Cationic Five-Coordinate Bis(butadiene)iridium(I) Complexes from the Highly Labile *cis*-$[Ir(\eta^2\text{-}C_8H_{14})_2(acetone)_2]^+$ Cation as the Precursor

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Dedicated to Professor Rudolf Taube on the occasion of his 70th birthday

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The cation *cis*-$[Ir(\eta^2\text{-}C_8H_{14})_2(acetone)_2]^+$, which is generated in situ from $[Ir(\mu\text{-}Cl)(\eta^2\text{-}C_8H_{14})_2]_2$ (**1**) and $AgPF_6$ in acetone, reacts with butadiene at room temperature to give the five-coordinate complex $[Ir(s\text{-}cis\text{-}\eta^4\text{-}C_4H_6)_2(\eta^2\text{-}C_8H_{14})]PF_6$ (**3**). The cyclooctene ligand of **3** is only weakly coordinated and easily displaced by P*i*Pr$_3$, As*i*Pr$_3$ and Sb*i*Pr$_3$ to afford the compounds $[Ir(s\text{-}cis\text{-}\eta^4\text{-}C_4H_6)_2(E\textit{i}Pr_3)]PF_6$ (**5**–**7**) in excellent yields. Alternatively, **5**–**7** can be prepared from $[IrCl(s\text{-}cis\text{-}\eta^4\text{-}C_4H_6)_2]$ (**4**) by stepwise treatment with $AgPF_6$ and E*i*Pr$_3$ (E = P, As, Sb). The X-ray crystal structure analysis of **5** revealed a square-pyramidal geometry of the cation with the phosphane ligand in the apical position.

Introduction

In the course of our investigations on the ability of sulfonatorhodium(I) compounds to catalyze C−C coupling reactions of olefins and other unsaturated substrates,[1] we recently found that the monomeric triflatorhodium(I) complex $[Rh\{\eta^2\text{-}O_2S(O)CF_3\}(P\textit{i}Pr_3)_2]$ is an active catalyst for the polymerization of butadiene.[2] Moreover, we observed that if instead of the bis(phosphane) compound the dimeric bis(cyclooctene) derivative $[Rh\{\mu\text{-}O_2S(O)CF_3\}(\eta^2\text{-}C_8H_{14})_2]_2$ is treated with C_4H_6, the five-coordinate bis(butadiene) complex $[Rh\{\eta^1\text{-}OS(O)_2CF_3\}(\eta^4\text{-}C_4H_6)_2]$ is formed, and this complex reacts with bulky phosphanes to give the corresponding cations $[Rh(\eta^4\text{-}C_4H_6)_2(PR_3)]^+$ in excellent yields by ligand displacement.[3] Since these cations readily undergo intramolecular C−C coupling reactions and are intermediates in the formation of the unusual cyclotetramer *cis*,*cis*,*trans*,*trans*-1,5,9,13-$C_{16}H_{24}$,[4] we became interested to find out whether analogous bis(butadiene)iridium(I) compounds would be accessible and what their reactivity compared to the rhodium counterparts is. In this paper we report the generation of the highly reactive bis(cyclooctene)iridium(I) cation *cis*-$[Ir(\eta^2\text{-}C_8H_{14})_2(acetone)_2]^+$ and its smooth conversion into cationic five-coordinate bis(butadiene) derivatives.

Results and Discussion

Our attempts to start the stepwise synthesis of the target compounds $[Ir(\eta^4\text{-}C_4H_6)_2(PR_3)]^+$ from the preparation of $[Ir\{\mu\text{-}O_2S(O)CF_3\}(\eta^2\text{-}C_8H_{14})_2]_2$, the analogue of the above-mentioned rhodium complex $[Rh\{\mu\text{-}O_2S(O)CF_3\}(\eta^2\text{-}C_8H_{14})_2]_2$, failed. Treatment of a suspension of $[Ir(\mu\text{-}Cl)(\eta^2\text{-}C_8H_{14})_2]_2$ (**1**) in acetone with two equivalents of AgO_3SCF_3 afforded a mixture of products which could not be separated either by fractional crystallization or chromatographic techniques.

Following earlier work by Schrock[5] and Muetterties,[6] we therefore used the dimeric chloro derivative **1** as the starting material. This compound reacts with $AgPF_6$ (molar ratio 1:2) in acetone to give an orange solution from which, even by evaporation of the solvent under very mild conditions, no analytically pure compound could be isolated. If, however, [D$_6$]acetone was used as the solvent, both the ^{1}H and the ^{13}C NMR spectra of the solution indicated that a bis(cyclooctene)iridium(I) cation had been generated. Although the NMR spectroscopic data did not allow us to determine the number of [D$_6$]acetone molecules coordinated to the metal center, we assume, in analogy to the more stable, isolated complex *cis*-$[Rh(\eta^2\text{-}C_8H_{14})_2(acetone)_2]PF_6$,[7] that the coordination geometry corresponds to a square plane with the cyclooctene and the [D$_6$]acetone ligands in *cis* positions (see Scheme 1). We note that in the ^{13}C NMR spectrum of **2** there is only one signal for the C=O moiety and one signal for the CH_3 carbon indicating that, at room temperature, a fast exchange between free and coordinated [D$_6$]acetone takes place.

Passing a slow stream of butadiene through a solution containing the in situ generated cation **2** for ten seconds, in the presence of excess cyclooctene, led to a quick change of color from orange to pale-yellow. After addition of pentane, a white, moderately air-sensitive solid precipitated which analyzed as $[Ir(s\text{-}cis\text{-}\eta^4\text{-}C_4H_6)_2(\eta^2\text{-}C_8H_{14})]PF_6$ (**3**). The ^{1}H NMR spectrum of **3** displays three well-separated resonances for the butadiene protons at δ = 6.10, 3.50 and 1.48 of which those for the *exo* and *endo* protons of the terminal CH_2 groups are split into doublets of doublets. The signal for the olefinic protons of the coordinated cyclooctene appears at δ = 5.66 and is thus shifted about 2.2 ppm down-

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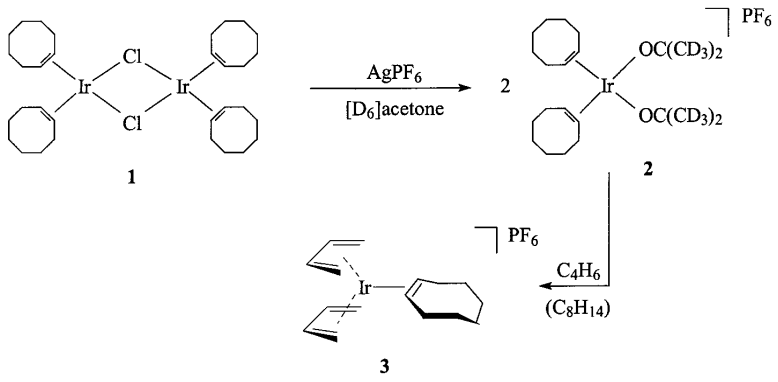


Scheme 1

field relative to **2**. A similar downfield shift is also observed in the ^{13}C NMR spectrum for the signal of the CH=CH carbon atoms of C_8H_{14}, which appears at $\delta = 81.9$ for **3** but at $\delta = 62.7$ for **2**. The increased electron density at the five-coordinate iridium(I) center of **3** could explain these observations.

The cyclooctene ligand of **3** is not strongly coordinated and can therefore be displaced by a better donor such as P*i*Pr$_3$ (Scheme 2). However, treatment of a solution of **3** in dichloromethane with *one* equivalent of the phosphane did not lead to a complete conversion and, after removal of the solvent, afforded a 1:1 mixture of **3** and **5**. An almost quantitative yield of the substitution product **5** could be achieved upon the addition of a second equivalent of P*i*Pr$_3$ to the 1:1 mixture of **3** and **5**. An alternative procedure to prepare **5** consists of the stepwise reaction of the mononuclear precursor **4**[8] with $AgPF_6$ and an equimolar amount of P*i*Pr$_3$. The yield here is also excellent. Compound **5** is a white solid that can be handled in air for a short period of time and can be stored under argon for weeks without decomposition. Similarly to **3**, the ^1H NMR spectrum of **5** displays three signals of equal intensity for the C_4H_6 protons and the ^{13}C NMR spectrum shows two resonances for the butadiene carbon atoms, one of which is split into a doublet due to ^{13}C-^{31}P coupling.

The molecular structure of the triisopropylphosphane complex **5** was determined by X-ray crystallography. There are two independent molecules, **5a** and **5b**, in the unit cell, of which **5a** is shown in Figure 1. The coordination geometry around the iridium center is square-pyramidal with the CH_2 groups of the butadiene ligands at the base of the pyramid. The apical position of the cationic species is occupied by the phosphorus atom of the P*i*Pr$_3$ ligand. The C−C bond lengths of the C_4H_6 moieties together with the bond angles C(1)−C(2)−C(3), C(4)−C(3)−C(2), C(5)−C(6)−C(7) and C(8)−C(7)−C(6) (all ≈120°) clearly indicate an η^4-coordination mode for the diene molecules. The distances between the metal and the CH and CH_2 units lie in the ranges 2.215(11)−2.205(11) and 2.184(11)−2.167(12) Å, respectively, and are quite similar to those found in other

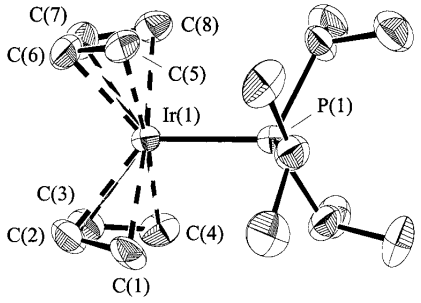
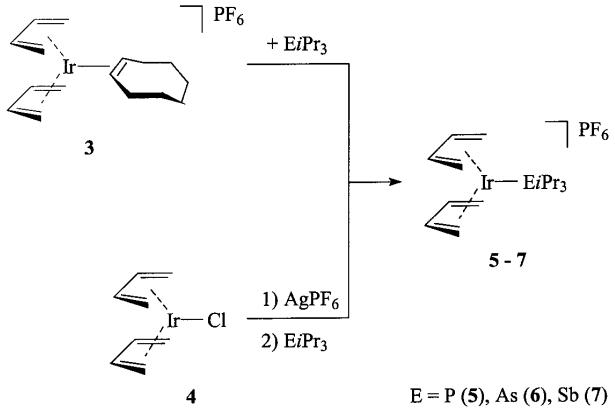


Figure 1. Molecular structure of **5a** (hydrogen atoms and anionic ligand omitted for clarity; there are two independent molecules **5a** and **5b** in the unit cell, the data for **5b** are given after the diagonal lines); principle bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Ir(1)−C(1) 2.206(11)/2.224(13), Ir(1)−C(2) 2.167(12)/2.166(12), Ir(1)−C(3) 2.184(11)/2.179(12), Ir(1)−C(4) 2.215(11)/2.216(11), Ir(1)−C(5) 2.205(11)/2.219(12), Ir(1)−C(6) 2.161(12)/2.187(13), Ir(1)−C(7) 2.178(13)/2.178(13), Ir(1)−C(8) 2.209(12)/2.212(12), C(1)−C(2) 1.424(18)/1.419(19), C(2)−C(3) 1.448(19)/1.436(19), C(3)−C(4) 1.414(18)/1.384(19), C(5)−C(6) 1.381(18)/1.418(19), C(6)−C(7) 1.430(19)/1.435(19), C(7)−C(8) 1.389(19)/1.388(18), Ir(1)−P(1) 2.394(3)/2.389(3); C(1)−Ir(1)−P(1) 90.4(3)/90.5(4), C(4)−Ir(1)−P(1) 94.4(4)/94.9(4), C(5)−Ir(1)−P(1) 91.1(3)/90.3(3), C(8)−Ir(1)−P(1) 95.1(4)/95.3(4), C(1)−C(2)−C(3) 116.8(12)/119.2(12), C(2)−C(3)−C(4) 117.5(12)/118.4(12), C(5)−C(6)−C(7) 118.4(12)/119.2(12), C(6)−C(7)−C(8) 118.5(12)/117.3(12)



Scheme 2

bis(diene)iridium(I) compounds.[9] Both butadiene ligands are nearly planar, as indicated by the torsional angles of −1.7(17)° for the plane [C(1)−C(2)−C(3)−C(4)] and 1.9(18)° for [C(6)−C(7)−C(8)−C(9)]. However, the two planes of the butadienes are not parallel to each other but tilted by 14.6(3)° which could be due to steric repulsion between the bulky phosphane and the diene systems. The Ir−P distance of 2.394(3) Å in **5a** is relatively long compared with the distances of [IrH(s-cis-η⁴-C_4H_6)(PiPr$_3$)$_2$] (2.30−2.32 Å)[10] and several square-planar iridium(I) compounds containing $trans$-[Ir(PiPr$_3$)$_2$] (average Ir−P distance 2.34 Å) as a molecular building block.[11]

The cycloocteneiridium(I) complex **3** also reacts with two equiv. of AsiPr$_3$ or SbiPr$_3$ in dichloromethane at room temperature. The substitution products **6** and **7** (see Scheme 2) can also be formed from **4**, $AgPF_6$ and triisopropylarsane or -stibane in the molar ratio of 1:1:1. Compounds **6** and **7** are white solids, with properties that are quite similar to those of the triisopropylphosphane analogue **5**. With regard to the ^{1}H NMR spectroscopic data of **6** and **7**, we note that the signal of the *endo* protons H_a (for assignment see Figure 2) appears at lower field than that of **5** while the resonances for the protons H_b and H_c are observed slightly upfield compared with the triisopropylphosphane counterpart.

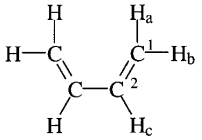


Figure 2. Assignment of the diene protons and carbon atoms in compounds **3**, **5**−**7**

The cations [Ir(s-cis-η⁴-C_4H_6)$_2$(EiPr$_3$)]$^+$ (E = P, As, Sb) are not only thermally quite stable (the PF_6^- salts decompose at about 150 °C) but, in contrast to the rhodium analogue [Rh(s-cis-η⁴-C_4H_6)$_2$(PiPr$_3$)]$^+$, they do not react upon heating by coupling of the two diene units to give an isomeric octadienediyliridium(III) derivative. We have already mentioned that the cationic bis(butadiene)rhodium(I) complex readily undergoes an intramolecular C−C coupling process in refluxing dichloromethane leading to [Rh(η³:η³-C_8H_{12})(PiPr$_3$)]$^+$, which is an intermediate in the rhodium-catalyzed cyclotetramerization of butadiene.[4] However, under the same conditions the iridium cations are completely inert and, even after stirring solutions of **5**, **6** or **7** in refluxing CH_2Cl_2 or CH_3NO_2 for 10−12 h, the starting materials could be quantitatively re-isolated. This inert behavior of the five-coordinate iridium(I) species is not only different to that of [Rh(s-cis-η⁴-C_4H_6)$_2$(PiPr$_3$)]$^+$ but also in contrast to the reactivity of some bis(butadiene)molybdenum and -ruthenium compounds which, in the presence of a Lewis base, undergo an intramolecular C−C coupling reaction.[12] Finally, we note that unlike [Rh(s-cis-η⁴-C_4H_6)$_2$(PiPr$_3$)]$^+$ the iridium counterpart does not react with excess PiPr$_3$ by either displacement of one of the diene ligands or attack of the phosphane at the coordinated butadiene to give a phosphoniumbutenylmetal cation.[3] The chemistry of diolefinrhodium(I) and diolefiniridium(I) compounds really is, as shown by several other examples,[13] not the same at all.

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The commercially available starting materials AgO_3SCF_3, $AgPF_6$ and butadiene were used without further purification. PiPr$_3$ was purchased from Strem Chemicals. The complexes [Ir(μ-Cl)(η²-C_8H_{14})$_2$]$_2$ (**1**)[14] and [IrCl(s-cis-η⁴-C_4H_6)$_2$] (**4**)[8] were prepared as described in the literature. The preparation of AsiPr$_3$ and SbiPr$_3$ was carried out as described for the n-propyl analogues.[15] NMR spectra were recorded at room temperature on Bruker AC 200 and Bruker AMX 400 instruments, unless otherwise stated. Abbreviations used: s, singlet; d, doublet; t, triplet; quin, quintet; sept, septet; m, multiplet; br, broadened signal. Melting and decomposition points were measured by differential thermal analysis (DTA).

Generation of cis-[Ir(η²-C_8H_{14})$_2$([D$_6$]acetone)$_2$]PF$_6$ (2): A suspension of **1** (60 mg, 0.07 mmol) in [D$_6$]acetone (1 mL) was treated with $AgPF_6$ (34 mg, 0.13 mmol) and stirred for 1 h at room temperature. A white solid precipitated, which was removed by filtration, and the clear orange solution was investigated by NMR spectroscopy. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 2.57 (br. s, 4 H, CH of C_8H_{14}), 2.06 (br. s, 4 H, =CHCH_2 of C_8H_{14}), 1.61 (m, 4 H, CH_2 of C_8H_{14}), 1.42 (m, 12 H, CH_2 of C_8H_{14}), 1.24 (m, 4 H, CH_2 of C_8H_{14}); ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 206.6 (s, C=O of [D$_6$]acetone), 62.7 (s, CH of C_8H_{14}), 29.8 [sept, ^1J(D,C) = 19.3 Hz; CD_3 of [D$_6$]acetone], 29.6, 28.3, 26.7 (all s, CH_2 of C_8H_{14}); ^{19}F NMR (376.4 MHz, [D$_6$]acetone): δ = −72.3 [d, ^1J(P,F) = 709.4 Hz]; ^{31}P NMR (162.0 MHz, [D$_6$]acetone): δ = −144.1 [sept, ^1J(F,P) = 709.4 Hz].

Preparation of [Ir(s-cis-η⁴-C_4H_6)$_2$(η²-C_8H_{14})]PF$_6$ (3): A suspension of **1** (207 mg, 0.23 mmol) in acetone (10 mL) was treated with $AgPF_6$ (117 mg, 0.46 mmol) and stirred for 1 h at room temperature. The solution was filtered, and cyclooctene (100 μL, 0.77 mmol) was added to the filtrate. After stirring for 2 min, a slow stream of butadiene was passed through the solution for 10 s. The gaseous diene was replaced by argon, the pale-yellow solution was stirred for 30 min at room temperature and then concentrated to ca. 2 mL in vacuo. Addition of pentane (20 mL) resulted in the precipitation of a white solid, which was separated from the mother liquor, washed with pentane (3 × 5 mL) and dried in vacuo; yield 114 mg (89%); m.p. 103 °C (decomp); ^{1}H NMR (200 MHz, [D$_6$]-acetone): δ = 6.10 (m, 4 H, H_c), 5.66 (m, 2 H, CH of C_8H_{14}), 3.50 [dd, ^3J(H,H) = 8.0, ^2J(H,H) = 1.8 Hz, 4 H, H_b], 2.50 (m, 2 H, CHCH_2 of C_8H_{14}), 2.17, 1.97, 1.87, 1.78, 1.57 (all m, 10 H, CH_2 of C_8H_{14}), 1.48 [dd, ^3J(H,H) = 9.0, ^2J(H,H) = 1.8 Hz, 4 H, H_a]; for the assignment of the butadiene protons and carbon atoms see Figure 2; ^{13}C NMR (100.6 MHz, [D$_6$]acetone, 308 K): δ = 87.9 (s, C^2), 81.9 (s, CH of C_8H_{14}), 49.8 (s, C^1), 32.6, 29.6, 26.8 (all s, CH_2 of C_8H_{14}); ^{19}F NMR (376.4 MHz, [D$_6$]acetone, 308 K): δ = −72.2 [d, ^1J(P,F) = 705.5 Hz]; ^{31}P NMR (162.0 MHz, [D$_6$]acetone, 308 K): δ = −144.1 [sept, ^1J(F,P) = 705.5 Hz]; $C_{16}H_{26}F_6IrP$ (555.6): calcd. C 34.59, H 4.72; found C 34.34, H 4.56.

Preparation of [Ir(s-cis-η⁴-C_4H_6)$_2$(PiPr$_3$)]PF$_6$ (5): a) A solution of **3** (87 mg, 0.16 mmol) in CH_2Cl_2 (10 mL) was treated with PiPr$_3$ (30 μL, 0.16 mmol) and stirred for 1 h at room temperature. After removal of the solvent in vacuo, the colorless solid residue was

washed with pentane (5 mL) and dried in vacuo. Since the ^1H and ^{13}C NMR spectroscopic data showed that the product is a 1:1 mixture of **3** and **5**, the residue was dissolved in CH_2Cl_2 (10 mL) and treated again with P*i*Pr$_3$ (30 μL, 0.16 mmol). After stirring for 30 min, pentane (20 mL) was added to afford a colorless suspension. The solvent was decanted, the residue was washed with pentane (3 × 5 mL) and dried in vacuo. White solid; yield 88 mg (91%).

b) A suspension of **4** (125 mg, 0.37 mmol) in acetone (15 mL) was treated with $AgPF_6$ (94 mg, 0.37 mmol) and the mixture stirred for 1 h at room temperature. After removal of the solvent in vacuo, the residue was suspended in CH_2Cl_2 (10 mL). The resulting suspension was treated with P*i*Pr$_3$ (72 μL, 0.37 mmol) and stirred for 1 h at room temperature. Filtration of the mixture afforded a clear orange-yellow solution which was concentrated to ca. 2 mL in vacuo. Addition of pentane (10 mL) led to the precipitation of a white solid, which was separated from the mother liquor, washed with pentane (3 × 5 mL) and dried in vacuo. Yield 206 mg (92%); m.p. 152 °C (decomp); ^1H NMR (400 MHz, [D$_3$]nitromethane): δ = 5.64 (m, 4 H, H$_c$), 3.25 [dd, ^3J(H,H) = 7.8, ^2J(H,H) = 2.3 Hz, 4 H, H$_b$], 2.78 (m, 3 H, PC*H*CH$_3$), 1.43 [dd, ^3J(P,H) = 14.1, ^3J(H,H) = 7.4 Hz, 18 H, PCHC*H*$_3$], 1.09 [ddd, ^3J(H,H) = ^3J(P,H) = 8.9, ^2J(H,H) = 2.3 Hz, 4 H, H$_a$]; for the assignment of the butadiene protons and carbon atoms see Figure 2; ^{13}C NMR (100.6 MHz, [D$_3$]nitromethane): δ = 82.2 (s, C^2), 39.8 [d, ^2J(P,C) = 4.1 Hz, C^1], 29.1 [d, ^1J(P,C) = 27.5 Hz, P*C*HCH$_3$], 20.7 [d, ^2J(P,C) = 2.0 Hz, PCH*C*H$_3$]; ^{19}F NMR (376.4 MHz, [D$_3$]nitromethane): δ = −72.6 [d, ^1J(P,F) = 706.9 Hz]; ^{31}P NMR (162.0 MHz, [D$_3$]nitromethane): δ = 11.2 (s, P*i*Pr$_3$), −144.6 [sept, ^1J(F,P) = 706.9 Hz, PF_6^-]; $C_{17}H_{33}F_6IrP_2$ (605.6): calcd. C 33.72, H 5.49; found C 33.56, H 5.21.

Preparation of [Ir(*s-cis*-η^4-C$_4$H$_6$)$_2$(As*i*Pr$_3$)]PF$_6$ (6): This was prepared as described for **5** (method a), from **3** (93 mg, 0.17 mmol) and two portions of As*i*Pr$_3$ (33 μL, 0.17 mmol). White solid; yield 98 mg (90%). Alternatively, **6** could also be prepared as described for **5** (method b), from **4** (125 mg, 0.37 mmol), $AgPF_6$ (94 mg, 0.37 mmol) and As*i*Pr$_3$ (73 μL, 0.37 mmol) as starting materials. White solid; yield 229 mg (95%); m.p. 156 °C (decomp); ^1H NMR (400 MHz, [D$_3$]nitromethane): δ = 5.58 (m, 4 H, H$_c$), 3.21 [dd, ^3J(H,H) = 7.8, ^2J(H,H) = 2.3 Hz, 4 H, H$_b$], 2.90 [sept, ^3J(H,H) = 7.1 Hz, 3 H, AsC*H*CH$_3$], 1.47 [d, ^3J(H,H) = 7.1 Hz, 18 H, AsCHC*H*$_3$], 1.22 [dd, ^3J(H,H) = 7.9, ^2J(H,H) = 2.3 Hz, 4 H, H$_a$]; for the assignment of the butadiene protons and carbon atoms see Figure 2; ^{13}C NMR (100.6 MHz, [D$_3$]nitromethane): δ = 81.0 (s, C^2), 37.0 (s, C^1), 29.6 (s, As*C*HCH$_3$), 21.0 (s, AsCH*C*H$_3$); ^{19}F NMR (376.4 MHz, [D$_3$]nitromethane): δ = −73.3 [d, ^1J(P,F) = 706.4 Hz]; ^{31}P NMR (162.0 MHz, [D$_3$]nitromethane): δ = −144.6 [sept, ^1J(F,P) = 706.4 Hz]; $C_{17}H_{33}AsF_6IrP$ (649.6): calcd. C 31.43, H 5.12; found C 31.19, H 5.45.

Preparation of [Ir(*s-cis*-η^4-C$_4$H$_6$)$_2$(Sb*i*Pr$_3$)]PF$_6$ (7): This was prepared as described for **5** (method a), from **3** (76 mg, 0.14 mmol) and two portions of Sb*i*Pr$_3$ (27 μL, 0.14 mmol). White solid; yield 85 mg (89%). Alternatively, **7** could also be prepared as described for **5** (method b), from **4** (203 mg, 0.60 mmol), $AgPF_6$ (153 mg, 0.60 mmol) and Sb*i*Pr$_3$ (120 μL, 0.60 mmol) as starting materials. White solid; yield 388 mg (93%); m.p. 150 °C (decomp); ^1H NMR (400 MHz, [D$_3$]nitromethane): δ = 5.54 (m, 4 H H$_c$), 3.07 [dd, ^3J(H,H) = 7.6, ^2J(H,H) = 2.2 Hz, 4 H, H$_b$], 2.92 [sept, ^3J(H,H) = 7.4 Hz, 3 H, SbC*H*CH$_3$], 1.55 [d, ^3J(H,H) = 7.4 Hz, 18 H, SbCHC*H*$_3$], 1.29 [dd, ^3J(H,H) = 7.6, ^2J(H,H) = 2.2 Hz, 4 H, H$_a$]; for the assignment of the butadiene protons and carbon atoms see Figure 2; ^{13}C NMR (100.6 MHz, [D$_3$]nitromethane): δ = 79.0 (s, C^2), 32.4 (s, C^1), 22.0 (s, SbCH*C*H$_3$), 21.6 (s, Sb*C*HCH$_3$); ^{19}F NMR (376.4 MHz, [D$_3$]nitromethane): δ = −73.3 [d, ^1J(P,F) = 706.4 Hz]; ^{31}P NMR (162.0 MHz, [D$_3$]nitromethane): δ = −144.6 [sept, ^1J(F,P) = 706.4 Hz]; $C_{17}H_{33}F_6IrPSb$ (696.4): calcd. C 29.32, H 4.78; found C 29.14, H 5.17.

Thermolysis Experiments: Solutions of **5** (45 mg, 0.07 mmol), **6** (50 mg, 0.08 mmol) and **7** (63 mg, 0.09 mmol) in [D$_3$]nitromethane (0.5 mL) were stirred for 6 h at 60 °C. During this time no change of color of the solutions could be observed. The ^1H and ^{31}P NMR spectra revealed that in all cases no reaction had taken place.

Determination of the X-ray Crystal Structure of 5: Single crystals were grown by slow diffusion of pentane (10 mL) into a saturated solution of **5** in acetone (2 mL) at room temperature. The white crystalline product was washed with pentane (2 × 2 mL) and dried under a stream of argon. Crystal data (from 23 reflections, 10.00° < Θ < 15.00°): triclinic; space group $P\bar{1}$ (No. 2); a = 9.929(2), b = 12.295(3), c = 17.370(4) Å, α = 89.91(3)°, β = 89.92(3)°, γ = 89.92(3)°; V = 2120.7(7) Å^3, Z = 4; $d_{calcd.}$ = 1.897 g cm^{-3}; μ(Mo-K_α) = 6.497 mm^{-1}; crystal size 0.19 × 0.16 × 0.15 mm; Enraf−Nonius CAD4, Mo-K_α radiation (0.71073 Å), graphite monochromator; T = 193(2) K; ω/Θ-scan, max. 2Θ = 44.92°; 5964 reflections measured, 5508 independent ($R_{int.}$ = 0.0435), 4470 with $I > 2\sigma(I)$. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied. The structure was solved by direct methods (SHELX-97).[16] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares method on F^2 (program package SDP (Enraf−Nonius) and SHELXL-97).[17] The asymmetric unit of **5** contains two formula units, each consisting of two moieties: a cationic iridium complex and a PF_6^- counterion. Both the PF_6^- ions are disordered occupying in both cases two geometrically independent positions. The site occupancy factors were refined with restrains on U_{ij} to values of 0.49:0.51 and 0.48:0.52, respectively. The positions of all hydrogen atoms were calculated according to ideal geometry and refined by using the riding method. Conventional R = 0.0461 [for 4470 reflections with $I > 2\sigma(I)$], and weighted wR_2 = 0.1342 for all 5964 located reflections; reflection/parameter ratio 10.0; residual electron density +1.997/−2.739 eÅ^{-3}.

Crystallographic data (excluding structure factors) for **5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-169995. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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