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*-$(Ph_3P)_2Ir(CO)(Cl)$ and *trans*-$(Ph_3P)_2Rh(CO)(Cl)$ with bis- and tris[phenyl(iodonium)] di- and triyne triflate salts $PhI{-}C{\equiv}C{-}R{-}C{\equiv}C{-}IPh{\cdot}2OTf$ ($R = p\text{-}C_6H_4$, $p\text{-}Me_4C_6H_4$, $4,4'\text{-}C_6H_4C_6H_4$, $o\text{-}C_6H_4$) and $1,3,5\text{-}(PhI{-}C{\equiv}C)_3C_6H_3{\cdot}3OTf$, 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]

$$L_nM{-}(C{\equiv}C)_{\overline{m}}{-}R \qquad L_nM{-}(C{\equiv}C)_{\overline{m}}{-}ML_n$$

1 **2**

$$R{-}C{\equiv}C{-}ML_{\overline{n}}{-}C{\equiv}C{-}R$$

3

$$L_nM{-}C{\equiv}C{-}R{-}C{\equiv}C{-}ML_n \qquad (L_nM{-}C{\equiv}C{-}R{-}C{\equiv}C{-})_m$$

4 **5**

Linear, conjugated C_2 and C_4 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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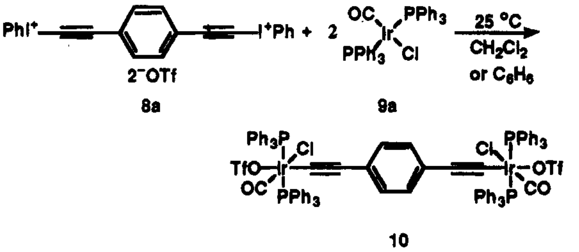
To date, the synthesis of metal complexes **1**−**5** has been primarily achieved via conventional nucleophilic acetylide ($RC{\equiv}C^-$) chemistry and by the formal oxidative addition of terminal acetylenes or alkynyl stannanes to the metal center. To complement these methods, the ability of alkynyl(phenyl)iodonium triflates **6** to serve as synthons for electrophilic acetylenes **7** may

$$\underset{\mathbf{6}}{PhI^+{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}I^+Ph\ 2^-OTf} \qquad \underset{\mathbf{7}}{\text{"}\ {}^+C{\equiv}C{-}Ar{-}C{\equiv}C^+\ \text{"}}$$

be exploited.[15] This is accomplished by the use of bis[phenyl(iodonium)] diyne triflate and tris[phenyl(iodonium)] triyne triflate salts in reactions with Vaska's complex *trans*-$(Ph_3P)_2Ir(CO)(Cl)$, **9a**, and its rhodium analogue **9b**. These investigations have resulted in the development of a single step procedure for the high yield synthesis of bi- and trimetallic, σ-acetylide complexes of iridium(III) and rhodium(III), where the alkyne moieties are separated by a variety of conjugated (aryl) and nonconjugated (alkyl) tethers.

Results and Discussion

The addition of **9a** to a stirred CH_2Cl_2 or benzene solution of bis[phenyl(iodonium)] triflate salt **8a** at ambient temperature resulted in the precipitation of a light yellow solid that proved to be completely insoluble in any organic solvent or water (eq 1). The IR spectrum of this product displayed C≡C and C≡O absorptions at 2143 and 2074 cm^{-1}, respectively. Furthermore, absorptions characteristic of a covalently bonded triflate at 1201, 1095, and 995 cm^{-1} were also observed. On the basis of this data, as well as previous results from this laboratory,[15] the product is presumed to be the bimetallic iridium triflate complex **10**. This structure assignment is also supported by proper combustion analysis.



(1)

To form complexes more amenable to characterization, displacement of the triflate anion by an alternative ligand (i.e., acetonitrile) was attempted.[16] The addition of **9a** to a stirred acetonitrile solution of the respective bis[phenyl(iodonium)] triflate salt **8a**−**d** resulted in the almost immediate formation of a clear yellow solution. Filtration to remove any undissolved solids and the subsequent addition of ether resulted in precipitation of the respective bimetallic iridium(III) complexes **11a**−**d** (Scheme 1). Likewise, reaction of tris[phenyl(iodonium)] triyne triflate **13** with 3 equiv of **9a** at room temperature afforded the trimetallic iridium(III) complex **14** as a stable microcrystalline solid.

In a similar manner, the addition of *trans*-$(Ph_3P)_2$-$Rh(CO)(Cl)$, **9b**, to a CH_3CN solution of the respective bis[phenyl(iodonium)] triflate **8a**−**c** resulted in the formation of a bright yellow solution from which small amounts of product generally began precipitating after several minutes (Scheme 1). The addition of ether effected complete precipitation, and subsequent filtration afforded the linear, bimetallic rhodium complexes **12a**−**c**, respectively, as yellow solids. Reaction of bis[phenyl(iodonium)] triflate **8d** and tris[phenyl(iodonium)] triflate **13** with **9b** under the same conditions, however, afforded impure rhodium complexes (~90% pure) that were unstable to further purification.

Complexes **11a**−**d**, **12a**−**c**, and **14** are characterized by multinuclear NMR and infrared spectroscopies, and selected structural and physical data are summarized in Table 1. Specifically, the IR spectra clearly show absorptions of the C≡O stretch at 2052−2102 cm^{-1} for **11a**−**d** and **14** and at 2111−2121 cm^{-1} for **12a**−**c**, highly characteristic of hexacoordinate Ir(III) and Rh(III) species, respectively. Moreover, the IR spectra show the C≡C stretch between 2126 and 2174 cm^{-1} and bands characteristic of the anionic triflate moiety at 1263−1267 and 1031−1032 cm^{-1}. The presence of the triflate counteranion is also confirmed by the characteristic ^{19}F NMR resonances between −78 and −79 ppm. The existence of the mutually *trans*-phosphines is indicated in the ^{31}P NMR spectra by the observance of a singlet between −10 and −12 ppm for complexes **11a**−**d** and **14** and the presence of a Rh-coupled doublet between 20 and 22 ppm ($J_{PRh} \approx 73$ Hz) for **12a**−**c**.

Further structural proof was provided by the ^{13}C NMR spectra. Particularly evident are resonances of the α- and β-acetylene carbon atoms at 47−56 ppm ($J_{CP} \approx 12$ Hz) and 96−109 ppm ($J_{CP} \approx 2$ Hz), respectively, for iridium complexes **11a**−**d** and **14**. The resonances of the carbon monoxide ligands are observed as triplets at 152−155 ppm ($J_{CP} \approx 6$ Hz). The ^{13}C NMR spectra of rhodium complexes **12a** and **12c** exhibit signals for the α-acetylene carbon atoms at 74−75 ppm with a carbon−rhodium coupling of 41−46 Hz and a carbon−phosphorus coupling of ~14 Hz. The β-acetylene carbon atoms resonate at 111−112 ppm with a carbon−rhodium coupling of ~9 Hz and carbon−phosphorus coupling of ~3 Hz. The carbon monoxide signals of **12a** and **12c** are observed at 177 ppm (J_{CRh} = 58−59 Hz, $J_{CP} \approx 9$

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Scheme 1

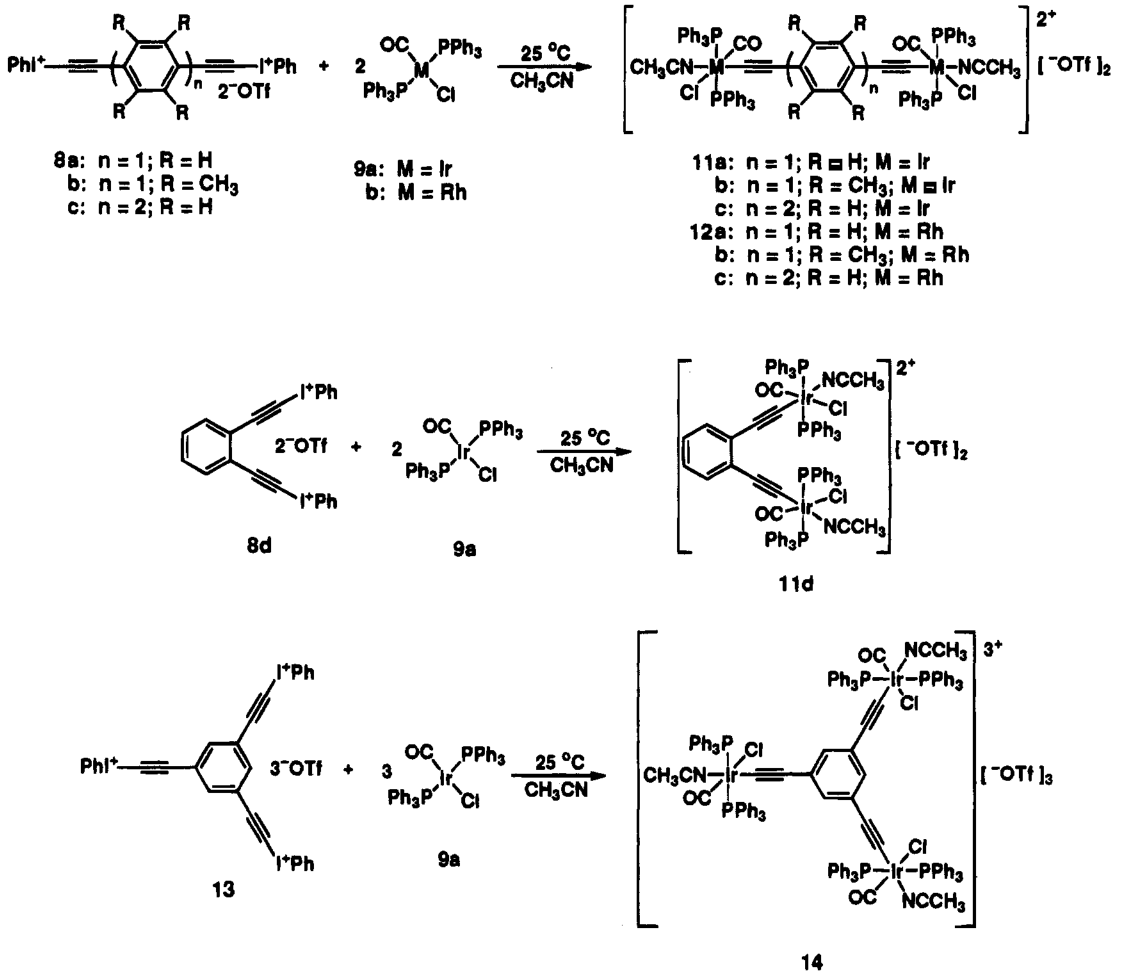


Table 1. Selected Physical and Structural Data for Iridium(III) and Rhodium(III) σ-Acetylide Complexes

cmpd	yield (%)	mp (dec) (°C)	IR (cm^{-1})		^{13}C{H} NMR (ppm)			^{31}P{H} NMR (ppm)
			C≡C	C≡O	C≡O	C≡CIr	C≡CIr	
10	88	204–206	2143	2074	*a*	*a*	*a*	*b*
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	*a*	*a*	*a*	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

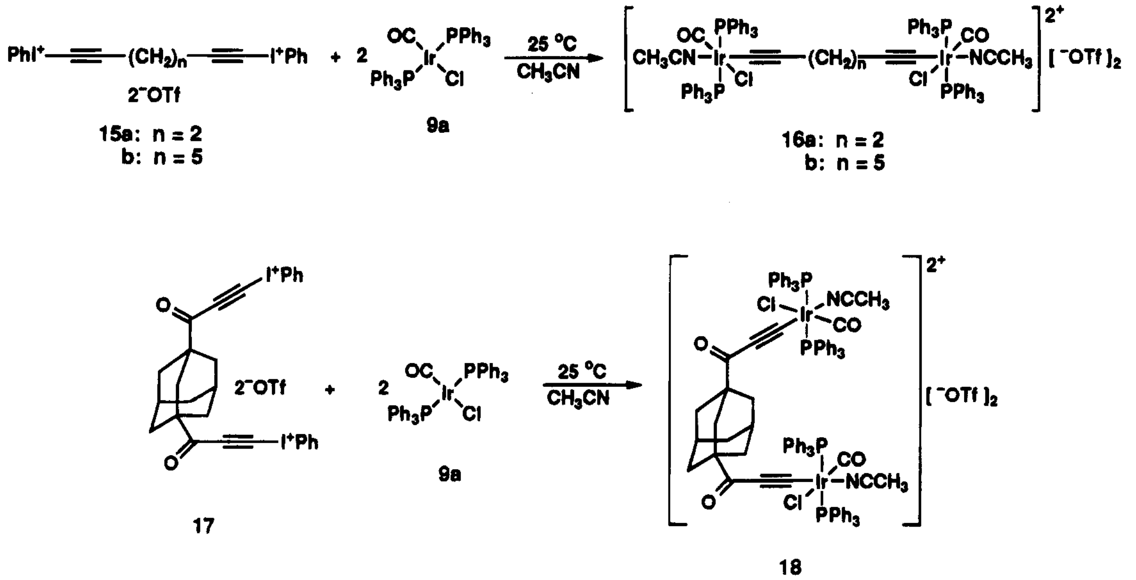
[a] Insufficiently soluble for ^{13}C NMR analysis. [b] Insufficiently soluble for ^{31}P NMR analysis.

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

The ^{1}H 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 ^{1}H 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, resolvation 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≡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, ^{1}H NMR, and ^{13}C 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 ^{13}C 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 alkynyliodonium 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 ^{1}H NMR spectra were recorded at 300 MHz, and chemical shifts were reported relative to $CDCl_3$ δ 7.24, CD_2Cl_2 δ 5.32, dimethyl sulfoxide-d_6 δ 2.49, or CD_3CN δ 1.93. The ^{13}C NMR spectra were recorded at 75 MHz, ^{1}H decoupled, and reported relative to $CDCl_3$ δ 77.0, CD_2Cl_2 δ 53.8, dimethyl sulfoxide-d_6 δ 39.5, or CD_3CN δ 1.30. The ^{19}F NMR spectra were recorded at 282 MHz, and chemical shifts were reported relative to external $CFCl_3$ (sealed capillary) in the appropriate deuterated solvent. The ^{31}P NMR spectra were recorded at 121 MHz, ^{1}H decoupled, and reported relative to external 85% H_3PO_4 (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 procedures[17] 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)acetylene[21] (1 mmol) in CH_2Cl_2 (10 mL) was added to a stirred suspension of PhI(CN)OTf[22] (2 mmol for **8b**, **8d**; 3 mmol for **13**) in CH_2Cl_2 (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 CH_3CN by the addition of CH_2Cl_2 and ether.

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1,4-Bis[[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodoniumyl]ethynyl]-2,3,5,6-tetramethylbenzene (8b). Reaction of 1,4-Bis[(tributylstannyl)ethynyl]-2,3,5,6-tetramethylbenzene[21] (1.37 g, 1.80 mmol) with PhI(CN)OTf[22] (1.36 g, 3.60 mmol) in 30 mL of CH_2Cl_2 gave 1.25 g (78%) of **8b** as a yellow microcrystalline solid, mp 116−121 °C dec: IR (CCl_4) 3068, 2927, 2157 (C≡C), 1211, 1161, 1021 cm^{-1}; ^{1}H NMR (DMSO-*d*$_6$/$CDCl_3$) 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); ^{13}C NMR (DMSO-*d*$_6$/$CDCl_3$) δ 137.4, 133.6, 132.0, 131.7, 122.1, 118.1, 102.9 (*C*≡CI), 45.3 (C≡*C*I), 17.5; FAB HRMS *m/z* 736.931606 [M - $CF_3SO_3^-$]$^+$, calcd for $C_{27}H_{22}F_3I_2O_3S$ 736.932880.

1,2-Bis[[phenyl[[(trifluoromethyl)sulfonyl])iodoniumyl]ethynyl]benzene (8d). Reaction of 1,2-bis[(tributylstannyl)ethynyl]benzene[21] (0.42 g, 0.60 mmol) with PhI(CN)OTf[22] (0.46 g, 1.2 mmol) gave 0.36 g (72%) of **8d** as a tan crystalline solid, mp 144−145 °C dec: IR (CCl_4) 3107, 3057, 2176 (C≡C), 1218, 1164, 1023 cm^{-1}; ^{1}H NMR (CD_3CN) 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); ^{19}F NMR (CD_3CN) δ −79.08; ^{13}C NMR (CD_3CN) δ 135.9, 134.8, 134.3, 133.8, 132.7, 124.2, 121.5 (q, J_{CF} = 320 Hz, $CF_3SO_3^-$), 118.0, 103.8 (*C*≡CI), 38.4 (C≡*C*I); FAB HRMS *m/z* 680.870433 [M - $CF_3SO_3^-$]$^+$, calcd for $C_{23}H_{14}F_3O_3SI_2$, 680.870280. Anal. Calcd for $C_{24}H_{14}F_6O_6S_2I_2$: C, 34.72; H, 1.70. Found: C, 34.69; H, 1.74.

1,3,5-Tris[[phenyl[[(trifluoromethyl)sulfonyl])oxy]iodoniumyl]ethynyl]benzene (13). Reaction of 1,3,5-tris[(tributylstannyl)ethynyl]benzene[21] (1.40 g, 1.38 mmol) with PhI(CN)OTf[22] (1.57 g, 4.14 mmol) in 20 mL of CH_2Cl_2, yielded 1.30 g (78%) of **13** as a yellow microcrystalline solid, mp 116−121 °C dec: IR (CCl_4) 3064, 2175, 1217, 1165, 1020 cm^{-1}; ^{1}H NMR (CD_3CN) 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); ^{13}C NMR (CD_3CN) δ 139.8, 136.1, 134.3, 133.7, 122.4, 121.5 (q, J_{CF} = 320 Hz, $CF_3SO_3^-$), 117.9, 103.1 (*C*≡CI), 37.0 (C≡*C*I); FAB MS *m/z* 1057 [M - $CF_3SO_3^-$]$^+$.

Bis[phenyl(iodonium)] Diyne Triflate (17). The reaction of 1,3-bis[[(tributylstannyl)ethynyl]carbonyl]adamantane[21] (2.7 g, 3.3 mmol) with PhI(CN)OTf[22] (2.5 g, 6.6 mmol) in 30 mL of CH_2Cl_2 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 CH_2Cl_2 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}; ^{1}H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) δ 189.1, 135.4, 132.7, 132.0, 119.6 (q, J_{CF} = 319.9 Hz, $CF_3SO_3^-$), 116.5, 99.4 (*C*≡CI$^+$), 47.5, 41.0, 36.8, 37.7, 35.2, 27.4. Anal. Calcd for $C_{30}H_{24}F_6I_2O_8S_2$: C, 38.15; H 2.56; S, 6.79. Found: C, 38.17; H, 2.57; S, 6.85.

$(F_3CO_2SO)(CO)(CI)(Ph_3P)_2IrC{\equiv}C(p\text{-}C_6H_4)C{\equiv}CIr(PPh_3)_2(CI)(CO)(OSO_2CF_3)$ (10). Vaska's complex **9a** (61 mg, 0.078 mmol) was added to a stirred CH_2Cl_2 (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 (CCl_4) 3066, 2143, 2074, 1312, 1201, 1095, 995 cm^{-1}. Anal. Calcd for $C_{86}H_{64}Cl_2F_6O_8P_4S_2Ir_2$: 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.

$(H_3CCN)(CO)(Cl)(Ph_3P)_2IrC{\equiv}C(p\text{-}C_6H_4)C{\equiv}CIr(PPh_3)_2(Cl)(CO)(NCCH_3){\cdot}2OSO_2CF_3$ (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 (CCl_4) 3058, 2156, 2100, 1264, 1032 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.0−7.9 (m, 24H), 7.50−7.62 (m, 36H), 6.82 (s, 4H), 1.66 (s, 6H); ^{19}F NMR (CD_3CN) δ −79.08; ^{13}C NMR (CD_3CN) 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 (N*C*CH_3), 108.9 (t, J_{PC} = 2 Hz, *C*≡CIr), 55.3 (t, J_{PC} = 11.5 Hz, C≡*C*Ir), 3.8 (NC*C*H_3); ^{31}P NMR (CD_3CN) δ − 9.85; FAB MS *m/z* 1916 [M − $CF_3SO_3^-$]$^+$. Anal. Calcd for $C_{90}H_{70}Cl_2F_6O_8N_2P_4S_2Ir_2$: C, 52.35; H, 3.42; S, 3.11. Found: C, 52.46; H, 3.42; S, 3.21.

$(H_3CCN)(CO)(Cl)(Ph_3P)_2IrC{\equiv}C(p\text{-}Me_4C_6)C{\equiv}CIr(PPh_3)_2(Cl)(CO)(NCCH_3){\cdot}2OSO_2CF_3$ (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 (CCl_4) 3059, 2139, 2052, 1271, 1033 cm^{-1}; ^{1}H NMR (DMSO-*d*$_6$/CD_3CN) δ 7.9−7.8 (m, 24H), 7.65−7.40 (m, 36H), 2.19 (s, 12H, Ar—CH_3), 1.68 (s, 6H, CH_3CN); ^{19}F NMR (DMSO-*d*$_6$/CD_3CN) δ −77.74; ^{13}C NMR (DMSO-*d*$_6$/CD_3CN) 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 (N*C*CH_3), 121.7 (q, J_{CF} = 321.5 Hz, $CF_3SO_3^-$), 107.1 (t, J_{PC} = 2.1 Hz, *C*≡CIr), 59.0 (t, J_{PC} = 12.1 Hz, C≡*C*Ir), 19.5 (Ar—*C*H_3), 3.6 (NC*C*H_3); ^{31}P NMR (DMSO-*d*$_6$/CD_3CN) δ − 11.65. Anal. Calcd for $C_{94}H_{78}Cl_2F_6O_8N_2P_4S_2Ir_2{\cdot}2H_2O$: C, 52.34; H, 3.83; S, 2.97. Found: C, 52.23; H, 3.76; S, 3.02.

$(H_3CCN)(CO)(Cl)(Ph_3P)_2IrC{\equiv}C(p\text{-}C_6H_4)_2C{\equiv}CIr(PPh_3)_2(Cl)(CO)(NCCH_3){\cdot}2OSO_2CF_3$ (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 (CCl_4) 3063, 2151, 2097, 1262, 1031 cm^{-1}; ^{1}H NMR (DMSO-*d*$_6$/$CDCl_3$) 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); ^{19}F NMR (DMSO-*d*$_6$/$CDCl_3$) δ −78.66; ^{13}C NMR (DMSO-*d*$_6$/$CDCl_3$) 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, $CF_3SO_3^-$), 118.80 (N*C*CH_3), 105.1 (*C*≡CIr), 52.9 (t, J_{PC} = 12.4 Hz, C≡*C*Ir), 1.04 (NC*C*H_3); ^{31}P NMR (DMSO-*d*$_6$/$CDCl_3$) δ −11.02. Anal. Calcd for $C_{96}H_{74}Cl_2F_6O_8N_2P_4S_2Ir_2{\cdot}2H_2O$: C, 52.96; H, 3.61; S, 2.95. Found: C, 52.80; H, 3.54; S, 2.91.

$(H_3CCN)(CO)(Cl)(Ph_3P)_2IrC{\equiv}C(o\text{-}C_6H_4)C{\equiv}CIr(PPh_3)_2(Cl)(CO)(NCCH_3){\cdot}2OSO_2CF_3$ (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 (CCl_4) 3063, 2124, 2092, 1264, 1031 cm^{-1}; ^{1}H NMR (CD_3CN) 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); ^{19}F NMR (CD_3CN) δ −78.82; ^{13}C NMR (CD_3CN) 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 (N*C*CH_3), 122.1 (q, J_{CF} = 320 Hz, $CF_3SO_3^-$), 109.2 (t, J_{PC} = 2 Hz, *C*≡CIr), 60.4 (t, J_{PC} = 11.2 Hz, C≡*C*Ir), 3.5 (NC*C*H_3); ^{31}P NMR (CD_3CN) δ −11.70; FAB MS *m/z* 1916.0 [M − $CF_3SO_3^-$]$^+$. Anal. Calcd for $C_{90}H_{70}Cl_2F_6O_8N_2P_4S_2Ir_2{\cdot}2H_2O$: C, 51.45; H, 3.55. Found: C, 51.16; H, 3.45.

$(H_3CCN)(CO)(Cl)(Ph_3P)_2RhC{\equiv}C(p\text{-}C_6H_4)C{\equiv}CRh(PPh_3)_2(Cl)(CO)(NCCH_3){\cdot}2OSO_2CF_3$ (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 (CCl_4) 3054, 2141, 2121, 1265,

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1031 cm^{-1}; ^{1}H 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, $^1J_{RhC}$ = 58.8 Hz, $^2J_{PC}$ = 8.6 Hz, $C\equiv O$), 135.4 (t, J_{PC} = 5.3 Hz), 132.3, 131.6, 129.8 (t, J_{PC} = 5.3 Hz), 129.4 (t, J_{PC} = 24.9 Hz), 110.9 (dt, $^2J_{RhC}$ = 8.5 Hz, $^3J_{PC}$ = 3.2 Hz, $C\equiv CIr$), 75.2 (dt, $^1J_{RhC}$ = 40.6 Hz, $^2J_{PC}$ = 14.0 Hz, $C\equiv CIr$); ^{31}P NMR (CD_3CN) δ 19.72 (d, J_{RhP} = 72.3 Hz). Anal. Calcd for $C_{90}H_{70}Cl_2F_6O_8N_2P_4S_2Rh_2\cdot 2H_2O$: C, 56.23; H, 3.88; S, 3.34. Found: C, 56.30; H, 3.71; S, 3.37.

$(H_3CCN)(CO)(Cl)(Ph_3P)_2)RhC\equiv C(p\text{-}Me_4C_6)C\equiv CRh(PPh_3)_2(Cl)(CO)(NCCH_3)\cdot 2OSO_2CF_3$ (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 bright yellow microcrystalline solid, mp 145−146 °C dec: IR (CCl_4) 3065, 3033, 2126, 2111, 1259, 1031 cm^{-1}; ^{1}H 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, Ar—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_{RhP} = 73.2 Hz). Anal. Calcd for $C_{94}H_{78}Cl_2F_6O_8N_2P_4S_2Rh_2$: C, 58.30; H, 4.05; S, 3.30. Found: C, 58.06; H, 4.10; S, 3.22.

$(H_3CCN)(CO)(Cl))Ph_3P)_2RhC\equiv C(p\text{-}C_6H_4)_2C\equiv CRh(PPh_3)_2(Cl)(CO)(NCCH_3)\cdot 2OSO_2CF_2CF_3$ (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}; ^{1}H 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, $^1J_{RhC}$ = 57.7 Hz, $^2J_{PC}$ = 8.5 Hz, $C\equiv O$), 139.9, 135.5 (t, J_{PC} = 5.3 Hz), 133.3, 132.3, 129.8 (t, J_{PC} = 5.3 Hz), 129.5 (t, J_{PC} = 27.8 Hz), 127.6, 125.5, 111.8 (dt, $^2J_{RhC}$ = 8.5 Hz, $^3J_{PC}$ = 3.2 Hz, $C\equiv CIr$), 73.8 (dt, $^1J_{RhC}$ = 45.5 Hz, $^2J_{PC}$ = 14.5 Hz, $C\equiv CIr$); ^{31}P NMR (CD_3CN) δ 19.70 (d, J_{RhP} = 73.3 Hz). Anal. Calcd for $C_{96}H_{74}Cl_2F_6O_8N_2P_4S_2Rh_2\cdot 2H_2O$: C, 57.70; H, 3.93; S, 3.21. Found: C, 57.81; H, 3.77; S, 3.20.

$(H_3CCN)(CO)(Cl)(Ph_3P)_2IrC\equiv CCH_2CH_2C\equiv CIr(PPh_3)_2(Cl)(CO)(NCCH_3)\cdot 2OSO_2CF_3$ (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}; ^{1}H NMR (DMSO-d_6/$CDCl_3$) δ 7.9−7.8 (m, 24H), 7.65−7.50 (m, 36H), 2.12 (s, 4H), 1.72 (s, 6H); ^{19}F NMR (DMSO-d_6/$CDCl_3$) δ −78.66; ^{13}C NMR (DMSO-d_6/$CDCl_3$) δ 155.1 (t, J_{PC} = 6.4 Hz, $C\equiv O$), 135.2 (t, J_{PC} = 5.2 Hz), 131.3, 129.6 (t, J_{PC} = 5.3 Hz), 128.4 (t, J_{PC} = 29.9 Hz), 122.1 (q, J_{PC} = 320 Hz, $CF_3SO_3^-$), 121.1 ($NCCH_3$), 106.2 (t, J_{PC} = 3.2 Hz, $C\equiv CIr$), 40.1 ($C\equiv CIr$), 22.4, 3.5 ($NCCH_3$); ^{31}P NMR (DMSO-d_6/$CDCl_3$) δ −9.97. Anal. Calcd for $C_{86}H_{70}Cl_2F_6O_8N_2P_4S_2Ir_2$: C, 51.22; H, 3.50; S, 3.18. Found: C, 50.96; H, 3.46; S, 3.18.

$(H_3CCN)(CO)(Cl)(Ph_3P)_2IrC\equiv C(CH_2)_5C\equiv CIr(PPh_3)_2(Cl)(CO)(NCCH_3)\cdot 2OSO_2CF_3$ (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}; ^{1}H 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_{PC} = 6.2 Hz, $C\equiv O$), 135.3 (t, J_{PC} = 5.3 Hz), 133.2, 129.7 (t, J_{PC} = 5.6 Hz), 128.3 (t, J_{PC} = 29.9 Hz), 122.2 (q, J_{CF} = 321.0 Hz, $CF_3SO_3^-$), 121.0 ($NCCH_3$), 108.1 ($C\equiv CIr$), 37.5 (t, J_{PC} = 12.3 Hz, $C\equiv CIr$), 29.6, 29.0, 21.3, 3.50 ($NCCH_3$); ^{31}P NMR (CD_3CN) δ −10.57. Anal. Calcd for $C_{89}H_{76}Cl_2F_6O_8N_2P_4S_2Ir_2$: 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 ($C=O$), 1224, 1154, 1033 cm^{-1}; ^{1}H 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 ($C=O$), 155.1 (t, J_{PC} = 6.4 Hz, $C\equiv O$), 135.8 (t, J_{PC} = 5.3 Hz), 134.1, 130.1 (t, J_{PC} = 5.7 Hz), 128.2 (t, J_{PC} = 29.9 Hz), 123.0 ($NCCH_3$), 122.8 (q, J_{CF} = 321.5 Hz, $CF_3SO_3^-$), 110.3 ($C\equiv CIr$), 68.6 (t, J_{PC} = 12.2 Hz, $C\equiv CIr$), 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 $C_{96}H_{80}Cl_2F_6O_{10}N_2P_4S_2Ir_2$: 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}; ^{1}H 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_{PC} = 6.4 Hz, $C\equiv O$), 134.2 (t, J_{PC} = 5.2 Hz), 133.4, 131.9, 127.3 (t, J_{PC} = 5.3 Hz), 126.8 (t, J_{PC} = 30 Hz), 125.6, 120.6, (q, J_{CF} = 320 Hz, $CF_3SO_3^-$), 120.1 ($NCCH_3$), 106.3 (t, J_{PC} = 2 Hz, $C\equiv CIr$), 55.7 (t, J_{PC} = 11.7 Hz, $C\equiv CIr$), 3.01 ($NCCH_3$); ^{31}P NMR (CD_3CN) δ −11.95.

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

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