane was added HC≡CPh (26 μL, 0.24 mmol). After stirring for 2 h, the solvent was removed, and the residue was extracted with 10 mL of pentane. The solution was led to dryness *in vacuo* to obtain a red oil. IR (pentane, cm^{-1}): ν(C≡C) 2085. ^1H NMR (300 MHz, C_6D_6): δ 7.6−6.9 (m, 5H, Ph), 5.24 (br, 2H, C*H* of TFB), 4.10 and 2.40 (both m, 2H each, =C*H* of TFB), 2.12 (m, 3H, PC*H*CH_3), 1.14 (dd, 18H, $J(PH) = 13.6$ Hz, $J(HH) = 7.2$ Hz, PCHC*H*$_3$). ^{19}F NMR (282 MHz, C_6D_6): δ −148.61 (second order spin system, 2F, TFB), −161.44 (second order spin system, 2F, TFB). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 34.8 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 130.8 (s, Ph), 128.7 (d, $J(PC) = 8.6$ Hz, C_β, C≡C), 128.3 (s, Ph), 125.5 (s, Ph), 125.2 (d, $J(PC) = 12.8$ Hz, C_α, C≡C), 63.5 (d, $J(PC) = 12.1$ Hz, =*C*H of TFB), 45.5 (s, *C*H of TFB), 40.9 (d, $J(PC) = 2.0$ Hz, =*C*H of TFB), 25.5 (d, $J(PC) = 26.7$ Hz, P*C*H), 19.9 (s, PCH*C*H_3).

X-ray Structure Analysis of $[Ir(TFB)(P\textit{i}Pr_3)_2]BF_4$ (2). Crystals suitable for the X-ray diffraction study were obtained from a dichloromethane/ethyl ether solution. A violet irregular

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block was mounted on a glass fiber. Crystal and collection data: space group *Pbca* (no. 61); $a = 20.420(3)$, $b = 13.415(2)$, $c = 24.192(4)$ Å; $V = 6627(2)$ Å (from 56 reflections $20 \leq 2\theta \leq 40°$); $Z = 8$; $D_{calcd} = 1.655$ g cm^{-3}; $\mu = 4.19$ mm^{-1}; crystal dimensions 0.47 × 0.36 × 0.22 mm; 4-circle Siemens-STOE AED-2 diffractometer, Mo K_α radiation (0.71073Å), graphite-oriented monochromator; $T = 273$ K; $\omega/2\theta$ scan method, max $2\theta = 50°$; 4353 measured and independent reflections of which 4342 were used in the refinement. Reflections were corrected for absorption by a semiempirical method (Ψ-scans).[15] The structure was solved by Patterson and conventional Fourier techniques. An isopropyl group of the P(2) phosphine ligand and the BF_4^- anion were observed disordered. These groups were refined with two sites of complementary occupancies (0.86 and 0.14(4)) for the isopropyl group, and with common boron and three sites for each fluorine atom of the anion. Anisotropic thermal parameters were used for all non hydrogen and non disordered atoms; hydrogens, except those bonded to disordered groups, were included in calculated positions[16] riding on carbon atoms with a common thermal parameter. Final $R1(F, F_o > 4.0\sigma(F_o))$ and $wR2(F^2$, all reflections) values were 0.0482 and 0.1164.

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Catalytic Hydrogenation Reactions. The catalytic reactions were followed by measuring the hydrogen consumption as a function of time on a gas buret. The analysis of the products of the catalytic reactions was carried out on a Perkin-Elmer Sigma 3 gas chromatograph with a flame ionization detector, connected to a LC1-100 integrator. A 15% β,β'-oxidipropionitrile on Chromosorb W 80/100 mesh (4 m × $^1/_8$ in.) column at 50 °C was used for analysis of the hydrogenation of olefins. An FFAP on Chromosorb GHP 80/100 mesh (3.6 m × $^1/_8$ in.) column at 150 °C was used for analysis of the hydrogenation of phenylacetylene and styrene. The reaction products were identified by comparison of their retention times with those observed for pure samples.

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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 (22 pages). Ordering information is given on any current masthead page.

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