

Alkynyl(phenyl) iodonium triflates as precursors to iridium(III) σ -acetylide complexes

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Dedicated to Professor Anastasios Varvoglis on the occasion of his 65th birthday

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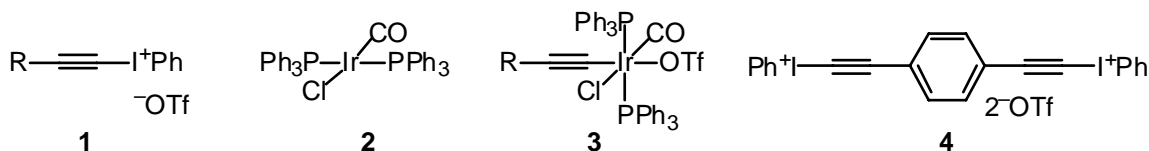
Abstract

The reaction of Vaska's complex **2** with alkynyl(phenyl)iodonium triflate salt **5** has been used to generate the Ir(III) σ -acetylide complex **6**. The labile triflate ligand is easily displaced from **6**, and this property has been used to explore the ability of a nitrile ligand to coordinate to the iridium center in exchange reactions, giving complexes **7a-d** in excellent yields. All complexes are stable under ambient conditions. The solid-state structure of alkynyl iodonium salt **5**, as well as complexes **7a** and **7d** have been investigated by single crystal X-ray crystallography.

Keywords: Alkynyl iodonium salts, σ -acetylide complexes, iridium(III)

Introduction

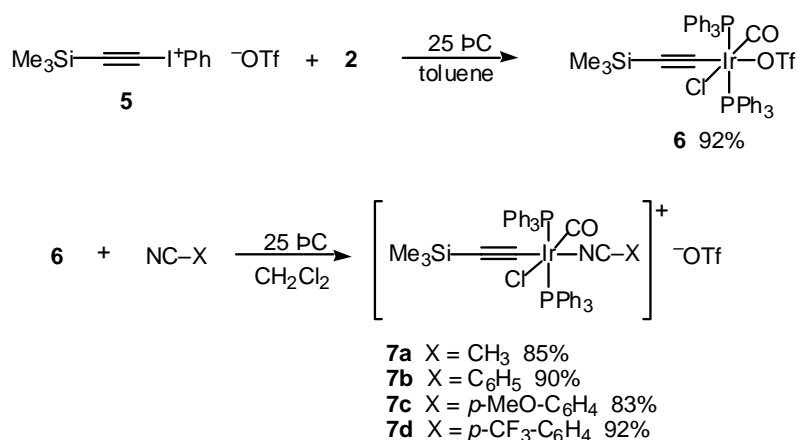
Alkynyl(aryl)iodonium salts are a versatile class of compounds that can function as precursors for the formation of a wide range of acetylenic derivatives.¹ They also serve well as a source of alkylidene carbene intermediates, which can be strategically trapped via intramolecular C-H bond insertion toward the formation of complex molecules.^{2,3} Several reports have also shown that alkynyl(aryl)iodonium triflates (**1**) can be effectively transformed into σ -acetylide complexes (**3**) through reaction with Vaska's complex (**2**) or its rhodium analogue.⁴ While a number of Ir(III) acetylide complexes have been successfully formed using this general methodology, the potential for elaboration of the products **3** has, surprisingly, gone unexplored.



We expected that the triflate ligand of complexes such as **3** should be easily displaced. Therefore, these complexes, and those derived from bis(alkynyl)iridium salts such as **4**,^{4a} could thus function as conjugated building blocks for the construction of coordination polymers and networks with potentially interesting structural, electronic, and optical properties.⁵ As the first step in this study, we report herein the successful derivatization of iridium triflate complexes such as **3** with alkyl and aryl nitriles.

Results and Discussion

Alkynyl iridium salt **5**⁶ was reacted at room temperature in toluene with Vaska's complex **2** to give acetylide complex **6** in 92% yield as a stable white solid (Scheme 1). Dissolving complex **6** in CH₂Cl₂, followed by the addition of CH₃CN results in the complete displacement of the triflate moiety by CH₃CN, and the resulting complex **7a** can be precipitated from this solution by the addition of hexanes. Using a similar protocol, addition of the appropriate aryl nitrile (in excess) to a CH₂Cl₂ solution of **6** resulted in the precipitation of the desired complexes **7b–d** over the period of approximately one hour. Hexanes were then added to ensure complete precipitation from the reaction mixture, and the complexes were isolated in good yields by filtration.



Scheme 1. Synthesis of Ir(III) acetylide complexes **6–7**.

All of the complexes **7** are off-white to pale yellow solids, are thermally stable to nearly 200 °C, and can be handled under ambient conditions with no noticeable decomposition. Several aspects of the IR and NMR spectra are particularly useful for structural characterization (Table 1). The IR spectrum for **7a** shows an absorbance for the C≡N stretch at 2336 cm⁻¹, and this absorbance for aryl nitriles of **7b–d** falls in the range of 2290–2300 cm⁻¹. The intense C≡C and C=O stretches appear at approximately 2110 and 2070 cm⁻¹, respectively.

Table 1. Selected spectroscopic data for σ -acetylide complexes **6** and **7a–d**

Cmpd	IR (cm ⁻¹)			¹³ C{H} NMR (ppm)			³¹ P{H} NMR (ppm)	
	C≡N	C≡C / C=O	C=O	NC	C≡CIr	C≡CIr		
6		2093	2069	154.5	—	110.3	62.8	-8.4
7a	2336	2104	2075	155.2	121.2	116.5	73.0	-11.4
7b	2290	2109	2080	154.2	120.5	116.2	71.6	-12.5
7c	2288	2108	2069	152.9	120.8	115.2	72.8	-12.6
7d	2300	2111	2071	152.0	118.7	115.2	72.2	-12.0

The ¹³C spectra show that the resonances of the C≡C–Ir carbons are shifted upfield, falling in the range of 72–73 ppm, with ²J_{CP} ~ 12 Hz. The resonances of the C=C–Ir carbons are found between 115–117 ppm, with ³J_{CP} = 2 Hz. The signals for the carbon monoxide ligand are seen as a triplet in the range of 152–155 ppm, with ²J_{CP} = 6 Hz, while the N≡C carbon resonates near 120 ppm. Somewhat surprisingly, there appears to be little variance in the NMR spectral data as a function of the electronic nature of the ancillary nitrile ligand. A weak trend in the ³¹P NMR data shows that the phosphorus resonance does shift to higher field as the nitrile's electron donating ability is increased in the series of **7d** → **7b** → **7c**.

Electrospray mass spectrometric analysis of complexes **6** and **7a–d** is particularly useful for confirming their composition and the association in solution of the nitrile ligand. These MS analyses show that the iridium complexes tend to form dimeric clusters under the analysis conditions used. Thus, the highest mass species detected in each case consists of [2M – TfO]⁺. The main spectrometric pattern in the lower *m/z* region for each complex includes a weak signal indicating [M – TfO]⁺, a slightly stronger signal *m/z* 877 ([M – RCN – TfO]⁺), and a base peak at *m/z* 849 ([M – RCN – CO – TfO]⁺). The [M – TfO]⁺ signal observed for each compound clearly displays an isotope pattern consistent with the proposed composition.

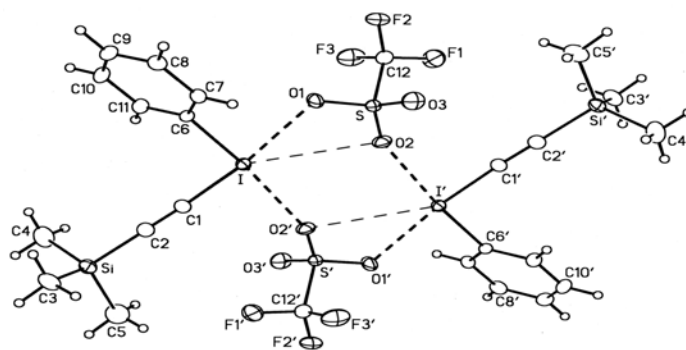


Figure 1. X-Ray crystal structure of **5** (20% probability level). Selected bond lengths [Å] and angles [°]: I–O(1) 2.664(2), I–O(2) 3.505(3), I–O(2') 2.839(2), I–C(1) 2.008(4), I–C(6) 2.124(3), C(1)–C(2) 1.197(5); C(1)–I–O(2') 81.89(11), C(1)–I–C(6) 92.76(13), C(6)–I–O(1) 79.21(10), O(1)–I–O(2') 106.19(7), I–C(1)–C(2) 177.3(3), C(1)–C(2)–Si 177.2(3).

The highly crystalline nature of **5** led us to investigate the solid-state characteristics of this alkynyl(iodonium) triflate salt.⁷ Single crystals of **5** were grown by the slow evaporation of a concentrated CDCl₃ solution at 4 °C. As is often observed in the solid state for iodonium triflate salts, secondary bonding interactions between the triflate anion and the I(III) center afford a dimeric structure, which is in the current case centrosymmetric. The overall core structure is nearly planar (excluding the phenyl group), with C(1), C(6) O(1), deviating less than 0.25 Å from a least squares plane composed of I, I', O(2), and O(2'). Nearly degenerate interactions are observed between I–O(1) (2.664(2) Å) and I–O(2') (2.839(2) Å), and a weaker secondary interaction is observed between I–O(2) (3.505(3) Å). The bonding orientation of the acetylene to the I(III) center is nearly linear, with the angle I–C(1)–C(2) at 177.3(3)°.

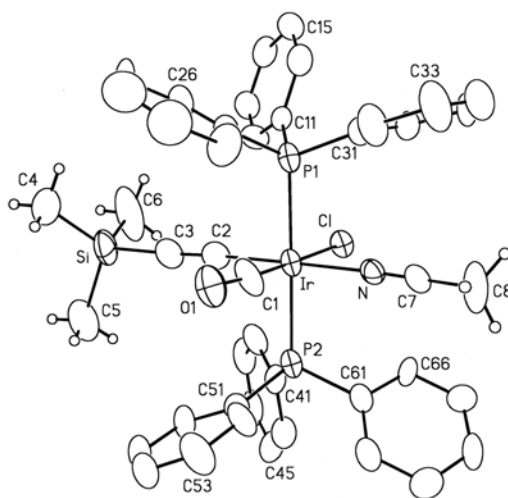


Figure 2. X-Ray crystal structure of **7a** with the co-crystallized hexane molecule and the triflate anion removed for clarity (20% probability level).

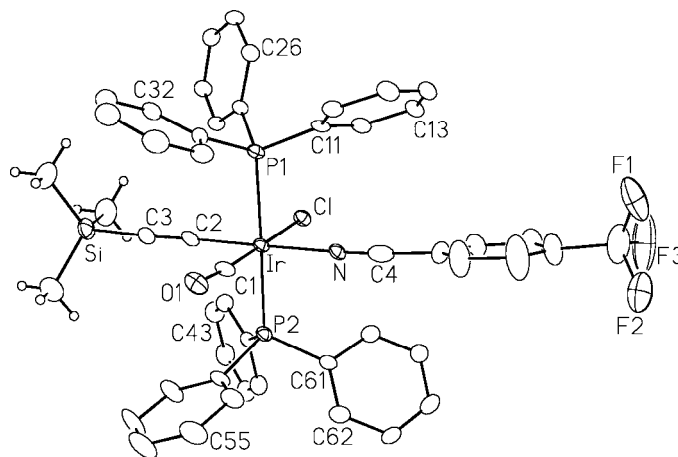


Figure 3. X-Ray crystal structure of **7d** with co-crystallized hexane molecule and the triflate anion removed for clarity (20% probability level).

Table 2. Selected bond lengths and angles for compounds **7a** and **7d**

Bond length	Compound 7a	Compound 7d
Ir–C(1)	1.83(2) Å	1.852(10) Å
Ir–Cl	2.375(4) Å	2.384(2) Å
Ir–C(2)	1.94(2) Å	1.965(11) Å
Ir–N	2.049(17) Å	2.047(8) Å
Ir–P(1)	2.388(6) Å	2.402(2) Å
Ir–P(2)	2.387(6) Å	2.408(2) Å
C(1)–O(1)	1.15(2) Å	1.164(12) Å
C(2)–C(3)	1.21(2) Å	1.209(14) Å
N–C(4)	1.15(2) Å	1.133(15) Å
Bond angle		
Ir–C(2)–C(3)	176.2(19)°	176.7(9)°
Ir–C(1)–O(1)	166(2)°	173.6(10)°
Ir–N–C(4)	174.2(15)°	177.5(9)°
P(1)–Ir–P(2)	175.33(16)°	174.72(8)°
Cl–Ir–C(1)	178.8(6)°	178.9(3)°
N–Ir–C(2)	177.5(7)°	178.9(4)°

Single crystals of σ -acetylide complexes **7a** and **7d** were each grown by diffusion of hexanes into a CHCl_3 solution, and each complex co-crystallizes with a half-equivalent of *n*-hexane. Although the refined structure of **7a** is of slightly lower quality than that of **7d**, structural comparisons are still possible (Table 2). The geometry about iridium in both cases is approximately octahedral, with the two triphenylphosphine groups occupying *trans*-positions. There is little significant variance in bond lengths between comparable bonds of the two structures, and the observed lengths are within expected ranges⁸. The Ir–C(2) distances, at 1.94(2) and 1.965(11), are somewhat shorter than other Ir(III) acetylide complexes that have been reported, but not remarkably (i.e., ≤ 0.1 Å).⁸ The coordination of the acetylene to iridium is essentially linear, as is the orientation of the nitrile moiety, in both cases. The most significant difference between the two structures is found in the geometry of the $\text{C}\equiv\text{O}$ ligand, with Ir–C(1)–O(1) angles at 166(2)° for **7a** and 173.6(10)° for **7d**.

Conclusions

Using an alkynyl(phenyl)iodonium triflate salt, **5**, the Ir(III) σ -acetylide complex **6** is formed via reaction with Vaska's complex. The triflate moiety of this complex is easily displaced with an alkyl- or aryl nitriles and affords complexes **7a–d**, which are stable microcrystalline solids.

Spectroscopic and solid state characterization demonstrate that the electronic influence of the nitrile ligand on the remainder of the molecule is minimal.

Experimental Section

General Procedures. Reagents and solvents were purchased reagent grade and used without further purification. CH₃CN, CH₂Cl₂, and hexanes were freshly distilled from CaH₂. Compounds **2**⁹ and **5**⁶ were prepared as previously described. Evaporation and concentration *in vacuo* was done at H₂O–aspirator pressure. All reactions were performed in flame–dried glassware under an inert atmosphere of N₂. Melting points: *Gallenkamp* apparatus; uncorrected. IR spectra (cm⁻¹): *Nicolet Magna–IR 750* (cast) or *Nic–Plan IR Microscope* (solids). ¹H and ¹³C NMR: *Varian Gemini–300*, *–400*, or *–500* and *Bruker AM–300* instruments, at rt in CD₃CN or CDCl₃; solvent peaks (1.94 and 7.24 ppm for ¹H; 1.3 and 77.0 ppm for ¹³C) as reference. ESI MS (*m/z*): *Micromass Zabspec oaTOF* or *PE Biosystems Mariner TOF* instruments; solvent: MeOH or MeOH/toluene 3:1. X-ray diffraction data: *Siemens P4/RA* instrument using Cu K α ($\lambda = 1.54178$ Å) (for **5** and **7a**) or Mo K α ($\lambda = 0.71073$ Å) (for **7d**) radiation (in each case the crystal was cooled to –60 °C under a cold nitrogen stream).

X–Ray crystal data for **5** (C₁₂H₁₄F₃IO₃SSi): monoclinic space group *P2_{1/c}* (No. 14), *D_c* = 1.716 g cm⁻³, *Z* = 4, *a* = 8.5211(14), *b* = 16.7310(12), *c* = 12.6973(11) Å, β = 105.613(9)°, *V* = 1743.4(3) Å³. Final *R(F)* = 0.0253 (for 2660 observations [$F_o^2 \geq 2\sigma(F_o^2)$]), *wR₂(F²)* = 0.0576 (for 3068 unique data with $F_o^2 \geq -3\sigma(F_o^2)$) with 190 parameters varied.

X–Ray crystal data for **7a** (C₄₈H₄₉ClF₃IrNO₄P₂SSi); monoclinic space group *C2/c* (No. 15), *D_c* = 1.362 g cm⁻³, *Z* = 8, *a* = 26.7317(17), *b* = 11.8425(9), *c* = 36.181(2) Å, β = 108.995(6)°, *V* = 10830.2(13) Å³. Final *R(F)* = 0.0883 (for 3794 observations [$F_o^2 \geq 2\sigma(F_o^2)$]), *wR₂(F²)* = 0.2834 (for 7316 unique data with $F_o^2 \geq -3\sigma(F_o^2)$) with 541 parameters varied.

X–Ray crystal data for **7d** (C₅₄H₅₀ClF₆IrNO₄P₂SSi); triclinic space group *P $\bar{1}$* (No. 2), *D_c* = 1.516 g cm⁻³, *Z* = 2, *a* = 11.9606(8), *b* = 13.8137(14), *c* = 18.1920(16) Å, α = 105.852(7), β = 92.846(6), γ = 108.109(6)°, *V* = 2718.2(4) Å³. Final *R(F)* = 0.0579 (for 5986 observations [$F_o^2 \geq 2\sigma(F_o^2)$]), *wR₂(F²)* = 0.1557 (for 7011 unique data with $F_o^2 \geq -3\sigma(F_o^2)$) with 622 parameters varied.

Crystallographic data (excluding structure factors) for all structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC–202855 (**5**), CCDC–202853 (**7a**), and CCDC–202854 (**7d**). These data can be obtained free of charge via www.ccdc.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223–336–033; e–mail: deposit@ccdc.cam.ac.uk).

Complex 6. To a solution of **5** (0.877 mg, 1.94 mmol) in toluene (50 mL) was added Vaska's complex **2** (1.52 g, 1.94 mmol) and the solution was allowed to stir for 1 hr. To the resulting

suspension was added hexanes (50 mL), and the precipitate was filtered to give **6** (1.85 g, 92%) as an off-white solid, mp 200–205 °C. IR (CH₂Cl₂ cast) 3061, 2955, 2093, 2069, 1573, 1246, 1198 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.05–7.9 (m, 12H), 7.65–7.50 (m, 18H), –0.15 (s, 9H); ¹³C NMR (75.5 MHz, CDCl₃) δ 154.5 (t, ²J_{PC} = 6 Hz, C≡O), 134.9 (t, J_{PC} = 5 Hz), 131.3, 128.1 (t, J_{PC} = 5 Hz), 126.2 (t, ¹J_{PC} = 29 Hz, C_i), 116.8 (q, ¹J_{CF} = 317 Hz, CF₃), 110.3 (t, ³J_{PC} = 2 Hz, C≡C_{Ir}), 62.8 (t, ²J_{PC} = 11 Hz, C≡C_{Ir}), 0.6 (SiCH₃); ¹⁹F NMR (376.5 MHz, CDCl₃) δ –76.5; ³¹P NMR (162 MHz, CDCl₃) δ –8.4. ESI MS *m/z*: 2013.3 ([2M – TfO]⁺, 1), 877.1 ([M – TfO]⁺, 30), 849.1 ([M – CO – TfO]⁺, 100).

General conditions for the formation of **7a–d**

To a solution of complex **6** in CH₂Cl₂ was added the appropriate nitrile (in excess). The reaction mixture was stirred at room temperature for approximately one hour, resulting in a suspension as the product normally precipitates from the reaction solution. Hexanes were then added to ensure complete precipitation of the product. The product was filtered, washed with hexanes (2 x 20 mL), and dried in vacuo.

Complex 7a. Reaction of acetonitrile (41 mg, 1.0 mmol) with complex **6** (103 mg, 0.100 mmol) in CH₂Cl₂ (5 mL) afforded **7a** (91 mg, 85%) as a pale yellow microcrystalline solid, mp 145 °C; IR (CH₂Cl₂ cast) 3061, 2336, 2104, 2075, 1587, 1266, 1031 cm⁻¹; ¹H NMR (300 MHz, CD₃CN) δ 8.05–7.9 (m, 12H), 7.65–7.50 (m, 18H), 0.03 (s, 9H); ¹³C NMR (75.5 MHz, CD₃CN) δ 155.2 (t, ²J_{PC} = 6 Hz, C≡O), 135.5 (t, ³J_{PC} = 5 Hz), 133.3, 129.7 (t, J_{PC} = 5 Hz), 128.2 (t, ¹J_{PC} = 30 Hz, C_i), 121.2 (t, ³J_{PC} = 2 Hz, NC), 116.5 (t, ³J_{PC} = 2 Hz, C≡C_{Ir}), 73.0 (t, ²J_{PC} = 12 Hz, C≡C_{Ir}), 1.0 (NCCH₃), 0.4 (SiCH₃); ¹⁹F NMR (376.5 MHz, CD₃CN) δ –79.7; ³¹P NMR (162 MHz, CD₃CN) δ –11.4. ESI MS *m/z*: 2013.3 ([2M – TfO]⁺, 1), 918.2 ([M – TfO]⁺, 12), 849.1 ([M – NCCH₃ – TfO]⁺, 55), 849.1 ([M – NCCH₃ – CO – TfO]⁺, 100).

Complex 7b. Reaction of benzonitrile (103 mg, 1.00 mmol) with complex **6** (100 mg, 0.0975 mmol) in CH₂Cl₂ (5 mL) afforded 99 mg (90%) of **7b** as a colorless microcrystalline solid, mp 190–195 °C dec; IR (CH₂Cl₂ cast) 3061, 2959, 2290, 2109, 2080, 1587, 1263, 1154 cm⁻¹; ¹H NMR (300 MHz, CH₂Cl₂) δ 7.95–8.05 (m, 12H), 7.65–7.50 (m, 18H), 7.17 (m, 5H), –0.04 (s, 9H); ¹³C NMR (75.5 MHz, CD₂Cl₂) δ 154.2 (t, ²J_{PC} = 7 Hz, C≡O), 136.1, 134.9 (t, J_{PC} = 5 Hz), 133.7, 132.4, 129.4, 129.1 (t, J_{PC} = 5 Hz), 127.5 (t, ¹J_{PC} = 30 Hz, C_i), 121.5 (q, ¹J_{CF} = 321 Hz, CF₃), 120.5 (NC), 116.2 (C≡C_{Ir}), 108.0, 71.6 (t, ²J_{PC} = 12 Hz, C≡C_{Ir}), 0.4 (SiCH₃); ¹⁹F NMR (376.5 MHz, CDCl₃) δ –78.3; ³¹P NMR (162 MHz, CDCl₃) δ –12.5. ESI MS *m/z*: 2109.3 ([2M – TfO]⁺, 1), 980.2 ([M – TfO]⁺, 12), 877.1 ([M – NCPH – TfO]⁺, 20), 849.1 ([M – NCPH – CO – TfO]⁺, 100).

Complex 7c. Reaction of *p*-methoxybenzonitrile (120 mg, 0.90 mmol) with complex **6** (45 mg, 0.043 mmol) in CH₂Cl₂ (5 mL) afforded **7c** (41 mg, 83%) as a colorless microcrystalline solid, mp 195–200 °C dec; IR (CH₂Cl₂ cast) 3064, 2961, 2288, 2108, 2069, 1602, 1265, 1149 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.96 (m, 12H), 7.39 (m, 18H), 7.02 (d, *J* = 8 Hz, 2H), 6.81 (d, *J* = 8 Hz, 2H), 3.84 (s, 3H), –0.07 (s, 9H); ¹³C NMR (75.5 MHz, CDCl₃) δ 164.8, 152.9 (t, ²J_{PC} = 7 Hz, C≡O), 136.0, 134.6 (t, J_{PC} = 5 Hz), 131.8, 128.6 (t, J_{PC} = 5 Hz), 127.3 (t, ¹J_{PC} = 30 Hz, C_i),

120.8 (t, $^3J_{PC} = 2$ Hz, NC), 115.2 (t, $^3J_{PC} = 2$ Hz, C≡C Ir), 114.6, 99.0, 72.8 (t, $^2J_{PC} = 12$ Hz, C≡C Ir), 55.9, 0.4 (SiCH₃); ^{19}F NMR (188 MHz, CDCl₃) δ -78.6; ^{31}P NMR (81 MHz, CDCl₃) δ -12.6; ESI MS m/z : 2169.4 ([2M - TfO]⁺, 1), 1010.2 ([M - TfO]⁺, 5), 877.1 ([M - *p*-CH₃OC₆H₄CN - TfO]⁺, 31), 849.1 ([M - *p*-CH₃OC₆H₄CN - CO - TfO]⁺, 100)

Complex 7d. Reaction of *p*-trifluoromethylbenzotrile (100 mg, 0.58 mmol) with complex **6** (100 mg, 0.0975 mmol) in CH₂Cl₂ (5 mL) afforded **7d** (108 mg, 92%) as a colorless microcrystalline solid, mp 200–205 °C dec; IR (CH₂Cl₂ cast) 3060, 2961, 2300, 2111, 2071, 1587, 1261, 1151 cm⁻¹; ^1H NMR (300 MHz, CDCl₃) δ 8.00 (m, 12H), 7.58 (d, $J = 8$ Hz, 2H), 7.40 (m, 18H), 7.33 (d, $J = 8$ Hz, 2H), 0.36 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl₃) δ 152.0 (t, $J_{PC} = 6$ Hz, C≡O), 135.2 (q, $J_{CF} = 5$ Hz), 134.8 (t, $J_{PC} = 5$ Hz), 131.4 (q, $^2J_{CF} = 45$ Hz), 131.7, 128.7 (t, $J_{PC} = 5$ Hz), 127.3 (t, $^1J_{PC} = 30$ Hz, C_i), 125.3 (q, $J_{CF} = 4$ Hz), 123.3 (q, $^1J_{CF} = 273$, ArCF₃), 118.7 (NC), 115.2 (C≡C Ir), 112.2, 72.2 (t, $^2J_{PC} = 12$ Hz, C≡C Ir), 0.4 (SiCH₃); ^{19}F NMR (376.5 MHz, CH₂Cl₂) δ -64.2 (CF₃Ar), -79.0 (OSO₂CF₃); ^{31}P NMR (162 MHz, CH₂Cl₂) δ -12.0. ESI MS m/z : 2245.3 ([2M - TfO]⁺, 1), 1048.2 ([M - TfO]⁺, 5), 877.1 ([M - *p*-CF₃C₆H₄CN - TfO]⁺, 23), 849.1 ([M - *p*-CF₃C₆H₄CN - CO - TfO]⁺, 100).

Acknowledgements

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