

Preparation of Rigid-Rod, Di- and Trimetallic, σ -Acetylide Complexes of Iridium(III) and Rhodium(III) via Alkynyl(phenyl)iodonium Chemistry

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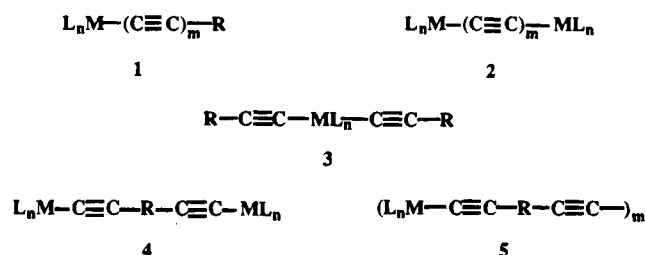
The reactions of *trans*-(Ph₃P)₂Ir(CO)(Cl) and *trans*-(Ph₃P)₂Rh(CO)(Cl) with bis- and tris-[phenyl(iodonium)] di- and triyne triflate salts PhI–C≡C–R–C≡C–IPh₂OTf (R = *p*-C₆H₄, *p*-Me₄C₆H₄, 4,4'-C₆H₄C₆H₄, *o*-C₆H₄) and 1,3,5-(PhI–C≡C)₃C₆H₃OTf, respectively, in acetonitrile afford high yields of the corresponding iridium(III) and rhodium(III) σ -acetylide complexes as stable, crystalline solids.

Introduction

Conjugated organic monomers and polymers have been extensively studied because of their interesting properties and potential applications to advanced materials.^{1,2} More recently, conjugated transition metal complexes have emerged as a promising class of molecules for use as advanced materials and, in particular, have shown promise in the areas of nonlinear optics, organic conductors, and liquid crystals.^{3,4} These properties result primarily from the ability of the metal to participate in π -delocalization, as well as the potential for interaction of the transition metal d-orbitals with the conjugated π -orbitals of the organic moiety.^{4,5} Furthermore, the ability of organometallic complexes to participate in metal-to-ligand and ligand-to-metal charge transfers allows significant reordering of the π -electron distribution,⁶ as well as manipulation of this electronic distribution via modification of the ligands coordinated to the metal center.⁷

Studies have recently shown that metallic σ -acetylide complexes exhibit particularly encouraging third-order NLO properties.^{4c,6,8} This has dramatically increased

interest in the synthesis and characterization of organometallic compounds with η^1 -acetylide ligands, 1.^{9,10}



Linear, conjugated C₂ and C₄ bridged bimetallic systems **2** have subsequently been formed, generally via interactions of complexes **1** with a second metal center.^{11,12} Numerous bis(acetylide)metal complexes **3** have also been synthesized via σ -coordination of two acetylene ligands to one metal center.¹³ Efforts toward the formation of metal acetylide complexes with even greater π -delocalization have afforded numerous bimetallic complexes **4** and polymetallic chains **5** linked by rigid, conjugated backbones such as –C≡C–aryl–C≡C–, and incorporating a variety of metals including Au, Co, Fe, Mn, Ni, Pd, Pt, Rh, and Ru.¹⁴

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(1) Prasad, P. N.; Williams, D. J. *Nonlinear Optical Effects in Molecules and Polymers*; John Wiley and Sons, Inc.: New York, 1991. Marder, T. B.; Lesley, G.; Yuan, Z.; Fyfe, H. B.; Chow, P.; Stringer, G.; Jobe, I. R.; Taylor, N. J.; Williams, I. D.; Kurtz, S. K. In *Materials for Nonlinear Optics: Chemical Perspectives*; Stucky, G. D., Marder, S. R., Sohn, J., Eds.; ACS Symposium Series 445; American Chemical Society: Washington, DC, 1991. Prasad, P. N.; Ulrich, D. R., Eds. *Nonlinear Optical and Electroactive Polymers*; Plenum: New York, 1988. Ferraro, J. R.; Williams, J. M. *Introduction of Synthetic Electrical Conductors*; Academic Press: Orlando, FL, 1987; Chapter 3.

(2) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923–949.

(3) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195–242. Hirsch, A.; Hanack, M. In *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics*; Bredas, J. L.; Chance, R. R., Eds.; Kluwer: New York, 1990.

(4) (a) Pollagi, T. P.; Stoner, T. C.; Dallinger, R. F.; Gilbert, T. M.; Hopkins, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 703–704. (b) Calabrese, J. C.; Cheng, L.-T.; Green, J. C.; Marder, S. R.; Tam, W. *J. Am. Chem. Soc.* **1991**, *113*, 7227–7232. (c) Meyers, L. K.; Langhoff, C.; Thompson, M. E. *J. Am. Chem. Soc.* **1992**, *114*, 7560–7561 and references therein.

(5) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276–3285. Lichtenberger, D. L.; Renshaw, S. K.; Wong, A.; Tagge, C. D. *Organometallics* **1993**, *12*, 3522–3526.

(6) Frazier, C. C.; Guha, S.; Chen, W. P.; Cockerham, M. P.; Porter, P. L.; Chaudard, E. A.; Lee, C. H. *Polymer* **1987**, *28*, 553–555 and references therein.

(7) Stoner, T. C.; Dallinger, R. F.; Hopkins, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 5651–5653.

(8) Guha, S.; Frazier, C. C.; Porter, P. L.; Kang, K.; Finberg, S. E. *Opt. Lett.* **1989**, *14*, 952–954. Blau, W. J.; Byrne, H. J.; Cardin, D. J.; Davey, A. P. *J. Mater. Chem.* **1991**, *1*, 245–249.

(9) Early reports of (σ -acetylide)metal complexes: Jolly, P. W.; Pettit, R. *J. Organomet. Chem.* **1968**, *12*, 491–495. Green, M. L. H.; Mole, T. J. *J. Organomet. Chem.* **1968**, *12*, 404–406. Collman, J. P.; Kang, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 844–851.

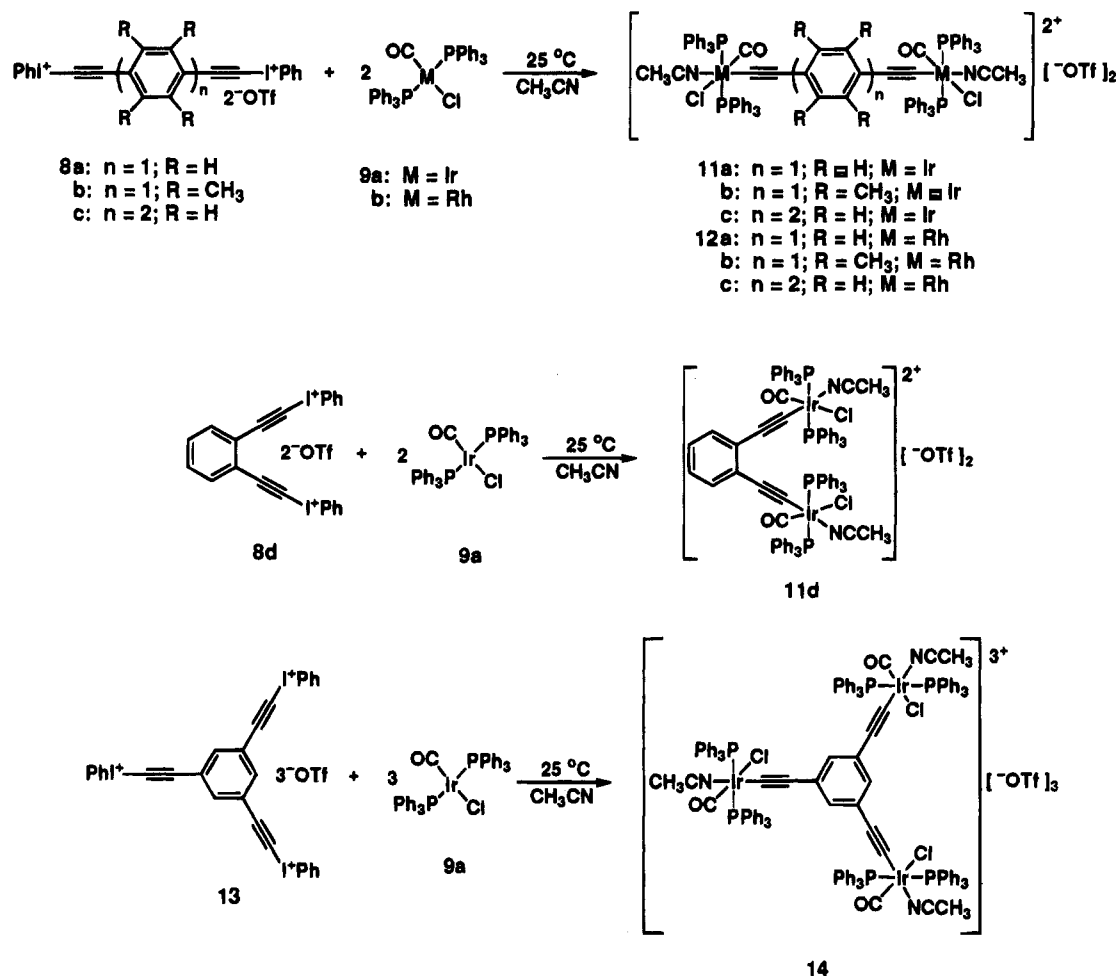
(10) Field, L. D.; George, A. V. *J. Organomet. Chem.* **1993**, *454*, 217–219. Ramsden, J. A.; Weng, W.; Gladysz, J. A. *Organometallics* **1992**, *11*, 3635–3645. Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Laschi, F.; Zanello, P.; Ottaviani, F. M. *Organometallics* **1990**, *9*, 360–371.

(11) Ramsden, J. A.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5890–5891. Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 8466–8477. Koutsantonis, G. A.; Selegue, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2316–2317 and references therein.

(12) Zhou, Y.; Seyler, J. F.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 8509–8510. Le Narvor, N.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 357–359. Crescenzi, R.; Lo Sterzo, C. *Organometallics* **1992**, *11*, 4301–4305. Wong, A.; Kang, P. C. W.; Tagge, C. D.; Leon, D. R. *Organometallics* **1990**, *9*, 1992–1994 and references therein.

(13) Leading references: Touchard, D.; Haquette, P.; Piro, N.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1993**, *12*, 3132–3139. Lewis, J.; Khan, M. S.; Kakkar, A. K.; Raithby, P. R.; Fuhrmann, K.; Friend, R. H. *J. Organomet. Chem.* **1992**, *433*, 135–139. Sun, Y.; Taylor, N. J.; Carty, A. J. *Organometallics* **1992**, *11*, 4293–4300. Field, L. D.; George, A. V.; Hambley, T. W.; Malouf, E. Y.; Young, D. L. *J. Chem. Soc., Chem. Commun.* **1990**, 931–933.

Scheme 1

Table 1. Selected Physical and Structural Data for Iridium(III) and Rhodium(III) σ -Acetylide Complexes

compd	yield (%)	mp (dec) ($^\circ C$)	IR (cm^{-1})		$^{13}C\{^1H\}$ NMR (ppm)			$^{31}P\{^1H\}$ NMR (ppm)
			$C\equiv C$	$C=O$	$C=O$	$C\equiv C Ir$	$C\equiv C Ir$	
10	88	204–206	2143	2074	<i>a</i>	<i>a</i>	<i>a</i>	<i>b</i>
11a	85	199–201	2156	2100	155	109	55	–9.9
11b	84	234–244	2139	2052	155	107	59	–11.7
11c	85	203–207	2151	2097	152	105	53	–11.0
11d	65	165–168	2124	2092	155	109	60	–11.7
12a	73	105–106	2141	2121	177	111	75	19.7 ($J_{RhP} = 72$ Hz)
12b	88	145–146	2126	2111	<i>a</i>	<i>a</i>	<i>a</i>	22.1 ($J_{RhP} = 73$ Hz)
12c	90	107–108	2174	2119	177	112	74	19.7 ($J_{RhP} = 73$ Hz)
14	73	196–197	2156	2095	153	106	56	–12.0
16a	83	197–200	2097	2069	155	106	40	–10.0
16b	77	142–143	2096	2048	156	108	38	–10.6
18	96	164–167	2125	2100	155	110	69	–9.4

^a Insufficiently soluble for ^{13}C NMR analysis. ^b Insufficiently soluble for ^{31}P NMR analysis.

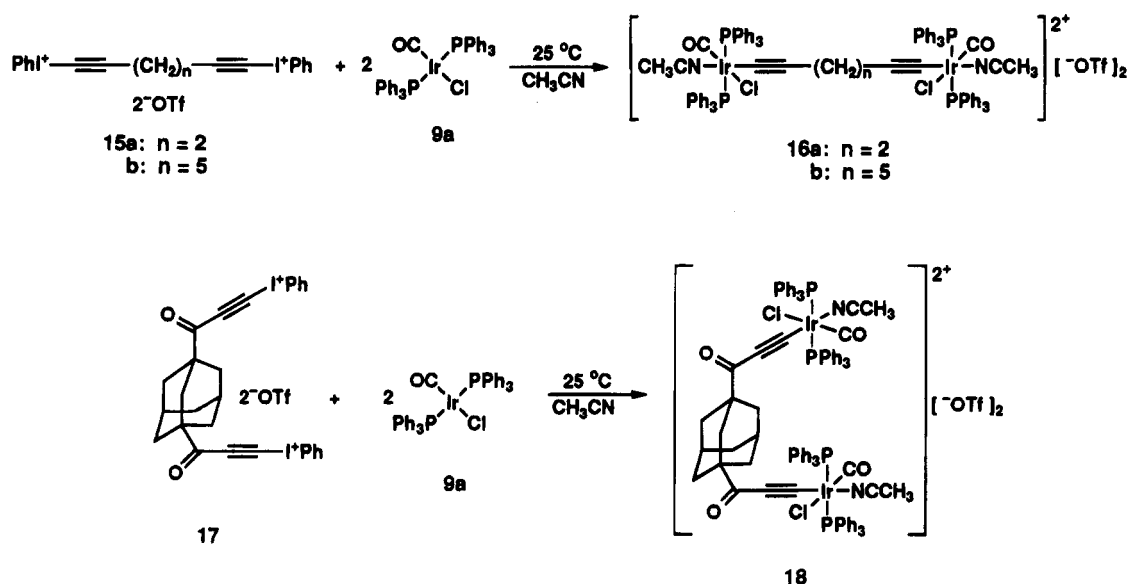
Hz). Complex **12b** proved insufficiently soluble for ^{13}C NMR analysis.

The 1H NMR analyses of **11a–d**, **12a–c**, and **14** provide information as to the lability of the acetonitrile ligands present in the iridium(III) and rhodium(III) complexes. The spectra of the iridium complexes **11a–d** and **14** clearly show singlets between 1.4 and 1.6 ppm integrating for 6 and 9 protons, respectively, for the acetonitrile ligands bonded to the iridium metal center. The consistent presence of this signal suggests the absence of exchange with the deuterated acetonitrile solvent. The 1H NMR analyses of rhodium complexes **12a–c**, however, reveal signals expected of acetonitrile solvent molecules at 1.9 ppm. Furthermore, the acetonitrile signals are absent from the proton spectra of

12a–c after removal of deuterated solvent in vacuo, resolution in CD_3CN , and subsequent NMR analysis. The ^{13}C NMR spectra furnish additional support of an acetonitrile exchange, showing signals at δ 120–122 ($C\equiv N$) and δ 3–4 (CH_3) for the acetonitrile ligands of **11a–d** and **14**. The analogous signals are absent in the ^{13}C NMR spectra of rhodium complexes **12a** and **12c**, where only the resonances of acetonitrile solvent at 118 and 1.3 ppm are observed.

This new methodology was also applied to the synthesis of bimetallic iridium complexes from bis[phenyl-(iodonium)] triflates **15a** and **15b**, where the alkyne functionalities are linked by nonconjugated alkyl tethers. Addition of **9a** to a CH_3CN solution of the respective iodonium salt at ambient temperature resulted in

Scheme 2



a clear solution after approximately 5 min (Scheme 2). The addition of ether and hexanes effected precipitation of iridium complexes **16a** and **16b**, as stable white solids in 83% and 77% yields, respectively. Likewise, the reaction of the keto-functionalized bis[phenyl(iodonium)] triflate salt **17** with **9a** resulted in a 96% yield of iridium complex **18**.

The IR, ¹H NMR, and ¹³C NMR spectral properties of complexes **16a,b** and **18** are similar to those of the conjugated iridium analogues **11a–d** and **14**. In the IR spectra, the C≡C and C=O stretches are found between 2096–2125 and 2048–2100 cm^{−1}, respectively. In the ¹³C NMR spectra, resonances of the C=O carbon atoms at 155 ppm ($J_{CP} \approx 6$ Hz) and of β -acetylene carbon atoms at 106–100 ppm are comparable to complexes **11a–d** and **14**. The signals observed for the α -acetylene carbons, however, are shifted upfield to 38–40 ppm for **16a** and **16b**, and the signal is shifted downfield to 69 ppm for **18** as a result of the significant electron withdrawing ability of the adjacent carbonyl.

Conclusions

The reactions of Vaska's complex with bis[phenyl(iodonium)] diyne triflate and tris[phenyl(iodonium)] triyne triflate salts have been utilized for the single-step synthesis of aryl and alkyl tethered, bi- and trimetallic, iridium(III) and rhodium(III) σ -acetylide complexes. The complexes are formed under extremely mild conditions and are isolated in good to excellent yields as microcrystalline solids. Furthermore, the pure solids are quite thermally stable and are also stable to air and moisture, allowing for facile handling and storage. This new method complements existing oxidative addition methods and represents a reversal of traditional metal acetylide chemistry by employing the organometallic species as a nucleophile and the alkynyl-iodonium salt as the alkynylating agent. Furthermore, the facile acetonitrile ligand exchange at the rhodium metal center of **12a–c** presents the opportunity for possible further derivatization of these linear complexes, particularly via the use of bidentate ligands toward the formation of organometallic polymers.

Experimental Section

General Comments. All melting points were obtained on a Mel-Temp capillary melting point apparatus and are uncorrected, IR spectra were recorded on a Mattson Polaris FTIR spectrometer, and NMR spectra were recorded on either a Varian Unity 300 or XL-300 spectrometer. The ¹H NMR spectra were recorded at 300 MHz, and chemical shifts were reported relative to CDCl₃ δ 7.24, CD₂Cl₂ δ 5.32, dimethyl sulfoxide-*d*₆ δ 2.49, or CD₃CN δ 1.93. The ¹³C NMR spectra were recorded at 75 MHz, ¹H decoupled, and reported relative to CDCl₃ δ 77.0, CD₂Cl₂ δ 53.8, dimethyl sulfoxide-*d*₆ δ 39.5, or CD₃CN δ 1.30. The ¹⁹F NMR spectra were recorded at 282 MHz, and chemical shifts were reported relative to external CFCl₃ (sealed capillary) in the appropriate deuterated solvent. The ³¹P NMR spectra were recorded at 121 MHz, ¹H decoupled, and reported relative to external 85% H₃PO₄ (sealed capillary) in the respective deuterated solvent. Mass spectra were recorded on either a Finigan MAT 95 high resolution GC/mass spectrometer or a VG Micromass 7050E double focusing high resolution mass spectrometer under positive ion fast atom bombardment (FAB) conditions at 8 keV. Elemental analyses were performed by Atlantic Microlab, Inc., of Norcross, GA. Solvents were purified according to established procedures¹⁷ or were high-purity HPLC grade solvents used as received. The syntheses of Vaska's complex **9a**,¹⁸ and its rhodium analogue **9b**,¹⁹ and bis[phenyl(iodonium)] diyne triflates **8a**, **8c**, and **15a–b**,²⁰ have been previously reported.

General Procedure for Synthesis of Bis- and Tris[phenyl(iodonium)] Triflates (8b**, **8d**, and **13**).** A solution of the appropriate bis- or tris(tributylstannyl)acetylene²¹ (1 mmol) in CH₂Cl₂ (10 mL) was added to a stirred suspension of PhI(CN)OTf²² (2 mmol for **8b**, **8d**; 3 mmol for **13**) in CH₂Cl₂ (50 mL) at −78 °C under nitrogen. The mixture was allowed to warm to room temperature and stirred for 30 min. Hexanes were added to complete precipitation, and the solid was filtered under nitrogen, washed with dry hexanes (100 mL) and dried *in vacuo*. Analytically pure materials were obtained by recrystallization from a concentrated solution of the iodonium salt in CH₃CN by the addition of CH₂Cl₂ and ether.

(17) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. W. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U.K., 1966.

(18) Vrieze, K.; Collman, J. P.; Sears, C. T.; Kubota, M. *Inorg. Synth.* **1968**, *11*, 101–104.

(19) Evans, J. A.; Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1968**, *11*, 99–101.

(20) Stang, P. J.; Tykwinski, R. R.; Zhdankin, V. V. *J. Org. Chem.* **1992**, *57*, 1861–1864.

(21) Tykwinski, R. R. Ph.D. Thesis, University of Utah, June, 1994.

1,4-Bis[[phenyl][(trifluoromethyl)sulfonyl]oxy]iodonium]ethynyl]-2,3,5,6-tetramethylbenzene (8b). Reaction of 1,4-Bis[(tributylstannyl)ethynyl]-2,3,5,6-tetramethylbenzene²¹ (1.37 g, 1.80 mmol) with PhI(CN)OTf²² (1.36 g, 3.60 mmol) in 30 mL of CH₂Cl₂ gave 1.25 g (78%) of **8b** as a yellow microcrystalline solid, mp 116–121 °C dec: IR (CCL₄) 3068, 2927, 2157 (C≡C), 1211, 1161, 1021 cm⁻¹; ¹H NMR (DMSO-*d*₆/CDCl₃) δ 7.89 (d, *J* = 7.8 Hz, 4H), 7.44 (t, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 4H), 2.01 (s, 12H); ¹³C NMR (DMSO-*d*₆/CDCl₃) δ 137.4, 133.6, 132.0, 131.7, 122.1, 118.1, 102.9 (C≡C), 45.3 (C≡C); FAB HRMS *m/z* 736.931606 [M - CF₃SO₃]⁺, calcd for C₂₇H₂₂F₃I₂O₃S 736.932880.

1,2-Bis[[phenyl][(trifluoromethyl)sulfonyl]iodonium]ethynyl]benzene (8d). Reaction of 1,2-bis[(tributylstannyl)ethynyl]benzene²¹ (0.42 g, 0.60 mmol) with PhI(CN)OTf²² (0.46 g, 1.2 mmol) gave 0.36 g (72%) of **8d** as a tan crystalline solid, mp 144–145 °C dec: IR (CCL₄) 3107, 3057, 2176 (C≡C), 1218, 1164, 1023 cm⁻¹; ¹H NMR (CD₃CN) δ 8.19 (d, *J* = 7.8 Hz, 4H), 7.77 (t, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.9 Hz, 4H), 7.59–7.54 (m, 4H); ¹⁹F NMR (CD₃CN) δ -79.08; ¹³C NMR (CD₃CN) δ 135.9, 134.8, 134.3, 133.8, 132.7, 124.2, 121.5 (q, *J*_{CF} = 320 Hz, CF₃SO₃⁻), 118.0, 103.8 (C≡C), 38.4 (C≡C); FAB HRMS *m/z* 680.870433 [M - CF₃SO₃]⁺, calcd for C₂₃H₁₄F₃O₃Si₂, 680.870280. Anal. Calcd for C₂₄H₁₄F₆O₆Si₂I₂: C, 34.72; H, 1.70. Found: C, 34.69; H, 1.74.

1,3,5-Tris[[phenyl][(trifluoromethyl)sulfonyl]oxy]iodonium]ethynyl]benzene (13). Reaction of 1,3,5-tris[(tributylstannyl)ethynyl]benzene²¹ (1.40 g, 1.38 mmol) with PhI(CN)OTf²² (1.57 g, 4.14 mmol) in 20 mL of CH₂Cl₂, yielded 1.30 g (78%) of **13** as a yellow microcrystalline solid, mp 116–121 °C dec: IR (CCL₄) 3064, 2175, 1217, 1165, 1020 cm⁻¹; ¹H NMR (CD₃CN) δ 8.20 (d, *J* = 7.6 Hz, 6H), 7.75 (t, *J* = 7.0 Hz, 3H), 7.73 (s, 3H), 7.60 (t, *J* = 7.5 Hz, 6H); ¹³C NMR (CD₃CN) δ 139.8, 136.1, 134.3, 133.7, 122.4, 121.5 (q, *J*_{CF} = 320 Hz, CF₃SO₃⁻), 117.9, 103.1 (C≡C), 37.0 (C≡C); FAB MS *m/z* 1057 [M - CF₃SO₃]⁺.

Bis[phenyl(iodonium)] Diyne Triflate (17). The reaction of 1,3-bis[(tributylstannyl)ethynyl]carbonyladamantane²¹ (2.7 g, 3.3 mmol) with PhI(CN)OTf²² (2.5 g, 6.6 mmol) in 30 mL of CH₂Cl₂ at -78 °C was warmed to 0 °C and stirred for 30 min. The addition of ether (10 mL) and hexanes (50 mL) gave a white solid which was filtered at -78 °C under nitrogen and immediately purified by recrystallization from CH₂Cl₂ by the addition of hexanes. Drying in vacuo gave 1.80 g (58%) of **17** as a light yellow solid, mp 126–128 °C: IR (neat) 3063, 2922, 2162 (C≡C), 1668 (C=O), 1273, 1173, 1016 cm⁻¹; ¹H NMR (CDCl₃) δ 8.15 (d, *J* = 7.9 Hz, 4H), 7.63 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 4H), 2.18 (bs, 2H), 2.09 (bs, 2H), 1.96 (m, 4H), 1.60 (m, 6H); ¹³C NMR (CDCl₃) δ 189.1, 135.4, 132.7, 132.0, 119.6 (q, *J*_{CF} = 319.9 Hz, CF₃SO₃⁻), 116.5, 99.4 (C≡C⁺), 47.5, 41.0, 36.8, 37.7, 35.2, 27.4. Anal. Calcd for C₃₀H₂₄F₆I₂O₆S₂: C, 38.15; H, 2.56; S, 6.79. Found: C, 38.17; H, 2.57; S, 6.85.

(F₃CO₂SO)(CO)(Cl)(Ph₃P)₂IrC≡C(p-C₆H₄)C≡C Ir(PPh₃)₂(Cl)(CO)(OSO₂CF₃) (10). Vaska's complex **9a** (61 mg, 0.078 mmol) was added to a stirred CH₂Cl₂ (5-mL) solution of bis(iodonium) salt **8a** (32 mg, 0.039 mmol) at ambient temperature and stirred for 10 min. The resulting precipitate was filtered out and washed with ether, giving 68 mg (88%) of **10** as a light yellow microcrystalline solid, mp 204–206 °C dec: IR (CCL₄) 3066, 2143, 2074, 1312, 1201, 1095, 995 cm⁻¹. Anal. Calcd for C₈₆H₆₄Cl₂F₆O₈P₄S₂Ir₂: C, 52.06; H, 3.27; S, 3.23. Found: C, 52.05; H, 3.35; S, 3.13.

General Procedure for the Formation of σ -Acetylide Complexes 11a–d, 12a–c, 16a,b, and 18. Vaska's complex **9a** (2 equiv), or the rhodium analogue **9b** (2 equiv), was added to a stirred suspension/solution of the respective bis[phenyl(iodonium)] diyne triflate (1 equiv) in ca. 5 mL of acetonitrile at ambient temperature and allowed to stir for 30 min.

Addition of diethyl ether (10–15 mL) and hexanes (10–15 mL) completed precipitation, and the solids were filtered out under nitrogen. Analytically pure material was obtained by recrystallization from a saturated acetonitrile solution by the addition of ether.

(H₃CCN)(CO)(Cl)(Ph₃P)₂IrC≡C(p-C₆H₄)C≡C Ir(PPh₃)₂(Cl)(CO)(NCCH₃)₂OSO₂CF₃ (11a). Reaction of Vaska's complex **9a** (26 mg, 0.033 mmol) with bis(iodonium) salt **8a** (55 mg, 0.066 mmol) gave 58 mg (85%) of **11a** as a light yellow microcrystalline solid, mp 199–201 °C dec: IR (CCL₄) 3058, 2156, 2100, 1264, 1032 cm⁻¹; ¹H NMR (CD₃CN) δ 8.0–7.9 (m, 24H), 7.50–7.62 (m, 36H), 6.82 (s, 4H), 1.66 (s, 6H); ¹⁹F NMR (CD₃CN) δ -79.08; ¹³C NMR (CD₃CN) δ 155.1 (t, *J*_{PC} = 6.0 Hz, C=O), 135.5 (t, *J*_{PC} = 5.1 Hz), 133.3, 131.9, 129.8 (t, *J*_{PC} = 5.3 Hz), 128.1 (t, *J*_{PC} = 30 Hz), 125.3, 121.6 (NCCH₃), 108.9 (t, *J*_{PC} = 2 Hz, C≡C Ir), 55.3 (t, *J*_{PC} = 11.5 Hz, C≡C Ir), 3.8 (NCCH₃); ³¹P NMR (CD₃CN) δ -9.85; FAB MS *m/z* 1916 [M - CF₃SO₃]⁺. Anal. Calcd for C₉₀H₇₀Cl₂F₆O₈N₂P₄S₂Ir₂: C, 52.35; H, 3.42; S, 3.11. Found: C, 52.46; H, 3.42; S, 3.21.

(H₃CCN)(CO)(Cl)(Ph₃P)₂IrC≡C(p-MeC₆H₄)C≡C Ir(PPh₃)₂(Cl)(CO)(NCCH₃)₂OSO₂CF₃ (11b). Reaction of Vaska's complex **9a** (50 mg, 0.064 mmol) with bis(iodonium) salt **8b** (28 mg, 0.032 mmol) gave 56 mg (84%) of **11b** as a light yellow microcrystalline solid, mp 234–244 °C dec: IR (CCL₄) 3059, 2139, 2052, 1271, 1033 cm⁻¹; ¹H NMR (DMSO-*d*₆/CD₃CN) δ 7.9–7.8 (m, 24H), 7.65–7.40 (m, 36H), 2.19 (s, 12H, Ar-CH₃), 1.68 (s, 6H, CH₃CN); ¹⁹F NMR (DMSO-*d*₆/CD₃CN) δ -77.74; ¹³C NMR (DMSO-*d*₆/CD₃CN) δ 154.5 (t, *J*_{PC} = 6.2 Hz, C=O), 135.9, 135.1 (t, *J*_{PC} = 2.1 Hz), 133.1, 129.6 (t, *J*_{PC} = 5.3 Hz), 127.8 (t, *J*_{PC} = 30 Hz), 124.5, 121.8 (NCCH₃), 121.7 (q, *J*_{CF} = 321.5 Hz, CF₃SO₃⁻), 107.1 (t, *J*_{PC} = 2.1 Hz, C≡C Ir), 59.0 (t, *J*_{PC} = 12.1 Hz, C≡C Ir), 19.5 (Ar-CH₃), 3.6 (NCCH₃); ³¹P NMR (DMSO-*d*₆/CD₃CN) δ -11.65. Anal. Calcd for C₉₄H₇₈Cl₂F₆O₈N₂P₄S₂Ir₂·2H₂O: C, 52.34; H, 3.83; S, 2.97. Found: C, 52.23; H, 3.76; S, 3.02.

(H₃CCN)(CO)(Cl)(Ph₃P)₂IrC≡C(p-C₆H₄)₂C≡C Ir(PPh₃)₂(Cl)(CO)(NCCH₃)₂OSO₂CF₃ (11c). Reaction of Vaska's complex **9a** (78 mg, 0.10 mmol) with bis(iodonium) salt **8c** (45 mg, 0.050 mmol) gave 91 mg (85%) of **11c** as a light yellow microcrystalline solid, mp 203–207 °C dec: IR (CCL₄) 3063, 2151, 2097, 1262, 1031 cm⁻¹; ¹H NMR (DMSO-*d*₆/CDCl₃) δ 8.05–7.9 (m, 24H), 7.65–7.50 (m, 36H), 7.44 (d, *J* = 8.2 Hz, 4H), 6.92 (d, *J* = 8.2 Hz, 4H), 1.85 (s, 6H); ¹⁹F NMR (DMSO-*d*₆/CDCl₃) δ -78.66; ¹³C NMR (DMSO-*d*₆/CDCl₃) δ 151.9 (t, *J*_{PC} = 6.1 Hz, C=O), 136.3, 132.2 (t, *J*_{PC} = 5.2 Hz), 130.3, 129.5, 126.9 (t, *J*_{PC} = 5.3 Hz), 124.9 (t, *J*_{PC} = 30 Hz), 124.4, 122.5, 118.81 (q, *J*_{CF} = 320 Hz, CF₃SO₃⁻), 118.80 (NCCH₃), 105.1 (C≡C Ir), 52.9 (t, *J*_{PC} = 12.4 Hz, C≡C Ir), 1.04 (NCCH₃); ³¹P NMR (DMSO-*d*₆/CDCl₃) δ -11.02. Anal. Calcd for C₉₆H₇₄Cl₂F₆O₈N₂P₄S₂Ir₂·2H₂O: C, 52.96; H, 3.61; S, 2.95. Found: C, 52.80; H, 3.54; S, 2.91.

(H₃CCN)(CO)(Cl)(Ph₃P)₂IrC≡C(o-C₆H₄)C≡C Ir(PPh₃)₂(Cl)(CO)(NCCH₃)₂OSO₂CF₃ (11d). Reaction of Vaska's complex **9a** (56 mg, 0.072 mmol) with bis(iodonium) salt **8d** (30 mg, 0.036 mmol) gave 48 mg (65%) of **11d** as a light yellow microcrystalline solid, which is slightly unstable in solution, mp 165–168 °C dec: IR (CCL₄) 3063, 2124, 2092, 1264, 1031 cm⁻¹; ¹H NMR (CD₃CN) δ 7.9–7.8 (m, 24H), 7.40–7.30 (m, 36H), 7.06 (m, 2H), 6.95 (m, 2H), 1.64 (s, 6H); ¹⁹F NMR (CD₃CN) δ -78.82; ¹³C NMR (CD₃CN) δ 155.4 (t, *J*_{PC} = 6.4 Hz, C=O), 136.7, 135.4 (t, *J*_{PC} = 5.3 Hz), 133.2, 129.8 (t, *J*_{PC} = 5.3 Hz), 127.7 (t, *J*_{PC} = 30 Hz), 127.5, 125.9, 122.3 (NCCH₃), 122.1 (q, *J*_{CF} = 320 Hz, CF₃SO₃⁻), 109.2 (t, *J*_{PC} = 2 Hz, C≡C Ir), 60.4 (t, *J*_{PC} = 11.2 Hz, C≡C Ir), 3.5 (NCCH₃); ³¹P NMR (CD₃CN) δ -11.70; FAB MS *m/z* 1916.0 [M - CF₃SO₃]⁺. Anal. Calcd for C₉₀H₇₀Cl₂F₆O₈N₂P₄S₂Ir₂·2H₂O: C, 51.45; H, 3.55. Found: C, 51.16; H, 3.45.

(H₃CCN)(CO)(Cl)(Ph₃P)₂RhC≡C(p-C₆H₄)C≡C Rh(PPh₃)₂(Cl)(CO)(NCCH₃)₂OSO₂CF₃ (12a). Reaction of **9b** (58 mg, 0.084 mmol) with bis(iodonium) salt **8a** (35 mg, 0.042 mmol) gave 58 mg (73%) of **12a** as a bright yellow microcrystalline solid, mp 105–106 °C dec: IR (CCL₄) 3054, 2141, 2121, 1265,

(22) Zhdankin, V. V.; Crittall, C. M.; Stang, P. J.; Zefirov, N. S. *Tetrahedron Lett.* **1990**, *31*, 4821–4824.

1031 cm^{-1} ; ^1H NMR (CD_3CN) δ 8.0–7.95 (m, 24H), 7.63–7.60 (m, 12H), 7.58–7.49 (m, 24H), 6.78 (s, 4H), 1.95 (s, 6H, NCCH_3); ^{19}F NMR (CD_3CN) δ -78.87; ^{13}C NMR (CD_3CN) δ 176.6 (dt, $^1J_{\text{RhC}} = 58.8$ Hz, $^2J_{\text{PC}} = 8.6$ Hz, $\text{C}=\text{O}$), 135.4 (t, $J_{\text{PC}} = 5.3$ Hz), 132.3, 131.6, 129.8 (t, $J_{\text{PC}} = 5.3$ Hz), 129.4 (t, $J_{\text{PC}} = 24.9$ Hz), 110.9 (dt, $^2J_{\text{RhC}} = 8.5$ Hz, $^3J_{\text{PC}} = 3.2$ Hz, $\text{C}=\text{C}(\text{Ir})$), 75.2 (dt, $^1J_{\text{RhC}} = 40.6$ Hz, $^2J_{\text{PC}} = 14.0$ Hz, $\text{C}=\text{C}(\text{Ir})$); ^{31}P NMR (CD_3CN) δ 19.72 (d, $J_{\text{RhP}} = 72.3$ Hz). Anal. Calcd for $\text{C}_{90}\text{H}_{70}\text{Cl}_2\text{F}_6\text{O}_8\text{N}_2\text{P}_4\text{S}_2\text{Rh}_2\cdot 2\text{H}_2\text{O}$: C, 56.23; H, 3.88; S, 3.34. Found: C, 56.30; H, 3.71; S, 3.37.

$(\text{H}_3\text{CCN})(\text{CO})(\text{Cl})(\text{Ph}_3\text{P})_2\text{RhC}=\text{C}(\text{p-Me}_6\text{C}_6)\text{C}=\text{CRh}(\text{PPh}_3)_2(\text{Cl})(\text{CO})(\text{NCCH}_3)_2\text{OSO}_2\text{CF}_3$ (12b). Reaction of **9b** (69 mg, 0.10 mmol) with bis(iodonium) salt **8b** (44 mg, 0.050 mmol) gave 85 mg (88%) of **12b** as a bright yellow microcrystalline solid, mp 145–146 °C dec: IR (CCl_4) 3065, 3033, 2126, 2111, 1259, 1031 cm^{-1} ; ^1H NMR (CD_3CN) δ 8.0–7.9 (m, 24H), 7.60–7.55 (m, 12H), 7.50–7.45 (m, 24H), 2.10 (s, 12H, $\text{Ar}-\text{CH}_3$), 1.95 (s, 6H, NCCH_3); ^{19}F NMR (CD_3CN) δ -78.89; ^{31}P NMR (CD_3CN) δ 22.14 (d, $J_{\text{RhP}} = 73.2$ Hz). Anal. Calcd for $\text{C}_{90}\text{H}_{78}\text{Cl}_2\text{F}_6\text{O}_8\text{N}_2\text{P}_4\text{S}_2\text{Rh}_2$: C, 58.30; H, 4.05; S, 3.30. Found: C, 58.06; H, 4.10; S, 3.22.

$(\text{H}_3\text{CCN})(\text{CO})(\text{Cl})(\text{Ph}_3\text{P})_2\text{RhC}=\text{C}(\text{p-C}_6\text{H}_4)_2\text{C}=\text{CRh}(\text{PPh}_3)_2(\text{Cl})(\text{CO})(\text{NCCH}_3)_2\text{OSO}_2\text{CF}_2\text{CF}_3$ (12c). Reaction of **9b** (31 mg, 0.044 mmol) with bis(iodonium) salt **8c** (20 mg, 0.022 mmol) gave 39 mg (90%) of **12c** as a bright yellow microcrystalline solid, mp 107–108 °C dec: IR (CCl_4) 3061, 3033, 2174, 2119, 1266, 1031 cm^{-1} ; ^1H NMR (CD_3CN) δ 8.02–7.00 (m, 24H), 7.55–7.50 (m, 36H), 7.44 (d, $J = 8.3$ Hz, 4H), 7.02 (d, $J = 8.3$ Hz, 4H), 1.95 (s, 6H, NCCH_3); ^{19}F NMR (CD_3CN) δ -78.89, ^{13}C NMR (CD_3CN) δ 176.6 (dt, $^1J_{\text{RhC}} = 57.7$ Hz, $^2J_{\text{PC}} = 8.5$ Hz, $\text{C}=\text{O}$), 139.9, 135.5 (t, $J_{\text{PC}} = 5.3$ Hz), 133.3, 132.3, 129.8 (t, $J_{\text{PC}} = 5.3$ Hz), 129.5 (t, $J_{\text{PC}} = 27.8$ Hz), 127.6, 125.5, 111.8 (dt, $^2J_{\text{RhC}} = 8.5$ Hz, $^3J_{\text{PC}} = 3.2$ Hz, $\text{C}=\text{C}(\text{Ir})$), 73.8 (dt, $^1J_{\text{RhC}} = 45.5$ Hz, $^2J_{\text{PC}} = 14.5$ Hz, $\text{C}=\text{C}(\text{Ir})$); ^{31}P NMR (CD_3CN) δ 19.70 (d, $J_{\text{RhP}} = 73.3$ Hz). Anal. Calcd for $\text{C}_{96}\text{H}_{74}\text{Cl}_2\text{F}_6\text{O}_8\text{N}_2\text{P}_4\text{S}_2\text{Rh}_2$: C, 57.70; H, 3.93; S, 3.21. Found: C, 57.81; H, 3.77; S, 3.20.

$(\text{H}_3\text{CCN})(\text{CO})(\text{Cl})(\text{Ph}_3\text{P})_2\text{IrC}=\text{CCH}_2\text{CH}_2\text{C}=\text{CIr}(\text{PPh}_3)_2(\text{Cl})(\text{CO})(\text{NCCH}_3)_2\text{OSO}_2\text{CF}_3$ (16a). Reaction of Vaska's complex **9a** (79 mg, 0.10 mmol) with bis(iodonium) salt **15a** (39 mg, 0.050 mmol) gave 83 mg (83%) of **16a** as a white microcrystalline solid, mp 197–200 °C dec: IR (CCl_4) 3061, 2097, 2069, 1262, 1031 cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6/\text{CDCl}_3$) δ 7.9–7.8 (m, 24H), 7.65–7.50 (m, 36H), 2.12 (s, 4H), 1.72 (s, 6H); ^{19}F NMR ($\text{DMSO}-d_6/\text{CDCl}_3$) δ -78.66; ^{13}C NMR ($\text{DMSO}-d_6/\text{CDCl}_3$) δ 155.1 (t, $J_{\text{PC}} = 6.4$ Hz, $\text{C}=\text{O}$), 135.2 (t, $J_{\text{PC}} = 5.2$ Hz), 131.3, 129.6 (t, $J_{\text{PC}} = 5.3$ Hz), 128.4 (t, $J_{\text{PC}} = 29.9$ Hz), 122.1 (q, $J_{\text{PC}} = 320$ Hz, CF_3SO_3^-), 121.1 (NCCH_3), 106.2 (t, $J_{\text{PC}} = 3.2$ Hz, $\text{C}=\text{C}(\text{Ir})$), 40.1 ($\text{C}=\text{C}(\text{Ir})$), 22.4, 3.5 (NCCH_3); ^{31}P NMR ($\text{DMSO}-d_6/\text{CDCl}_3$) δ -9.97. Anal. Calcd for $\text{C}_{86}\text{H}_{70}\text{Cl}_2\text{F}_6\text{O}_8\text{N}_2\text{P}_4\text{S}_2\text{Ir}_2$: C, 51.22; H, 3.50; S, 3.18. Found: C, 50.96; H, 3.46; S, 3.18.

$(\text{H}_3\text{CCN})(\text{CO})(\text{Cl})(\text{Ph}_3\text{P})_2\text{IrC}=\text{C}(\text{CH}_2)_5\text{C}=\text{CIr}(\text{PPh}_3)_2(\text{Cl})(\text{CO})(\text{NCCH}_3)_2\text{OSO}_2\text{CF}_3$ (16b). Reaction of Vaska's complex

9a (39 mg, 0.050 mmol) with bis(iodonium) salt **15b** (21 mg, 0.025 mmol) gave 44 mg (77%) of **16b** as a white microcrystalline solid, mp 141–142 °C dec: IR (CCl_4) 3057, 2096, 2048, 1263, 1150, 1031 cm^{-1} ; ^1H NMR (CD_3CN) δ 7.98–7.91 (m, 24H), 7.53–7.45 (m, 36H), 2.18 (m, 4H), 1.57 (s, 6H), 1.14 (m, 4H), 1.07 (m, 2H); ^{19}F NMR (CD_3CN) δ -78.89; ^{13}C NMR (CD_3CN) δ 155.5 (t, $J_{\text{PC}} = 6.2$ Hz, $\text{C}=\text{O}$), 135.3 (t, $J_{\text{PC}} = 5.3$ Hz), 133.2, 129.7 (t, $J_{\text{PC}} = 5.6$ Hz), 128.3 (t, $J_{\text{PC}} = 29.9$ Hz), 122.2 (q, $J_{\text{CF}} = 321.0$ Hz, CF_3SO_3^-), 121.0 (NCCH_3), 108.1 ($\text{C}=\text{C}(\text{Ir})$), 37.5 (t, $J_{\text{PC}} = 12.3$ Hz, $\text{C}=\text{C}(\text{Ir})$), 29.6, 29.0, 21.3, 3.50 (NCCH_3); ^{31}P NMR (CD_3CN) δ -10.57. Anal. Calcd for $\text{C}_{89}\text{H}_{76}\text{Cl}_2\text{F}_6\text{O}_8\text{N}_2\text{P}_4\text{S}_2\text{Ir}_2$: C, 51.92; H, 3.72; S, 3.11. Found: C, 51.69; H, 3.71; S, 3.06.

Bis(iridium) Complex 18. Reaction of Vaska's complex **9a** (39 mg, 0.050 mmol) with bis(iodonium) salt **17** (25 mg, 0.025 mmol) gave 52 mg (96%) of **18** as a white microcrystalline solid, mp 164–167 °C dec: IR (CCl_4) 3060, 2125, 2100, 1647 ($\text{C}=\text{O}$), 1224, 1154, 1033 cm^{-1} ; ^1H NMR (CD_3CN) δ 7.93–7.86 (m, 24H), 7.458–7.48 (m, 36H), 1.88 (s, 2H), 1.66 (s, 6H), 1.47 (m, 2H), 1.43 (bs, 6H), 1.28 (bs, 2H), 1.24 (bs, 2H); ^{19}F NMR (CD_3CN) δ -78.82; ^{13}C NMR (CD_3CN) δ 191.9 ($\text{C}=\text{O}$), 155.1 (t, $J_{\text{PC}} = 6.4$ Hz, $\text{C}=\text{O}$), 135.8 (t, $J_{\text{PC}} = 5.3$ Hz), 134.1, 130.1 (t, $J_{\text{PC}} = 5.7$ Hz), 128.2 (t, $J_{\text{PC}} = 29.9$ Hz), 123.0 (NCCH_3), 122.8 (q, $J_{\text{CF}} = 321.5$ Hz, CF_3SO_3^-), 110.3 ($\text{C}=\text{C}(\text{Ir})$), 68.6 (t, $J_{\text{PC}} = 12.2$ Hz, $\text{C}=\text{C}(\text{Ir})$), 47.4, 39.3, 38.5, 36.3, 29.0, 4.40 (NCCH_3); ^{31}P NMR (CD_3CN) δ -9.42. Anal. Calcd for $\text{C}_{96}\text{H}_{80}\text{Cl}_2\text{F}_6\text{O}_{10}\text{N}_2\text{P}_4\text{S}_2\text{Ir}_2$: C, 52.92; H, 3.70; S, 2.94. Found: C, 52.82; H, 3.66; S, 3.03.

Tris(iridium) Complex 14. Reaction of Vaska's complex **9a** (68 mg, 0.087 mmol) with tris(iodonium) salt **13** (35 mg, 0.029 mmol) in ca. 5 mL of acetonitrile at ambient temperature for 10 min resulted in a clear yellow solution. Addition of ether (10 mL) and hexanes (15 mL), followed by filtration gave 79 mg (73%) of **14** as a light yellow microcrystalline solid, mp 196–197 °C dec: IR (CCl_4) 3058, 2156, 2095, 1263, 1031 cm^{-1} ; ^1H NMR (CD_3CN) δ 8.0–7.93 (m, 36H), 7.35–7.30 (m, 54H), 6.57 (s, 3H), 1.63 (s, 9H); ^{19}F NMR (CD_3CN) δ -78.50; ^{13}C NMR (CD_3CN) δ 152.9 (t, $J_{\text{PC}} = 6.4$ Hz, $\text{C}=\text{O}$), 134.2 (t, $J_{\text{PC}} = 5.2$ Hz), 133.4, 131.9, 127.3 (t, $J_{\text{PC}} = 5.3$ Hz), 126.8 (t, $J_{\text{PC}} = 30$ Hz), 125.6, 120.6, (q, $J_{\text{CF}} = 320$ Hz, CF_3SO_3^-), 120.1 (NCCH_3), 106.3 (t, $J_{\text{PC}} = 2$ Hz, $\text{C}=\text{C}(\text{Ir})$), 55.7 (t, $J_{\text{PC}} = 11.7$ Hz, $\text{C}=\text{C}(\text{Ir})$), 3.01 (NCCH_3); ^{31}P NMR (CD_3CN) δ -11.95.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra for compounds **8b**, **13**, and **14** (6 pages). Ordering information is given in any current masthead page.

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