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Synthesis, Structures, and Oxidation of Iridium(III) Alkyl Compounds Containing Thiolate and Dithiolate Ligands

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Treatment of [Ir(dtbpy){$CH_2CMe_2C^c{}_6H_4$(*Ir*–*C*^{c})}(C_6H_4tBu-2)] (**1**) (dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl) with the dichalcogenides R_2Q_2 in refluxing toluene afforded the chalcogenolate-bridged dinuclear complexes [Ir(dtbpy){$CH_2CMe_2C^c{}_6H_4$(*Ir*–*C*^{c})}]$_2$(μ-QR)$_2$ [RQ = *p*TolS (**2**), PhSe (**3**)]. Similarly, heating a solution of [Rh(dtbpy){$CH_2CMe_2C^c{}_6H_4$(*Ir*–*C*^{c})}(CH_2CMe_2Ph)] and *p*-tolyl sulfide in toluene at reflux gave [Rh(dtbpy){$CH_2CMe_2C^c{}_6H_4$(*Ir*–*C*^{c})}]$_2$(μ-S*p*Tol)$_2$ (**4**). Treatment of [Ir(dtbpy)(CH_2CMe_2Ph)Cl]$_2$(μ-Cl)$_2$ with Na(Sxyl) (xyl = 2,6-dimethylphenyl) and Na_2(S^S) afforded [Ir(dtbpy)(CH_2CMe_2Ph)(Sxyl)$_2$]$_2$ (**5**) and [Ir(dtbpy)(CH_2CMe_2Ph)(S^S)]$_2$ {S^S^{2-} = maleonitriledithiolate (**6**), toluene-3,4-dithiolate (**7**), benzene-1,2-dithiolate (**8**)}. Oxidation of compound **8** with AgOTf (OTf$^-$ = triflate) resulted in dimerization of the bdt^{2-} ligand by S–S bond formation and the isolation of [Ir$_2$(dtbpy)$_2$(CH_2Me_2Ph)$_2${(bdt)$_2$}][OTf]$_2$ (**9**). The solid-state structures of compounds **2**, **3**, **4**, **7**, and **9** were determined.

Introduction

Organoiridium compounds containing 2,2′-bipyridyl (bpy) and related ligands are of interest due to the findings that Ir(bpy) compounds can catalyze selective borylation of arenes under mild conditions.[1,2] It is believed that Ir(bpy)-catalyzed borylation involves the oxidative addition of an Ir^{III}(bpy) boryl species with arene C–H bonds and subsequent reductive elimination of boronate esters.[3] Thus, understanding of organometallic chemistry of higher valent Ir(bpy) compounds can help develop new Ir catalysts for C–H activation and functionalization.

Few stable Ir^{IV} alkyls and aryls have been isolated,[4,5] presumably because of the stability of low-spin d^6 Ir^{III} compounds, which renders their oxidation difficult. Recently, we synthesized the irida(III)cycle [Ir(dtbpy){$CH_2CMe_2C^c{}_6H_4$(*Ir*–*C*^{c})}(C_6H_4tBu-2)] (dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl) (**1**) by alkylation of [Ir(dtbpy)Cl_3(dmf)] (dmf = *N*,*N*-dimethylformamide) with $PhMe_2CCH_2MgCl$. Compound **1** could be oxidized reversibly to an Ir^{IV} species, which was found to decompose in solutions to give the Ir^{III} starting material.[6] In an attempt to enhance the stability of the Ir^{IV} state, we sought to synthesize Ir^{III} alkyl complexes with thiolate and dithiolate ligands that are known to stabilize metal ions in unusual oxidation states.[7,8] Of special interest are metal complexes with benzene-1,2-dithiolate (bdt) due to their interesting redox behavior.[8–10] The electronic structures of oxidized forms of metal–bdt complexes were studied in detail recently.[10] Although Ir^{IV} species have been generated in solutions by electrochemical oxidation of Ir^{III} tris(dithiocarbamate) complexes,[11] analogous Ir–bdt complexes have not been isolated. In this paper, we describe the synthesis and crystal structures of Ir^{III} dtbpy alkyl complexes containing thiolate and dithiolate ligands. It was found that instead of formation of Ir^{IV} species oxidation of the Ir^{III} bdt alkyl complex led to dimerization of the bdt^{2-} ligand by formation of a S–S bond.

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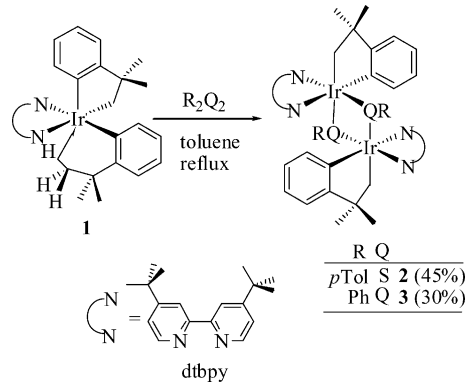
Results and Discussion

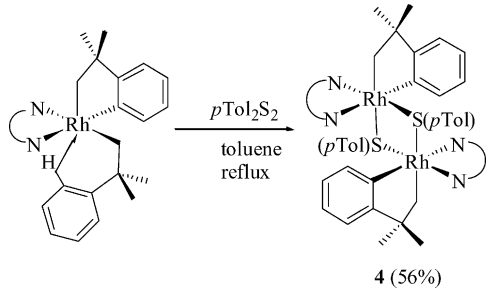
Iridacyclic Thiolate Complexes

In an attempt to synthesize high-valent Ir alkyl compounds, the oxidative addition of iridacycle **1** with disulfides was studied. Reaction of compound **1** with *p*-tolyl disulfide in refluxing toluene resulted in a dark material. Column chromatography on silica led to isolation of the dinuclear thiolate compound [Ir(dtbpy){$CH_2CMe_2C^c{}_6H_4$(*Ir*–*C*^{c})}]$_2$(μ-S*p*Tol)$_2$ (**2**) in 45% yield along with unreacted **1** (ca. 40%). Similarly, the selenolate-bridged dimer [Ir(dtbpy){$CH_2CMe_2C^c{}_6H_4$(*Ir*–*C*^{c})}]$_2$(μ-SePh)$_2$ (**3**) was synthesized from compound **1** and Ph_2Se_2 (Scheme 1). This synthetic route can also be used for Rh thiolate alkyl compounds. Thus, heating a solution of [Rh(dtbpy)-

$\{CH_2CMe_2C^c{}_6H_4(Rh–C^c)\}(CH_2CMe_2Ph)]$[12] and *p*-tolyl disulfide in toluene at reflux led to formation of the Rh^{III} thiolate complex $[Rh(dtbpy)\{CH_2CMe_2C^c{}_6H_4(Rh–C^c)\}]_2(\mu\text{-}Sp\text{Tol})_2$ (**4**) (Scheme 2). Heating compound **1** with Ph_2Te_2 in toluene at reflux resulted in a brown oil possibly containing an Ir^{III} tellurolate complex. We have not been able to purify this brown oily material for further analysis. Oxidative addition of low-valent metal centers with disulfides to give metal bis(thiolate) complexes[13] and C–S reductive elimination from organometallic thiolate complexes[14] is well documented. Thus, it seems reasonable to assume that the formation of compound **2** involves the oxidative addition of **1** with the S–S bond. Reductive elimination of 2-*tert*-butylphenyl *p*-tolyl sulfide from the Ir^{V} bis(thiolate) intermediate gives the Ir^{III} thiolate product (Scheme 3). It may be noted that the Ir^{III} thiolate complexes $[Ir(CO)(PPh_3)X(SAr)]_2(\mu\text{-}Ar)_2$ (X = halide, Ar = 4-substituted 2,6-dinitrophenyl) were synthesized from oxidative addition of *trans*-$[Ir(CO)X(PPh_3)_2]$ with Ar_2S_2.[15]

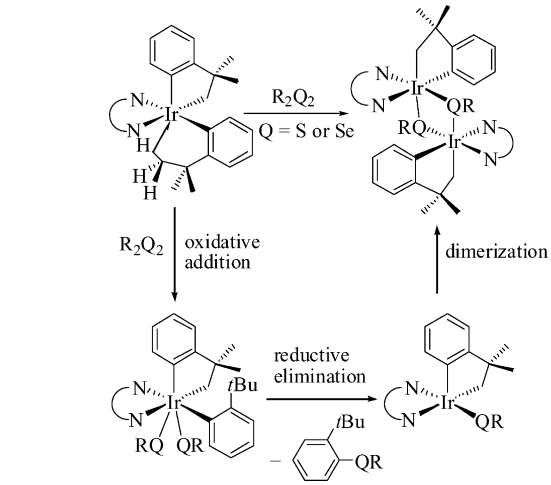


Scheme 1. Reaction of complex **1** with dichalcogenides.



Scheme 2. Synthesis of complex **4**.

Compounds **2**–**4** are remarkably stable in both the solid state and CH_2Cl_2 solutions. They could be purified by column chromatography on silica in air. The ^1H NMR spectrum of compound **2** shows two doublets at δ = 1.17 and 1.87 ppm (J = 6.0 Hz) and two singlets at δ = 0.42 and 0.47 ppm, which are assigned to the diastereotopic methylene (H^a) and methyl (H^b) protons of the iridacycle (see atom labeling scheme in the Experimental Section), respectively. The corresponding resonances for compound **3** were found at δ = 1.23 (d), 1.95 (d), 0.48 (s) and 0.56 (s) ppm, whereas those for compound **4** occurred at δ = 0.90 (d), 1.90 (d), 0.45 (s) and 0.57 (s) ppm. Consistent with the solid-state structures (see below), the two *tert*-butyl groups of the dtbpy ligand in these complexes are magnetically in-



Scheme 3. Proposed mechanism for the formation of complexes **2** and **3**.

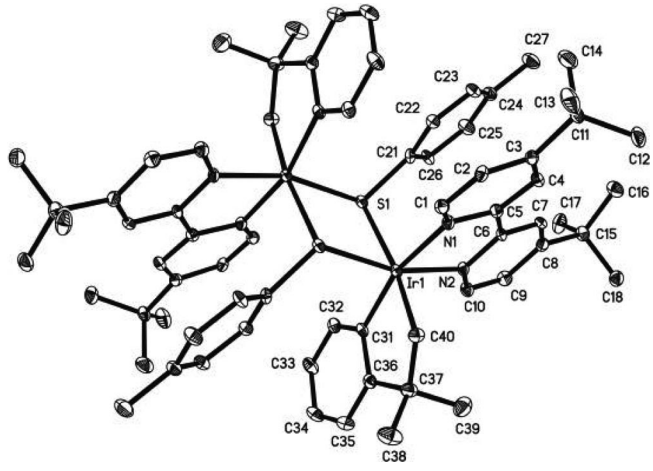


Figure 1. Molecular structure of $[Ir(dtbpy)\{CH_2CMe_2C^c{}_6H_4(Ir–C^c)\}]_2(\mu\text{-}Sp\text{Tol})_2$ (**2**). The ellipsoids are drawn at the 30% probability level.

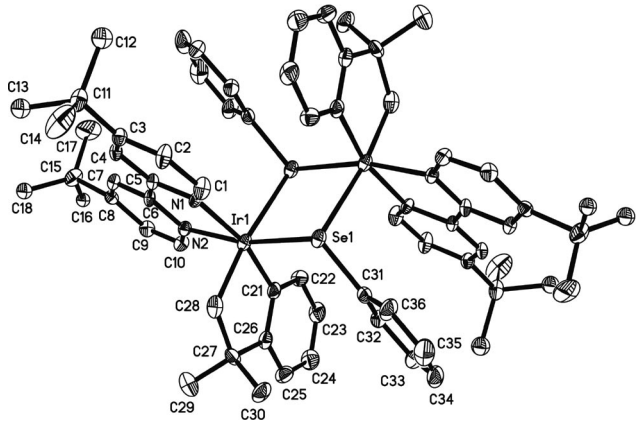


Figure 2. Molecular structure of $[Ir(dtbpy)\{CH_2CMe_2C^c{}_6H_4(Ir–C^c)\}]_2(\mu\text{-}SePh)_2$ (**3**). The ellipsoids are drawn at the 30% probability level.

equivalent and appear as two singlets in the ^{1}H NMR spectra.

Compounds **2**–**4** were characterized by X-ray crystallography (Figures 1, 2, and 3, respectively). Selected bond lengths and angles are summarized in Table 1. The structure of each of these complexes can be viewed as consisting of two symmetry-related {M(dtbpy)[$CH_2CMe_2C^cH_4$(*M*–*C*^{c})](QR)} (M = Ir or Rh, RQ = *p*TolS or PhSe) fragments that are linked together by M–Q–M′ bridges. Contrary to compound **1**, the phenyl ring of the metallacycle in compounds **2** and **3** is opposite to a pyridyl nitrogen atom, whereas the methylene group is *trans* to a M–Q bond. The same arrangement was found for Rh compound **4**. In compound **2**, the Ir–S bond opposite the carbon atom [2.495(1) Å] is longer than that opposite the nitrogen atom [2.345(1) Å] due to the *trans* influence of the methylene group. Similar asymmetric M–Q–M′ bridges were found in compounds **3** [2.575(1) and 2.490(9) Å] and **4** [2.544(7) and 2.344(7) Å]. It may be noted that the Ir–S distances in **2** are shorter than the Ir–Se distances in **3** but comparable to the Rh–S distances in **4**. The Ir–C(phenyl) [2.044(4) and 2.024(9) Å] and Ir–C(methylene) [2.077(4) and 2.022(9) Å] distances of compounds **2** and **3** compare well with those of compound **1** [2.022(4) and 2.073(4) Å, respectively]. The corresponding distances for compound **4** [2.019(3) and 2.056(3) Å, respectively] are in good agreement with those of [Rh(dtbpy){$CH_2CMe_2C^cH_4$(*Rh*–*C*^{c})}-(CH_2CMe_2Ph)].[12] The long M–M separations in these complexes (3.696, 3.877, and 3.706 Å) indicate the absence of any direct metal–metal bond.

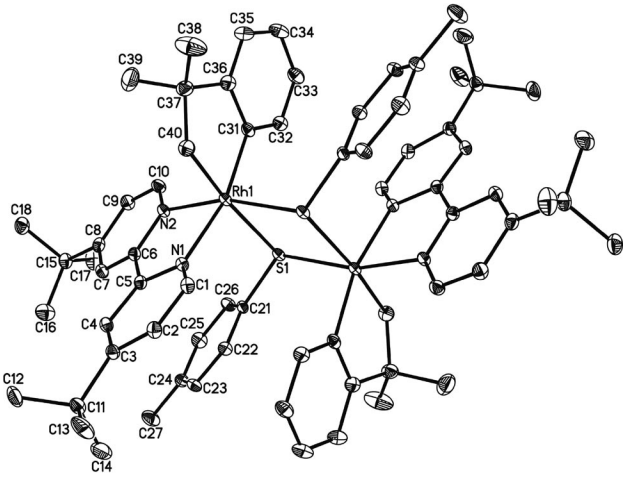


Figure 3. Molecular structure of [Rh(dtbpy){$CH_2CMe_2C^cH_4$(*Rh*–*C*^{c})}]$_2$(μ-S*p*Tol)$_2$ (**4**). The ellipsoids are drawn at the 30% probability level.

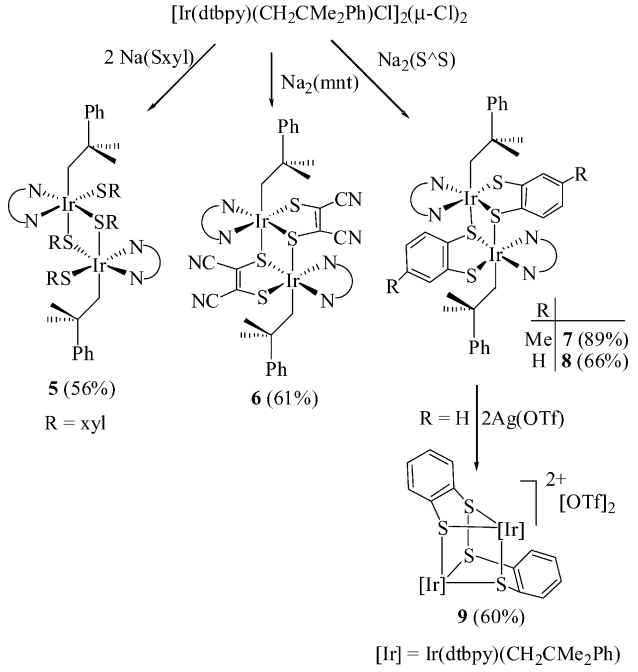
Table 1. Selected bond lengths [Å] and angles [°] for [M(dtbpy)-{$CH_2CMe_2C^cH_4$(*M*–*C*^{c})}]$_2$(μ-QR)$_2$.

	M = Ir, RQ = *p*TolS (**2**)	M = Ir, RQ = PhSe (**3**)	M = Rh, RQ = *p*TolS (**4**)
M–N(*trans* to phenyl)	2.046(3)	2.054(5)	2.057(2)
M–N′(*trans* to Q)	2.108(4)	2.109(6)	2.133(2)
M–C(phenyl)	2.044(4)	2.024(9)	2.019(3)
M–C(methylene)	2.077(4)	2.029(9)	2.542(7)
M–Q	2.495(1)	2.575(1)	2.542(7)
M–Q′	2.345(1)	2.490(9)	2.344(7)
M–M′	3.696	3.877	3.706
C(phenyl)–M–N′	96.2(2)	94.7(3)	96.3(9)
C(phenyl)–M–C(methylene)	81.5(2)	82.1(4)	81.7(1)
N′–M–C(methylene)	98.7(2)	94.7(3)	97.9(1)
C(phenyl)–M–N	165.0(2)	166.8(3)	165.4(1)
N–M–N′	77.6(1)	76.9(2)	77.7(8)
C(methylene)–M–N	86.0(2)	88.4(3)	85.9(1)
C(phenyl)–M–Q	96.8(1)	96.8(2)	96.4(7)
N′–M–Q	163.5(1)	166.5(2)	164.1(6)
C(methylene)–M–Q	93.3(1)	93.9(2)	93.4(9)
N–M–Q	92.0(1)	93.0(2)	92.1(6)
C(phenyl)–M–Q′	94.7(1)	93.9(3)	95.9(8)
N(2)–M–Q′	88.3(1)	92.0(2)	87.8(6)
C(methylene)–M–Q′	172.3(1)	172.5(2)	174.0(8)
N–M–Q′	98.7(1)	96.5(2)	97.2(6)
Q–M–Q′	80.5(4)	80.1(3)	81.4(2)

Ir Neophyl Thiolate and Dithiolate Complexes

Ir(dbpy) neophyl thiolate and dithiolate complexes were synthesized by reaction of [Ir(dtbpy)(CH_2CMe_2Ph)Cl]$_2$(μ-Cl)$_2$ with sodium salts of thiol and dithiol. Thus, treatment of [Ir(dtbpy)(CH_2CMe_2Ph)Cl]$_2$(μ-Cl)$_2$ with 2 equivalents of NaSxyl (xyl = 2,6-dimethylphenyl) afforded the thiolate-bridged dinuclear compound [Ir(dtbpy)(CH_2CMe_2Ph)-(Sxyl)]$_2$(μ-Sxyl)$_2$ (**5**), whereas that with equimolar amounts of Na_2(S^S) gave dimeric [Ir(dtbpy)(CH_2CMe_2Ph)(S^S)]$_2$ {S^S^{2-} = maleonitriledithiolate (mnt^{2-}) (**6**), toluene-3,4-dithiolate (tdt^{2-}) (**7**), benzene-1,2-dithiolate (bdt^{2-}) (**8**)} (Scheme 4). The ^{1}H NMR spectra for compounds **5**–**8** show two singlets due to the *tert*-butyl protons, indicating that the two thiolate groups of the S^S ligand in each of these complexes are inequivalent. The methylene protons (H^a) in compound **5** appear as two doublets δ = 1.03 and 1.48 ppm, whereas those for compounds **6** (δ = 1.52 and 2.48 ppm), **7** (δ = 1.40 and 1.82 ppm), and **8** (δ = 1.38 and 1.84 ppm) were found at more upfield positions. The methyl protons of the neophyl ligand for compounds **6**–**8** appear as singlets at δ = 1.35, 1.17, and 1.14 ppm, respectively.

Compound **7** was characterized by X-ray crystallography (Figure 4). Selected bond lengths and angles are listed in Table 2. The structure consists of two symmetry-related {Ir(dtbpy)(CH_2CMe_2Ph)(tdt)} fragments that are linked together by two Ir–S–Ir′ bridges. Such a thiolate-bridged dimeric structure is well known for metal bis(dithiolene) compounds.[16] The tdt^{2-} ligand is opposite the dtbpy ligand, whereas the neophyl ligand is *trans* to the bridged Ir–S bond. A similar arrangement is expected for **6** and **8** given their similar NMR spectral patterns. The two Ir–S(*trans* to N) distances [2.324(2) and 2.343(2) Å] in **7** are similar to those in [Ir_2(tdt)$_3$(CO)$_2$(PPh_3)$_2$][17] but shorter than the Ir–S(*trans* to C) distance [2.491(2) Å] presumably due to the *trans* influence of the neophyl group. The Ir–C distance of 2.088(8) Å compares well with that in [Ir(dtbpy)-(CH_2CMe_2Ph)Cl]$_2$(μ-Cl)$_2$ [2.132(5) Å].[6]



Scheme 4. Syntheses of complexes **5**–**9**.

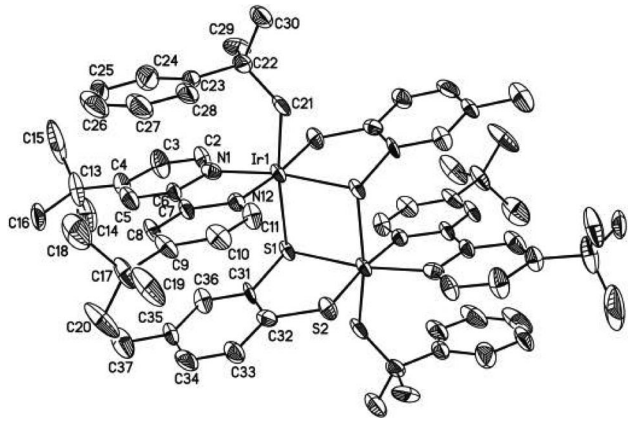


Figure 4. Molecular structure of $[Ir(dtbpy)(CH_2CMe_2Ph)(tdt)]_2$ (**7**). The ellipsoids are drawn at the 30% probability level.

Table 2. Selected bond lengths [Å] and angles [°] for $[Ir(dtbpy)(CH_2CMe_2Ph)(tdt)]_2$ (**7**).[a]

Ir1–N1	2.023(7)	Ir1–N12	2.045(7)
Ir1–C21	2.088(8)	Ir1–S1#1	2.324(2)
Ir1–S2#1	2.343(2)	Ir1–S1	2.491(2)
Ir1–Ir1#1	3.548		
N1–Ir1–N12	78.5(3)	N1–Ir1–C21	101.6(3)
N12–Ir1–C21	88.5(3)	N1–Ir1–S1#1	171.1(2)
N12–Ir1–S1#1	99.3(2)	C21–Ir1–S1#1	86.8(3)
N1–Ir1–S2#1	95.9(2)	N12–Ir1–S2#1	173.8(2)
C21–Ir1–S2#1	90.1(3)	S1#1-Ir1–S2#1	86.7(8)
N1–Ir1–S1	86.5(2)	N12–Ir1–S1	94.6(2)
C21–Ir1–S1	171.7(2)	S1#1-Ir1–S1	85.1(7)
S2#1-Ir1–S1	87.6(8)		

[a] Symmetry operator: #1: $-x + 1, -y + 1, -z + 1$.

Oxidation of Complex 8

No observable change was found when compound **6** was treated with Ag(OTf). In contrast, treatment of compound **8** with Ag(OTf) (2 equiv.) afforded a diamagnetic species characterized as $[Ir_2(dtbpy)_2(CH_2CMe_2Ph)_2\{(bdt)_2\}][OTf]_2$ (**9**) containing the binucleating bis(mercaptophenyl) disulfide ligand $[(bdt)_2]^{2-}$ (Scheme 4) The ^1H NMR spectrum of compound **9** displays well-resolved signals in the normal region, indicative of diamagnetic nature of the compound. Unlike compound **8**, only two resonances were found for the bdt protons in **9**. It seems likely that the chemical environments of the thiolate groups in the bdt ligands in **9** are similar, and thus resulting in the accidental degeneracy. Oxidation-induced dimerization of coordinated benzenedithiolates is well precedented.[18] Liaw and coworkers synthesized $[Mn_2(CO)_6\{(bdt)_2\}]$ by reaction of $[Mn(CO)_3(bdt)]$ with HBF_4 or $[Cp_2Fe][BF_4]$.[18a] Rosenberg and coworkers reported that oxidation of $[M_2(CO)_{10}]$ (M = Mn or Re) with triethylamine oxide followed by treatment with 3,4-toluenedithiol gave $[M_2(CO)_6\{(tdt)_2\}]$.[18b] The cyclic voltammogram of **8** in CH_2Cl_2 solution (working electrode: glassy carbon, supporting electrolyte: 0.1 M $[nBu_4N][PF_6]$) displays a reversible couple at ca. –0.45 V vs. $Cp_2Fe^{+/0}$, which is tentatively assigned as bdt-based oxidation. Under the same conditions, the metal-centered Ir^{IV}–Ir^{III} couple for the iridacycle $[Ir(dtbpy)\{CH_2CMe_2C^c{}_6H_4(Ir–C^c)\}(C_6H_4tBu\text{-}2)]$ was observed at a higher potential (0.02 V vs. $Cp_2Fe^{+/0}$).[6] Thus, it seems reasonable to assume that the Ag^I oxidation of **8** resulted in a transient Ir^{III}–thiyl radical cation species that dimerized by formation of an S–S disulfide bond.

The identity of **9** was established by X-ray diffraction analysis. Figure 5 shows the structure of the dication $[Ir_2(dtbpy)_2(CH_2CMe_2Ph)_2\{(bdt)_2\}]^{2+}$; selected bond lengths and angles are listed in Table 3. The structure of the dication can be viewed as consisting of two $\{Ir(dtbpy)(CH_2CMe_2Ph)(bdt)\}^+$ fragments linked together by two Ir–S–Ir′ bridges and an S–S bond. The geometry around each Ir is roughly octahedral with the neophyl group opposite the bridged thiolate group. The S–S distance of the $[(bdt)_2]^{2-}$ ligand in **9** [2.317(4) Å] is longer than those in $[Mn_2(CO)_6\{(bdt)_2\}]$[2.222(1) Å],[18a] $[Mn_2(CO)_6\{(tdt)_2\}]$ [2.2235(8) Å], and $[Re_2(CO)_6\{(tdt)_2\}]$ [2.235(2) Å],[18b] probably because of steric effects. Unlike complex **8**, in which the two bdt–Ir chelate rings are placed side by side, the chelate rings in **9** are rather superimposed, resulting in a distorted Ir_2S_4 trigonal prism. As pointed out by one referee of this paper, the bonding in **9** can also be described in terms of π*–π* interaction of the two IrS_2 moieties in view of the rather long disulfide S–S distance and the increased separation between both Ir(bdt) chelate rings. The Ir1–Ir2 separation in compound **9** (3.415 Å) is shorter than that in compound **7** (3.548 Å) presumably due to the formation of the S–S bond and/or cationic charge of the complex. Ir–S(Ir′) distances [2.341(3) and 2.333(4) Å] are longer than the Ir–S(disulfide) distances [2.271(3) and 2.259(3) Å]. A similar result was found for analogous Mn complexes.[18] The Ir′–S(*trans* to C) distances [2.515(3) and 2.509(3) Å] are similar to that in **7**.

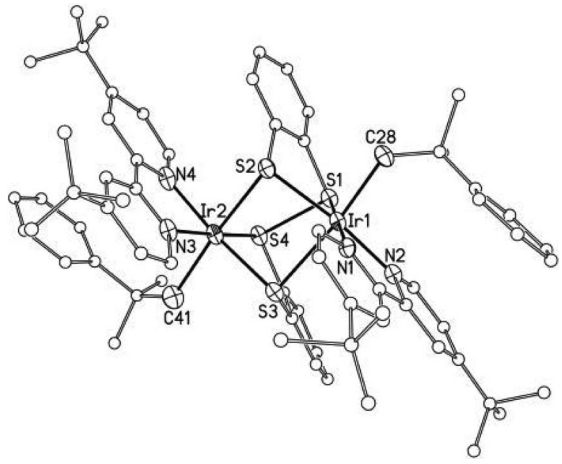


Figure 5. Molecular structure of the complex dication in **9**. The ellipsoids are drawn at the 20% probability level.

Table 3. Selected bond lengths (Å) and angles [°] for $[Ir_2(dtbpy)_2(CH_2CMe_2Ph)_2\{(bdt)_2\}][OTf]_2$ (**9**).

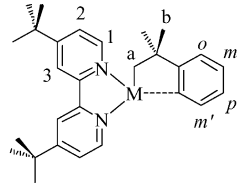
Ir1–N2	2.043(10)	Ir1–N1	2.051(10)
Ir2–N3	2.073(10)	Ir2–N4	2.061(12)
Ir1–C28	2.137(12)	Ir2–C41	2.146(14)
Ir1–S1	2.271(3)	Ir1–S2	2.341(3)
Ir1–S3	2.509(3)	Ir2–S4	2.259(3)
Ir2–S3	2.333(4)	Ir2–S2	2.515(3)
S1–S4	2.317(4)	Ir1–Ir2	3.415
N1–Ir1–N2	77.9(4)	N2–Ir1–C28	99.1(5)
N1–Ir1–C28	89.7(5)	N2–Ir1–S1	99.7(3)
N1–Ir1–S1	177.4(3)	C28–Ir1–S1	91.7(4)
N2–Ir1–S2	172.9(3)	N1–Ir1–S2	98.9(3)
C28–Ir1–S2	87.1(4)	S1–Ir1–S2	83.46(12)
N2–Ir1–S3	88.0(3)	N1–Ir1–S3	82.9(3)
C28–Ir1–S3	168.5(3)	S1–Ir1–S3	96.04(11)
S2–Ir1–S3	85.36(11)		
N4–Ir2–N3	77.9(4)	N4–Ir2–C41	100.6(5)
N3–Ir2–C41	88.2(5)	N4–Ir2–S4	99.0(3)
N3–Ir2–S4	176.8(3)	C41–Ir2–S4	92.1(4)
N4–Ir2–S3	172.3(3)	N3–Ir2–S3	99.3(3)
C41–Ir2–S3	86.4(4)	S4–Ir2–S3	83.90(12)
N4–Ir2–S2	87.2(3)	N3–Ir2–S2	83.5(3)
C41–Ir2–S2	167.2(4)	S4–Ir2–S2	96.70(11)
S3–Ir2–S2	85.40(11)		

Conclusions

We synthesized Ir^{III} alkyl thiolate/dithiolate compounds by (a) reaction of iridacycle **1** with *p*-tolyl disulfide and (b) chloride substitution of $[Ir(dtbpy)(CH_2CMe_2Ph)Cl]_2(\mu\text{-}Cl)_2$ with sodium thiolate/dithiolate. X-ray crystallography confirmed that oxidation of Ir^{III} bdt complex **8** with silver triflate resulted in oxidation of the bdt^{2-} ligand that underwent dimerization by formation of an S–S bond.

Experimental Section

General Remarks: All manipulations were performed under an atmosphere of nitrogen by standard Schlenk techniques. Solvents were purified, distilled and degassed prior to use. ^1H NMR spectra were measured with a Varian Mercury 300 spectrometer operating at 300 MHz. ^1H chemical shifts are reported in ppm relative to $SiMe_4$ (δ = 0 ppm) and were referenced to the proton solvent residue. Infrared spectra were recorded with a Perkin–Elmer 16 PC FTIR spectrophotometer, and mass spectra were recorded with a Finnigan TSQ 7000 spectrometer. Elemental analyses were performed by Medac Ltd., Surrey, UK. The compounds $[Ir(dtbpy)\{CH_2CMe_2C^c{}_6H_4(Ir\text{–}C^c)\}(C_6H_4t\text{Bu-}2)]$ (**1**), $[Ir(dtbpy)(CH_2CMe_2Ph)Cl]_2(\mu\text{-}Cl)_2$,[6] and $[Rh(dtbpy)\{CH_2CMe_2C^c{}_6H_4(Rh\text{–}C^c)\}(CH_2CMe_2Ph)]$[12] were prepared as described elsewhere. The ligand Na_2mnt [mnt^{2-} = maleonitriledithiolate] was prepared according to a literature method.[19] Hydrogen atom labeling schemes for the dtbpy and neophyl ligands are shown below.



$[Ir(dtbpy)\{CH_2CMe_2C^c{}_6H_4(Ir\text{–}C^c)\}]_2(\mu\text{-}QR)_2$ [RQ = *p*TolS (2), PhSe (3)]: To a solution of compound **1** (100 mg, 0.138 mmol) in toluene (25 mL) was added R_2Q_2 (0.069 mmol), and the mixture was heated under reflux overnight. The volatiles were removed in vacuo, and the residue was purified by silica gel column chromatography (Et_2O/hexane, 7:3). Recrystallization from CH_2Cl_2/hexane gave green crystals suitable for X-ray diffraction analysis.

2: Yield: 45 mg, 45%. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 0.42 (s, 6 H, H^b), 0.47 (s, 6 H, H^b), 1.24 (s, 18 H, *t*Bu), 1.48 (s, 18 H, *t*Bu), 1.17 (d, J = 6.0 Hz, 2 H, H^a), 1.87 (d, J = 6.0 Hz, 2 H, H^a), 2.03 (s, 6 H, Me of *p*Tol), 5.56 (d, J = 8.1 Hz, 4 H, H_{ortho} of *p*Tol), 5.85 (d, J = 8.1 Hz, 4 H, H_{meta} of *p*Tol), 6.47 (dd, J = 7.2 and 1.2 Hz, 2 H, H_{ortho}), 6.84–6.87 (m, 4 H, H_{meta}), 6.96 (t, J = 6.9 Hz, 2 H, H_{para}), 7.05 (d, J = 1.8 Hz, 2 H, H^3), 7.38 (d, J = 1.8 Hz, 2 H, H^3), 7.67 (dd, J = 5.7 and 1.8 Hz, 2 H, H^2), 8.57 (d, J = 6.3 Hz, 2 H, H^1), 8.96 (dd, J = 5.7 and 1.8 Hz, 2 H, H^2), 10.34 (d, J = 6.3 Hz, 2 H, H^1) ppm. MS (FAB): m/z = 715.2 $[M/2 + 1]^+$. $C_{70}H_{86}Ir_2N_4S_2\cdot CH_2Cl_2\cdot H_2O$ (1534.97): calcd. C 55.56, H 5.91, N 3.65; found C 55.64, H 5.88, N 3.67.

3: Yield: 32 mg, 30%. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 0.48 (s, 6 H, H^b), 0.57 (s, 6 H, H^b), 1.46 (s, 18 H, *t*Bu), 1.62 (s, 18 H, *t*Bu), 1.94 (d, J = 9.9 Hz, 2 H, H^a), 3.14 (d, J = 9.9 Hz, 2 H, H_{ortho} of PhSe), 5.60 (d, J = 7.2 Hz, 4 H, H_{meta} of PhSe), 5.85 (t, J = 7.2 Hz, 6 H, H_{para} of PhSe), 6.47 (dd, J = 6.0 and 2.0 Hz, 2 H, H_{ortho}), 6.81–6.84 (m, 4 H, H_{meta}), 6.92 (t, J = 6.9 Hz, 2 H, H_{para}), 7.15 (d, J = 2 Hz, 2 H, H^3), 7.30 (d, J = 2 Hz, 2 H, H^3), 7.99 (dd, J = 5.7 and 2.0 Hz, 2 H, H^2), 8.71 (d, J = 6.0 Hz, 2 H, H^1), 9.52 (dd, J = 5.7 and 2.0 Hz, 2 H, H^2), 10.20 (d, J = 6.0 Hz, 2 H, H^1) ppm. MS (FAB): m/z = 750.2 $[M/2 + 1]^+$. $C_{68}H_{82}Ir_2N_4Se_2\cdot 0.5C_6H_{14}$ (1540.85): calcd. C 55.34, H 5.82, N 3.64; found C 55.29, H 5.77, N 3.34.

$[Rh(dtbpy)\{CH_2CMe_2C^c{}_6H_4(Rh\text{–}C^c)\}]_2(\mu\text{-}S$*p*$Tol)_2$ (4): To a solution of $[Rh(dtbpy)\{CH_2CMe_2C^c{}_6H_4(Rh\text{–}C^c)\}(CH_2CMe_2Ph)]$ (100 mg, 0.157 mmol) in toluene (25 mL) was added *p*-tolyl disulfide (20 mg, 0.081 mmol), and the mixture was heated at reflux overnight. The volatiles were removed in vacuo, and the residue was purified by silica gel column chromatography (Et_2O/hexane, 7:3). Recrystallization from CH_2Cl_2/hexane afforded orange crystals suitable for X-ray diffraction analysis (yield: 55 mg, 56%). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 0.42 (s, 6 H, H^b), 0.47 (s, 6 H, H^b), 1.24 (s, 18 H, *t*Bu), 1.48 (s, 18 H, *t*Bu), 1.20 (d, J = 6.0 Hz, 2 H, H^a), 1.93 (d, J = 6.0 Hz, 2 H, H^a), 2.03 (s, 6 H, Me of *p*Tol), 5.53 (d, J = 7.8 Hz,

4 H, *p*Tol), 5.83 (d, *J* = 8.1 Hz, 4 H, *p*Tol), 6.48 (dd, *J* = 7.5 and 1.2 Hz, 2 H, H_{ortho}), 6.86 (t, *J* = 6.0 Hz, 2 H, H_{meta}), 6.94 (dd, *J* = 6.0 and 1.8 Hz, 2 H, $H_{meta'}$), 6.98 (t, *J* = 7.5 Hz, 2 H, H_{para}), 7.06 (d, *J* = 1.8 Hz, 2 H, H^3), 7.41 (d, *J* = 1.8 Hz, 2 H, H^3), 7.68 (dd, *J* = 7.2 and 1.8 Hz, 2 H, H^2), 8.37 (d, *J* = 5.7 Hz, 2 H, H^1), 9.02 (dd, *J* = 7.2 and 1.8 Hz, 2 H, H^2), 10.20 (d, *J* = 5.7 Hz, 2 H, H^1) ppm. MS (FAB): *m*/*z* = 622.2 [M/2 + 1]$^+$. $C_{70}H_{86}N_4Rh_2S_2{\cdot}CH_2Cl_2$ (1338.33): calcd. C 63.72, H 6.63, N 4.19; found C 64.15, H 7.15, N 3.99.

[Ir(dtbpy)(CH$_2$CMe$_2$Ph)(Sxyl)$_2$]$_2$ (5): To a suspension of NaH (60% in mineral oil, 3 mg, 0.080 mmol) in tetrahydrofuran (10 mL) at 0 °C was added 2,6-dimethylbenzenethiol (10 mg, 0.072 mmol), and the mixture was slowly warmed to room temperature and stirred for 2 h. The mixture was cooled to 0 °C and [Ir(dtbpy)(CH$_2$CMe$_2$Ph)Cl]$_2$(μ-Cl)$_2$ (50 mg, 0.036 mmol) was added. After stirring at room temperature overnight, the volatiles were removed in vacuo, and the residue was washed with hexane. Recrystallization from Et_2O at 0 °C afforded a green powder (yield: 35 mg, 56% with respect to Ir). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.03 (d, *J* = 16.2 Hz, 2 H, H^a), 1.28 (s, 18 H, *t*Bu), 1.35 (s, 18 H, *t*Bu), 1.41 (s, 12 H, H^b), 1.48 (d, *J* = 16.2 Hz, 2 H, H^a), 2.25 (s, 6 H, Me of xyl), 2.27 (s, 6 H, Me of xyl), 2.33 (s, 6 H, Me of xyl), 2.38 (s, 6 H, Me of xyl), 5.53 (d, *J* = 7.2 Hz, 4 H, xyl), 5.76 (t, *J* = 6.9 Hz, 2 H, xyl), 6.34 (d, *J* = 7.5 Hz, 4 H, H_{ortho}), 6.54 (t, *J* = 6.9 Hz, 4 H, H_{meta}), 6.67 (t, *J* = 7.2 Hz, 2 H, H_{para}), 6.78 (t, *J* = 6.9 Hz, 2 H, xyl), 6.89 (d, *J* = 7.2 Hz, 4 H, xyl), 6.92 (d, *J* = 2.2 Hz, 2 H, H^3), 7.11 (d, *J* = 2.2 Hz, 2 H, H^3), 7.21 (dd, *J* = 7.2 and 1.8 Hz, 2 H, H^2), 7.27 (dd, *J* = 7.2 and 1.8 Hz, 2 H, H^2), 9.01 (d, *J* = 6.8 Hz, 2 H, H^1), 9.68 (d, *J* = 6.8 Hz, 2 H, H^1) ppm. MS (FAB): *m*/*z* = 731.3 [M/2 – Sxyl]$^+$. $C_{88}H_{110}Ir_2N_4S_4{\cdot}2CHCl_3$ (1971.26): calcd. C 54.84, H 5.52, N 2.84; found C 54.91, H 5.57, N 2.83.

[Ir(dtbpy)(CH$_2$CMe$_2$Ph)(mnt)]$_2$ (6): To a solution of [Ir(dtbpy)(CH$_2$CMe$_2$Ph)Cl]$_2$(μ-Cl)$_2$ (50 mg, 0.036 mmol) in CH_2Cl_2 (20 mL) was added Na_2(mnt) (15 mg, 0.081 mmol), and the mixture was stirred at room temperature overnight. The volatiles were removed in vacuo, and the residue was washed with hexane and Et_2O. Recrystallization from CH_2Cl_2/hexane gave a red powder (yield: 32 mg, 61% with respect to Ir). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.04 (s, 6 H, H^b), 1.35 (s, 6 H, H^b), 1.45 (s, 18 H, *t*Bu), 1.46 (s, 18 H, *t*Bu), 1.52 (d, *J* = 10.1 Hz, 2 H, H^a), 2.48 (d, *J* = 10.1 Hz, 2 H, H^a), 6.19 (d, *J* = 8.1 Hz, 4 H, H_{ortho}), 6.47 (t, *J* = 7.5 Hz, 4 H, H_{meta}), 6.72 (t, *J* = 7.2 Hz, 2 H, H_{para}), 7.47 (d, *J* = 5.4 Hz, 2 H, H^2), 7.54 (d, *J* = 1.8 Hz, 2 H, H^3), 9.05 (d, *J* = 5.4 Hz, 2 H, H^1) ppm. MS (FAB): *m*/*z* = 734.7 [M/2 + 1]$^+$. IR (KBr): $\tilde{\nu}$ = 2188 [ν(CN)] cm^{-1}. $C_{64}H_{74}Ir_2N_8S_4$ (1468.02): calcd. C 52.36, H 5.08, N 7.63; found C 52.35, H 5.39, N 7.86.

[Ir(dtbpy)(CH$_2$CMe$_2$Ph)(tdt)]$_2$ (7): To a suspension of NaH (60% in mineral oil, 3 mg, 0.080 mmol) in thf (10 mL) at 0 °C was added 3,4-toluenedthiol (0.037 mmol) over 1 h, and the mixture was slowly warmed to room temperature and stirred for 2 h. The mixture was cooled to 0 °C and [Ir(dtbpy)(CH$_2$CMe$_2$Ph)Cl]$_2$(μ-Cl)$_2$ (50mg, 0.036mmol) was added. After stirring at room temperature overnight, the volatiles were removed in vacuo, and the residue was washed with hexane. Recrystallization from CH_2Cl_2/hexane afforded dark-yellow crystals suitable for X-ray diffraction (yield: 48 mg, 89% with respect to Ir). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 0.65 (s, 6 H, H^b), 1.17 (s, 6 H, H^b), 1.40 (d, *J* = 10.8 Hz, 2 H, H^a), 1.43 (s, 18 H, *t*Bu), 1.45 (s, 18 H, *t*Bu), 1.82 (d, *J* = 10.8 Hz, 2 H, H^a), 2.66 (s, 6 H, Me of tdt), 5.16 (s, 2 H, tdt), 5.84 (d, *J* = 7.2 Hz, 2 H, tdt), 6.10 (d, *J* = 7.5 Hz, 4 H, H_{ortho}), 6.25 (t, *J* = 7.5 Hz, 4 H, H_{meta}), 6.34 (t, *J* = 7.2 Hz, 2 H, H_{para}), 6.48 (d, *J* = 7.5 Hz, 2 H, tdt), 6.78 (d, *J* = 2.4 Hz, 2 H, H^3), 7.14 (d, *J* = 2.4 Hz, 2 H, H^3), 7.20 (dd, *J* = 6.3 and 1.8 Hz, 2 H, H^2), 7.26 (dd, *J* = 6.3 and 1.8 Hz, 2 H, H^2), 9.04 (d, *J* = 6.0 Hz, 2 H, H^1), 9.68 (d, *J* = 6.0 Hz, 2 H, H^1) ppm. MS (FAB): *m*/*z* = 748.5 [M/2 + 1]$^+$. $C_{70}H_{86}Ir_2N_4S_4{\cdot}CH_2Cl_2$ (1581.09): calcd. C 53.94, H 5.61, N 3.54; found C 53.85, H 5.80, N 3.76.

[Ir(dtbpy)(CH$_2$CMe$_2$Ph)(bdt)]$_2$ (8): This compound was prepared similarly as for compound **7** by using 1,2-benzenedithiol in place of 3,4-toluenedithiol (yield: 36 mg, 60% with respect to Ir). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 0.63 (s, 6 H, H^b), 1.14 (s, 6 H, H^b), 1.38 (d, *J* = 11.1 Hz, 2 H, H^a), 1.43 (s, 18 H, *t*Bu), 1.45 (s, 18 H, *t*Bu), 1.84 (d, *J* = 11.1 Hz, 2 H, H^a), 5.28 (d, *J* = 7.5 Hz, 2 H, bdt), 5.99 (t, *J* = 6.9 Hz, 2 H, bdt), 6.16 (d, *J* = 7.5 Hz, 4 H, H_{ortho}),

Table 4. Crystallographic data for complexes **2**–**4**, **7**, and **9**.

	2	**3**	**4**	**7**	**9**
Formula	$C_{70}H_{86}Ir_2N_4S_2$	$C_{68}H_{82}Ir_2N_4Se_2$	$C_{70}H_{86}N_4Rh\ S_2$	$C_{70}H_{86}Ir_2N_4S_4$	$C_{70}H_{82}F_6Ir_2N_4O_6S_6$
Molecular weight	1431.95	1497.70	1253.37	1496.07	1766.16
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a [Å]	12.9414(18)	11.439(2)	12.8896(8)	9.8899(9)	16.4417(14)
b [Å]	19.004(3)	14.471(3)	19.0136(12)	12.4739(12)	24.827(2)
c [Å]	13.5637(18)	18.817(4)	13.6123(9)	26.240(3)	20.6900(17)
α [°]	90	90	90	90	90
β [°]	112.984(2)	93.912(4)	113.023(1)	99.343(2)	102.751(2)
γ [°]	90	90	90	90	90
V [Å^3]	3071.0(7)	3107.6(11)	3070.3(3)	3194.1(5)	8237.4(12)
Z	2	2	2	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.549	1.601	1.356	1.556	1.424
T [K]	100(2)	100(2)	100(2)	100(2)	293(2)
μ [mm^{-1}]	4.442	5.492	0.650	4.337	3.439
F(000)	1440	1480	1312	1504	
No. of reflections	16456	16428	16362	15514	14418
No. of indep. reflections	6013	6017	5970	5585	7074
R_{int}	0.0504	0.0765	0.0269	0.0715	
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.0316, 0.0670	0.0492, 0.0687	0.0378, 0.0860	0.0467, 0.0888	0.0609, 0.1994
R_1, wR_2 (all data)	0.0482, 0.0715	0.1272, 0.0773	0.0432, 0.0882	0.0918, 0.0983	0.1503, 0.1479
Goodness of fit	0.998	0.995	1.098	1.003	

[a] $R_1 = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|)$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

6.28–6.35 (m, 6 H, H_{meta} and H_{para}), 6.53 (t, J = 7.5 Hz, 2 H, bdt), 6.69 (d, J = 8.1 Hz, 2 H, bdt), 6.76 (d, J = 2.4 Hz, 2 H, H^3), 7.09 (d, J = 2.4 Hz, 2 H, H^3), 7.15 (dd, J = 6.3 and 1.8 Hz, 2 H, H^2), 7.22 (dd, J = 6.3 and 1.8 Hz, 2 H, H^2), 9.06 (d, J = 6.0 Hz, 2 H, H^1), 9.72 (d, J = 6.0 Hz, 2 H, H^1) ppm. $C_{68}H_{82}Ir_2N_4S_4 \cdot 0.5CH_2Cl_2$ (1510.57): calcd. C 54.47, H 5.54, N 3.71; found C 54.31, H 5.53, N 3.96.

$[Ir_2(dtbpy)_2(CH_2CMe_2Ph)_2\{(bdt)_2\}][OTf]_2$ (9): To a solution of **8** (51 mg, 0.034 mol) in CH_2Cl_2 was added silver triflate (18 mg, 0.068 mmol, 2 equiv.), and the mixture was stirred at room temperature for 2 h. Recrystallization from CH_2Cl_2/hexane afforded brown crystals (yield: 36 mg, 60%) that were suitable for X-ray diffraction. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 0.50 (s, 6 H, H^b), 0.76 (s, 6 H, H^b), 0.96 (d, J = 11.6 Hz, 2 H, H^a), 1.44 (s, 18 H, *t*Bu), 1.62 (s, 18 H, *t*Bu), 2.15 (d, J = 11.6 Hz, 2 H, H^a), 5.99 (d, J = 7.9 Hz, 4 H, bdt), 6.44 (d, J = 7.4 Hz, 4 H, bdt), 6.72 (d, J = 7.5 Hz, 2 H, H_{ortho}), 6.81 (d, J = 7.5 Hz, 2 H, H_{ortho}), 6.88 (d, J = 6.1 Hz, 2 H, H^2), 7.08 (t, J = 7.5 Hz, 2 H, H_{para}), 7.51–7.56 (m, 4 H, H_{meta}), 7.75 (s, 2 H, H^3), 7.92 (d, J = 6.1 Hz, 2 H, H^2), 7.98 (s, 2 H, H^3), 8.70 (d, J = 7.7 Hz, 2 H, H^1), 8.80 (d, J = 5.9 Hz, 2 H, H^1) ppm. $C_{70}H_{82}F_6Ir_2N_4O_6S_6 \cdot CH_2Cl_2$ (1851.17): calcd. C 46.07, H 4.57, N 3.03; found C 46.43, H 4.72, N 3.02.

X-ray Crystallography: Crystallographic data and structure refinement parameters for compounds **2**–**4**, **7**, and **9** are summarized in Table 4. Intensity data were collected with a Bruker SMART APEX 1000 CCD diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The data was corrected for absorption by using the program SADABS.[20] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 by using the SHELXTL software package.[21] In compound **3**, the *tert*-butyl groups of the dtbpy ligand were found to be disordered. The C12 carbon atom is split into two sites with 0.6 and 0.4 occupancies, whereas C13, C16, and C18 are split into two sites with 50% occupancy each. In compound **9**, the disordered triflate anions were refined isotropically. Selected bond lengths and angles for **2**–**4**, **7**, and **9** are listed in Tables 1, 2, and 3, respectively. CCDC-683524 (for **2**), -683525 (for **3**), -683526 (for **4**), -683527 (for 7), and -683528 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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