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Annulation of an Iridabenzene through Formal Cycloaddition Reactions with Organonitriles

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The cationic iridacyclopentadiene complex $[Ir(C_4H_4)(CS)(MeCN)(PPh_3)_2][CF_3SO_3]$ (**2**), which is derived from the reaction between $[Ir(CS)(MeCN)(PPh_3)_2][CF_3SO_3]$ (**1**) and ethyne, undergoes a thermally induced migratory insertion reaction involving the thiocarbonyl ligand to form the cationic iridabenzene $[Ir(C_5H_4\{S\text{-}1\})(MeCN)(PPh_3)_2][CF_3SO_3]$ (**3**) in very high yield. The addition of methyl triflate to this iridabenzene in the presence of NCMe results in methylation of the sulfur atom, and the red dicationic iridabenzene $[Ir(C_5H_4\{SMe\text{-}1\})(MeCN)_2(PPh_3)_2][PF_6]_2$ (**4**) is obtained after the addition of NH_4PF_6. Upon treatment of **3** with RCN (R = Me or *p*-tolyl) and acid, a cyclization reaction ensues between the organonitrile and the η^2-C(S)Ir function of the iridabenzene to give the corresponding iridabenzothiazolium complexes $[Ir(C_5H_4\{NH{=}C(R)S\text{-}1\})(RCN)(PPh_3)_2][PF_6]_2$ [R = Me (**6a**); *p*-tolyl (**6b**)], where the iridium occupies a ring junction position.

Introduction

Metallabenzenes have now become a well-established class of metalla-aromatic compounds, and a considerable number of papers have appeared addressing the syntheses, structures, reactions, and bonding of these compounds.[1] In contrast, stable metallabenzenoids with fused benzene or heterocyclic rings are much rarer. Reported examples include an iridanaphthalene[2] and an osmanaphthalene,[3] an iridabenzothiophene,[4] as well as ruthena-[5,6] and osmabenzofurans.[7] The fused heterocyclic ring metallabenzenes were prepared using two different synthetic approaches. The iridabenzothiophene was obtained by the cycloaddition of two methylpropiolate molecules to a thiocarbonyl ligand to form a fused iridacyclobutadiene iridathiophene complex followed by the insertion of both carbon atoms of a third methylpropiolate into the four-membered iridacyclic ring.[4] The metallabenzofurans formally resulted from metal-mediated cyclization reactions of methylpropiolate and coordination to the metal center of the carbonyl oxygen of incipient metallabenzene ester substituents.[5,7] Metallabenzenes with saturated tethering arms have also been formed by C-protonation of the metallafuran rings of these metallabenzofurans.[6,7] In this paper, we now report that the new fused heterocyclic ring metallabenzenes, the cationic iridabenzothiazolium complexes $[Ir(C_5H_4\{NH{=}C(R)S\text{-}1\})(RCN)(PPh_3)_2][PF_6]_2$ [R = Me (**6a**); *p*-tolyl (**6b**)], can be prepared by the formal [2 + 3] cycloaddition reaction between organonitriles and the η^2-C(S)Ir function of the cationic iridabenzene $[Ir(C_5H_4\{S\text{-}1\})(MeCN)(PPh_3)_2][CF_3SO_3]$ (**3**) in the presence of acid. The crystal structures of **3** and **6b** are also reported.

Results and Discussion

In a recent paper, we noted that the neutral thiocarbonyl iridacyclopentadiene $Ir(C_4H_4)Cl(CS)(PPh_3)_2$ can be prepared by the treatment of $[Ir(CS)(MeCN)(PPh_3)_2][CF_3SO_3]$ (**1**) first with ethyne and then chloride.[8] $Ir(C_4H_4)Cl(CS)(PPh_3)_2$ resists rearrangement on heating in solution, but when heated in the presence of methyl triflate, S-methylation and migratory insertion ensues, and after the addition of chloride, the neutral iridabenzene $Ir(C_5H_4\{SMe\text{-}1\})Cl_2(PPh_3)_2$ can be isolated.[8] We have investigated this reaction in more detail with the aim of discovering a way to induce a migratory insertion reaction of the iridacyclopentadiene and CS groups without concomitant alkylation of the sulfur atom. Our interest in this approach was inspired by the expectation that the η^2-C(S) function of the resulting iridabenzene could serve as an important reaction center for the development of new metallabenzene chemistry. Because migratory insertions of σ-organyl and CS ligands may be more favorable in cationic complexes,[9] we focused our

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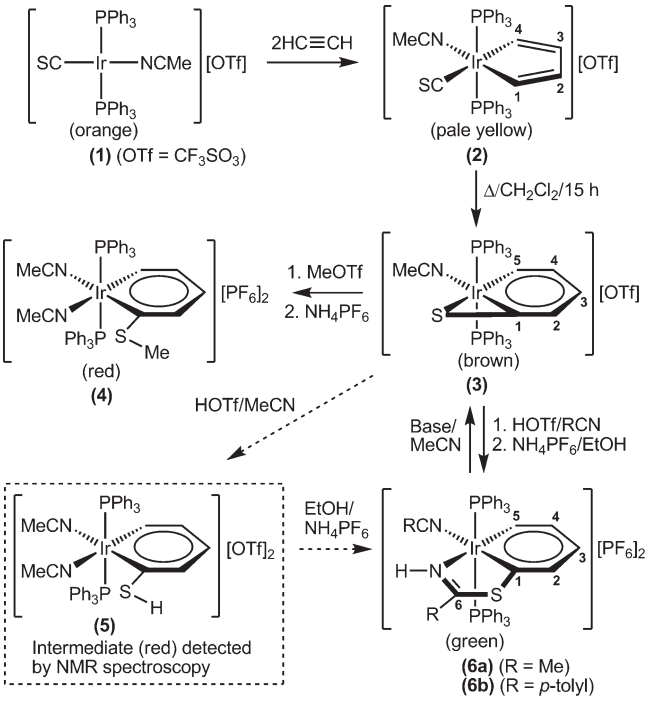
Scheme 1



studies on the cationic thiocarbonyl iridacyclopentadiene $[Ir(C_4H_4)(CS)(MeCN)(PPh_3)_2][CF_3SO_3]$ (**2**).

Complex **2** is formed when a solution of **1** is treated with ethyne, and isolation of pure samples is possible by the careful addition of hexane (see Scheme 1). Characterizing data for **2** and the other new compounds are given in the Experimental Section. The ring-numbering system used for discussion of the NMR spectra is indicated in Scheme 1.

The metal-bound carbon atoms of the iridacyclopentadiene ring in **2** appear in the ^{13}C NMR spectrum at 152.6 and 136.0 ppm, and the signals for the protons attached to these carbon atoms are observed in the ^{1}H NMR spectrum at 7.20 and 6.53 ppm. Unlike the related neutral complex $Ir(C_4H_4)Cl(CS)(PPh_3)_2$,[8] we have found that pure samples of **2** undergo migratory insertion on heating under reflux in dichloromethane and that complete rearrangement to the cationic iridabenzene **3** occurs after 15 h under these conditions (see Scheme 1). The metal-bound carbon atoms in the iridabenzene **3** display low-field resonances in the ^{13}C NMR spectrum at 243.9 (C1) and 176.9 (C5) ppm. The proton H5 that is attached to C5 also gives rise to a very low-field signal in the ^{1}H NMR spectrum at 12.47 ppm.

These resonances, which are shifted conspicuously downfield compared to those observed for the corresponding nuclei in the iridacyclopentadiene **2**, are consistent with increased π bonding between the metal and ring carbon atoms in **3** and are a characteristic feature of metallabenzenes.[1] As expected, the other metallabenzene ring atoms in **3** give rise to signals in the ^{1}H and ^{13}C NMR spectra that fall in the normal aromatic regions [7.50 (H3), 6.81 (H4), and 6.24 (H2) ppm and 153.9 (C3), 127.4 (C4), and 117.6 (C2) ppm, respectively]. The single resonance observed for the two triphenylphosphine ligands in the ^{31}P NMR spectrum at 5.77 ppm indicates that these groups are mutually trans in solution. One important aspect of the synthesis of **3** is that the three steps starting from $IrCl(CS)(PPh_3)_2$ can be carried out in one pot without isolation and purification of **1** and **2** (see the Experimental Section). When carried out in this way, the overall yield of pure **3** based on $IrCl(CS)(PPh_3)_2$ is 91%, and this is one of the highest percentages reported for a metallabenzene synthesis.

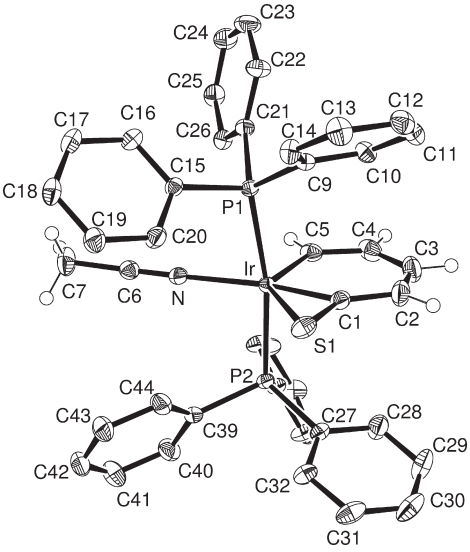


Figure 1. Molecular structure of **3** with thermal ellipsoids at the 50% probability level. Hydrogen atoms on the phenyl rings and the triflate counterion have been omitted for clarity.

The crystal structure of **3** has been determined, and the molecular structure is shown in Figure 1 (crystal data for **3** as well as **6b** are given in the Supporting Information). The metallabenzene ring and the acetonitrile ligand occupy the equatorial positions, and the two *trans*-PPh_3 ligands are axial with P1−Ir−P2 = 169.768(16)°. The iridabenzene ring is nearly planar, with the iridium atom deviating the most [0.039(1) Å] from the mean plane through Ir, C1−C5, and S(1). The Ir−C1 [1.933(2) Å] and Ir−C5 [1.989(2) Å] distances are relatively short and are consistent with these bonds having some multiple character.

There is a very slight but significant alternation in the length of the C−C distances within the iridabenzene ring [C1−C2, 1.398(3) Å; C2−C3, 1.366(4) Å; C3−C4, 1.421(4) Å; C4−C5, 1.365(3) Å], although all distances clearly fall in the aromatic range and are typical of those observed in other metallabenzenes.[1]

An important aspect of the structure of **3** is the η^2-C(S) function associated with the iridabenzene ring. Within this group, the Ir−S distance is 2.6325(6) Å, the C1−S distance is 1.664(2) Å, and the Ir−C1−S angle is 93.80(9)°. In comparison, for the related neutral osmabenzene $Os(C_5H_2\{S\text{-}1\}\{Me\text{-}2\}\{Me\text{-}5\})(CO)(PPh_3)_2$,[10] the Os−S distance is shorter [2.4990(12) Å], the Os−C(S) distance is longer [1.689(6) Å], and the Os−C−S angle is smaller (84.00°). This indicates that in **3** the sulfur of the η^2-C(S) function does not interact as strongly with the metal as it does in the related osmabenzene. The Ir−S interaction in **3** is also weaker than that found in the *dihapto*thiocarbamoyl complex $Ir(\eta^2\text{-}C(S)NMe_2)Cl_2(PPh_3)_2$,[11] where the relevant parameters are as follows: Ir−S, 2.4265(17) Å; C−S, 1.704(7) Å; Ir−C−S, 82.3(3)°.

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Although the iridabenzene **3** is cationic, the sulfur atom of the η^2-C(S) function still shows significant nucleophilic character, and this is probably enhanced as a result of the relatively weak Ir−S interaction noted above. The addition of methyl triflate to **3** in a dichloromethane solution containing acetonitrile results in S-methylation, and the red dicationic iridabenzene $[Ir(C_5H_4\{SMe\text{-}1\})(MeCN)_2(PPh_3)_2][PF_6]_2$ (**4**) can be isolated after the addition of NH_4PF_6 in ethanol (see Scheme 1). In the ^{1}H NMR spectrum, the iridabenzene protons of **4** appear at 11.59 (H5), 7.03 (H4), 6.90 (H3), and 6.29 (H2) ppm and the methyl protons of the two inequivalent acetonitrile ligands are observed at 2.17 and 1.99 ppm. In the ^{31}P NMR spectrum, a singlet at −2.45 ppm is observed for the two mutually trans phosphorus atoms.

Attempts were made to synthesize the analogue of **4** that has an SH rather than an SMe iridabenzene ring substituent by treating a dichloromethane/acetonitrile solution of **3** with triflic acid. The brown solution of **3** immediately turned red upon the addition of the acid, but a pure sample of the red product could not be obtained either by solvent evaporation or by the addition of a precipitating solvent such as hexane. In an attempt to isolate the product in this red solution as a hexafluorophosphate salt, an ethanol solution of NH_4PF_6 was added. Unexpectedly, this caused the red solution to quickly turn deep green, and upon removal of the dichloromethane solvent under reduced pressure, dark-green crystals of the iridabenzothiazolium complex $[Ir(C_5H_4\{NH{=}C(Me)S\text{-}1\})(MeCN)(PPh_3)_2][PF_6]_2$ (**6a**) were isolated in high yield (see Scheme 1). The ν(NH) band of **6a** is observed in the IR spectrum at 3289 cm^{-1}. In the ^{1}H and ^{13}C NMR spectra, the chemical shifts of the iridabenzene ring protons [12.35 (H5), 6.86 (H2), 6.75 (H4), and 6.55 (H3) ppm] and carbon atoms [232.3 (C1), 210.9 (C5), 170.2 (C3), 127.2 (C4), 125.5 (C2), and 123.5 ppm] are very close to those observed in **3** and **4**, suggesting that the aromatic character of this six-membered ring is not diminished by the fused thiazolium ring. The NH signal is observed in the ^{1}H NMR spectrum as a broad singlet at 10.23 ppm that integrates for one proton. The thiazolium ring carbon atom, C6, is observed at 190.0 ppm in the ^{13}C NMR spectrum, a position considerably downfield from the nitrile carbon (C8, 128.3 ppm) of the coordinated acetonitrile ligand.

The cyclization reaction that produces the fused thiazolium ring is not restricted to acetonitrile. If a dichloromethane solution of **3** containing *p*-tolunitrile is treated first with triflic acid and then an ethanol solution of NH_4PF_6, the iridabenzothiazolium complex $[Ir(C_5H_4\{NH{=}C(p\text{-}tolyl)S\text{-}1\})(p\text{-}tolylCN)(PPh_3)_2][PF_6]_2$ (**6b**) can be isolated from the solution (see Scheme 1) in good yield. Complex **6b** is an analogue of **6a**, and the ^{1}H and ^{13}C NMR chemical shifts for the corresponding ring protons and carbon atoms in the fused iridabenzothiazolium ring are very similar. The crystal structure of **6b** has been determined, and the molecular structure is shown in Figure 2. The solution of the structure was complicated because there was disorder involving the solvents of crystallization, one PF_6^- anion, and two of the phenyl rings on the PPh_3 ligands. Details of how each of these disorder problems was resolved are given in the Supporting Information. There was no disorder associated with the iridabenzothiazolium group.

The geometry about iridium is approximately octahedral, with the two PPh_3 ligands mutually trans. The fused five- and six-membered metallacyclic rings form an essentially planar bicyclic ring system (the maximum deviation from the mean plane through Ir, C1−C6, S, and N1 is 0.064(3) Å for N1), with iridium occupying a ring junction position. The Ir−C1 [1.953(5) Å] and Ir−C5 [2.009(5) Å] distances are similar to those found in **3** and the related neutral iridabenzene $Ir[C_5H_4(SMe\text{-}1)]Cl_2(PPh_3)_2$ [Ir−C1, 1.993(4) Å; Ir−C5, 1.992(4) Å].[8] The C−C distances around the iridabenzene ring of **6b** [C1−C2 1.396(7) Å; C2−C3, 1.385(7) Å; C3−C4, 1.402(7) Å; C4−C5, 1.360(7) Å] are all close to normal aromatic bond lengths and show no significant bond-length alternation. Within the iridathiazolium ring, the C1−S and S−C6 distances are 1.754(5) and 1.757(5) Å, respectively. These are similar to the distances recorded for the corresponding bonds in the 2-methylbenzo[*d*]thiazolium cation [1.717(9) and 1.741(9) Å, respectively].[12] The C6−N1 distance within the iridathiazolium ring of **6b** is 1.290(6) Å, which is consistent with a C−N double bond. The corresponding C−N bond distance in the 2-methylbenzo[*d*]thiazolium cation is 1.278(11) Å.[12] One of the PF_6^- anions in **6b** makes a close approach to N1 (see Figure 2). The fluorine atoms of this PF_6^- anion are disordered over two sites and were refined with occupancies of 0.669 (F1−6) and 0.331 (F1a−6a). The F1···N1 distance of 2.969(9) Å is smaller than the sum of the covalent radii of N and F (ca. 3.15 Å)[13] and is close to the upper range of N−H···F hydrogen-bonded distances,[14,15] pointing to the presence of a weak hydrogen bond between these atoms. The F1a···N1 distance, however, is longer at 3.45(2) Å, indicating that there is no significant interaction in this case.

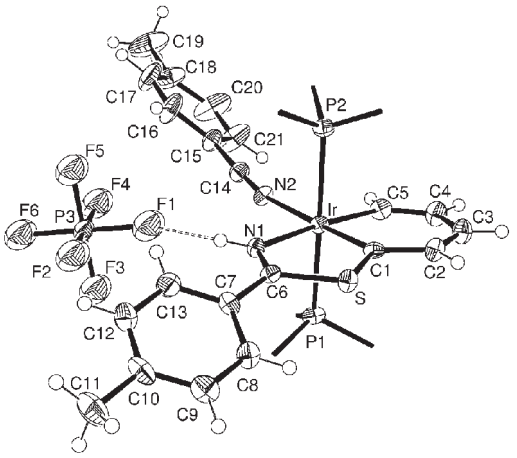

Figure 2. Molecular structure of **6b** with thermal ellipsoids at the 50% probability level. The triphenylphosphine phenyl rings and one hexafluorophosphate counterion have been omitted for clarity. The included PF_6^- anion is disordered over two sites, and only the most popular orientation is depicted.

In order to learn more about the cyclization reactions that produce these iridabenzothiazolium cations, the conversion of **3** to **6a** was followed by ^{1}H NMR spectroscopy. A sample of the cationic iridabenzene **3** was dissolved in CD_2Cl_2 containing 10 equiv of NCMe. Upon the addition of 5 equiv of CF_3SO_3H to this brown solution, the color immediately changed to bright red. On the basis of the ^{1}H and ^{31}P NMR

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spectra of this solution, the red product formed was tentatively formulated as the SH-substituted iridabenzene $[Ir(C_5H_4\{SH\text{-}1\})(MeCN)_2(PPh_3)_2][CF_3SO_3]_2$ (**5**) (see Scheme 1). The ^1H NMR spectrum revealed new signals at 11.50 (1H, H5), 7.23 (1H, S*H*), 7.04 (1H, H4), 6.90 (1H, H3), 6.89 (1H, H2), 2.03 (3H, NCCH_3), and 2.02 (3H, NCCH_3) ppm. In the ^{31}P NMR spectrum, a singlet at −0.83 ppm was observed for the two PPh_3 ligands. These signals are remarkably similar to those observed for the red SCH_3-substituted iridabenzene **4** described above, with the exception that the SCH_3 signal in **4** was replaced by a new signal at 7.23 ppm (SH) and the resonance for H2, which is vicinal to SH, shows a slight downfield shift. If protected from the atmosphere, solutions of **5** formed in this way are stable for days. The addition of ethanol (ca. 15 equiv) to a red CD_2Cl_2 solution of **5** caused the color to turn deep green rapidly, and signals identical with those observed for **6a** were observed in the ^1H and ^{31}P NMR spectra. This transformation to **6a** was also brought about by the addition of water (ca. 15 equiv) to the acidic CD_2Cl_2 solution. These results confirm that NH_4PF_6, which is added in the synthesis of **6a** and **6b** to facilitate the isolation of crystalline products, does not play a role in the formation of the iridabenzothiazolium cations. We do not have any evidence concerning the mechanism for the conversion of **5** into **6a**. However, one possibility is that the addition of the proton acceptors ethanol or water to the solution containing **5** facilitates partial deprotonation of the SH group. The deprotonated sulfur atom then attacks the adjacent coordinated nitrile carbon atom, and the nitrogen atom is protonated to form **6a**. Ample precedents for reactions of this type are provided by the numerous addition reactions that have been reported for metal-activated organonitriles with water, alcohols, amines, and related compounds.[16] It has also been reported recently that acetonitrile can undergo a formal [2 + 4] cycloaddition reaction with an osmium hydride, vinylcarbyne complex to give an osmapyridinium derivative.[17] Deprotonation of the nitrogen in this metallacycle with *n*-butyllithium gives the corresponding osmapyridine without promoting any reversal of the cycloaddition. Metal-coordinated organonitriles have also been reported to undergo [2 + 3] cycloaddition reactions with azides or nitrones to form tetrazoles or oxadiazolines, respectively.[16] The overall transformation of **3** into **6a**, which can be described as a metal-mediated formal [2 + 3] cycloaddition between acetonitrile and the η^2-C(S)Ir group, is most closely related to these latter reactions.

The iridabenzothiazolium complexes **6a** and **6b** are stable for days in solutions that contain traces of acid, even upon exposure to the atmosphere. However, in the absence of acid, the stability of these compounds in solution is much reduced. Upon the addition of bases such as NEt_3 or NaO_2CCH_3 to solutions of **6a** (or **6b** in the presence of acetonitrile), the iridathiazolium nitrogen atom is rapidly deprotonated and the iridabenzene **3** is reformed almost quantitatively. The cycloaddition reactions that form **6a** and **6b** are therefore reversible, unlike the situation with the osmapyridinium complex described above.

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Concluding Remarks

In conclusion, the cationic iridabenzene **3** can be formed in high yield through a one-pot reaction sequence starting from $IrCl(CS)(PPh_3)_2$. The nucleophilic sulfur atom in **3** is rapidly alkylated by methyl triflate, leading to the iridabenzene **4**. However, upon treatment of **3** with acetonitrile, triflic acid, and ethanol, the iridabenzothiazolium complex **6a** is formed in high yield. The analogue **6b** is obtained if the acetonitrile in this reaction is replaced by *p*-tolunitrile. The reactions that form these new fused heterocyclic ring iridabenzenes involve formal [2 + 3] cycloaddition reactions between the organonitrile and the η^2-C(S)Ir group of **3**. This cycloaddition reaction is reversible, and upon treatment of **6a** or **6b** with base in the presence of acetonitrile, the iridathiazolium nitrogen is deprotonated and **3** is returned quantitatively.

Experimental Section

General Comments. Standard laboratory procedures were followed, as have been described previously.[18] In addition, acetonitrile was distilled from calcium hydride before use. $IrCl(CS)(PPh_3)_2$ was prepared by the literature method.[19]

IR spectra (4000−400 cm^{-1}) of solid samples were recorded on a Perkin-Elmer Spectrum 400 spectrometer using an ATR accessory. NMR spectra were obtained on a Bruker Avance 300 at 25 °C. ^1H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were obtained by operating at 300.13 (^1H NMR), 75.48 (^{13}C NMR), 121.50 (^{31}P NMR), and 282.4 (^{19}F NMR) MHz, respectively. Resonances are quoted in ppm and ^1H NMR spectra referenced to either tetramethylsilane (0.00 ppm) or the proteoimpurity in the solvent (7.25 ppm for $CHCl_3$). ^{13}C NMR spectra were referenced to $CDCl_3$ (77.00 ppm), ^{31}P NMR spectra to 85% orthophosphoric acid (0.00 ppm) as an external standard, and ^{19}F NMR spectra to $CFCl_3$ (0.00 ppm) as an external standard. Mass spectra were recorded using the fast atom bombardment technique with a Varian VG 70-SE mass spectrometer. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

$[Ir(MeCN)(CS)(PPh_3)_2][CF_3SO_3]$ (1). An improved procedure for the synthesis of **1**[8] is as follows. With rigorous exclusion of moisture, $IrCl(CS)(PPh_3)_2$ (1.500 g, 1.88 mmol) and $AgCF_3SO_3$ (0.489 g, 1.90 mmol, 1.01 equiv) were added to a flask followed by acetonitrile (75 mL). A precipitate of silver chloride formed immediately, and the solution turned bright orange. The mixture was stirred for 20 min, then the acetonitrile removed *in vacuo*, and the orange solid dried under vacuum for a further 1 h. The residue was extracted with dichloromethane (70 mL) and filtered through a Celite pad to remove AgCl. Pure **1** was crystallized as a bright-orange crystalline solid by the slow addition of *n*-hexane (yield = 1.362 g, 76%). Anal. Calcd for $C_{40}H_{33}F_3IrNO_3P_2S_2$: C, 50.52; H, 3.50; N, 1.47. Found: C, 50.38; H, 3.43; N, 1.46. The spectral data were identical with those previously reported.[8]

$[Ir(C_4H_4)(CS)(MeCN)(PPh_3)_2][CF_3SO_3]$ (2). Ethyne was slowly bubbled at atmospheric pressure through a dichloromethane solution (70 mL) containing **1** (1.79 g, 1.88 mmol) for 1 h at 10 °C, turning the solution yellow. Pure **2** was crystallized as a yellow solid by the slow addition of *n*-hexane at low temperature to prevent isomerization to the iridabenzene **3** (see below) (yield = 1.36 g, 72%). Anal. Calcd for $C_{44}H_{37}NO_3F_3IrP_2S_2 \cdot H_2O$: C, 51.76; H, 3.85; N, 1.37. Found: C, 51.97; H, 4.01; N, 1.33 (NMR spectroscopy showed the presence of ca. 1 mol equiv of water in the analytical sample). MS (FAB^+,

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NBA). Calcd for $C_{43}H_{37}{}^{193}IrNP_2S$ [M − $(CF_3SO_3^-)$]$^+$: *m*/*z* 854.17514. Found: *m*/*z* 854.17604. IR (cm^{-1}): 2291 *ν*(CN); 1305 *ν*(CS); 1264, 1141, 1028, 636 ($CF_3SO_3^-$). ^{1}H NMR ($CDCl_3$, *δ*): 7.13−7.75, m, 30H (P*Ph*$_3$), 7.20 (partially obscured by phenyl, d(from DQF-COSY), H1 or H4), 6.53 (d, $^3J_{HH}$ = 6.0 Hz, 1H, H1 or H4), 5.84 (m, 2H, H2 and H3), 1.94 (s, 3H, C*H*$_3$CN). ^{13}C NMR ($CDCl_3$, *δ*): 279.1 (t, $^2J_{CP}$ = 8.3 Hz, *C*S), 152.6 (t, $^2J_{CP}$ = 10.6 Hz, C1 or C4), 144.5 (t, $^3J_{CP}$ = 3.0 Hz, C2 or C3), 142.4 (s, C2 or C3), 136.0 (t, $^2J_{CP}$ = 6.8 Hz, C1 or C4), 134.7 (t′, ^{18} $^{3,5}J_{CP}$ = 10.6 Hz, *m*-PPh$_3$), 131.4 (s, *p*-PPh$_3$), 128.0 (t′, $^{2,4}J_{CP}$ = 10.6 Hz, *o*-PPh$_3$), 126.8 (t′, $^{1,3}J_{CP}$ = 58.9 Hz, *i*-PPh$_3$), 123.9 (s, CH$_3$*C*N), 2.9 (s, *C*H$_3$CN). ^{31}P NMR ($CDCl_3$, *δ*): 5.80. ^{19}F NMR ($CDCl_3$, *δ*): −78.99.

[Ir(C$_5$H$_4${S-1})(MeCN)(PPh$_3$)$_2$][CF$_3$SO$_3$] (3). 2 (1.89 g, 1.88 mmol) was dissolved in dichloromethane (70 mL) and the solution heated under reflux for 15 h, over which time the solution turned brown. The solution was cooled to room temperature and *n*-hexane slowly added to afford brown crystals of pure **3** (1.72 g, 91%). Anal. Calcd for $C_{44}H_{37}F_3IrNO_3P_2S_2$: C, 52.69; H, 3.72; N, 1.40. Found: C, 52.66; H, 3.86; N, 1.38. The crystal used for X-ray structure determination was grown from dichloromethane/*n*-hexane and contained one molecule of dichloromethane per molecule of complex. MS (FAB$^+$, NBA). Calcd for $C_{41}H_{34}{}^{193}IrNP_2S^+$ [M − $(CF_3SO_3^-)$ − MeCN]$^+$: *m*/*z* 813.14859. Found: *m*/*z* 813.14834. IR (cm^{-1}): 1261, 1150, 1030, 637 ($CF_3SO_3^-$). ^{1}H NMR ($CDCl_3$, *δ*): 12.47 (d, $^3J_{HH}$ = 6.3 Hz, 1H, H5), 7.27−7.50 (m, 30H, P*Ph*$_3$), 7.50 (partially obscured by phenyl, m, 1H, H3), 6.81 (apparent t, 7.8 Hz, 1H, H4), 6.24 (d, $^3J_{HH}$ = 9.0 Hz, 1H, H2), 1.83 (s, 3H, C*H*$_3$CN). ^{13}C NMR ($CDCl_3$, *δ*): 243.9 (t, $^2J_{CP}$ = 5.3 Hz, C1), 176.9 (t, $^2J_{CP}$ = 8.3 Hz, C5), 153.9 (s, C3), 134.2 (t′, $^{3,5}J_{CP}$ = 10.6 Hz, *m*-PPh$_3$), 131.5 (s, *p*-PPh$_3$), 128.5 (t′, $^{2,4}J_{CP}$ = 10.6 Hz, *o*-PPh$_3$), 126.8 (t′, $^{1,3}J_{CP}$ = 56.6 Hz, *i*-PPh$_3$), 127.5 (s, CH$_3$*C*N), 127.4 (t, $^3J_{CP}$ = 1.9 Hz, *C*H$_3$CN), 117.6 (s, C2) 2.4 (s, C7). ^{31}P NMR ($CDCl_3$, *δ*): 5.77. ^{19}F NMR ($CDCl_3$, *δ*): −79.03.

One-Pot Synthesis of 3 Starting from IrCl(CS)(PPh$_3$)$_2$. The procedures for synthesizing **1** and **2** detailed above were followed except that solid products were not isolated. Instead, the dichloromethane solutions of **1** and **2** obtained were used directly in the subsequent reactions. Compound **3** was prepared from the dichloromethane solution of **2** and isolated as indicated above in an overall yield of 91% based on IrCl(CS)(PPh$_3$)$_2$.

[Ir(C$_5$H$_4${SMe-1})(MeCN)$_2$(PPh$_3$)$_2$][PF$_6$]$_2$ (4). 3 (100 mg, 0.100 mmol) was dissolved in dichloromethane (5 mL), and acetonitrile (52 *μ*L, 1.0 mmol) and then methyl triflate (23 *μ*L, 0.20 mmol) were added. The solution instantly turned red upon the addition of methyl triflate. After 15 min, ammonium hexafluorophosphate (81 mg, 0.50 mmol) dissolved in ethanol (5 mL) was added to the stirred solution and dichloromethane removed under reduced pressure. Maroon crystals of pure **4** were collected by filtration and washed with ethanol (2 × 3 mL, 103 mg, 86%). Anal. Calcd for $C_{46}H_{43}F_{12}IrN_2P_4S$: C, 46.04; H, 3.61; N, 2.33. Found: C, 45.74; H, 3.48; N, 2.33. MS (FAB$^+$, NBA). Calcd for $C_{46}H_{43}{}^{193}IrN_2PSF_6$ [M − (PF_6^-)]$^+$: *m*/*z* 1055.189 35. Found: *m*/*z* 1055.186 92. IR (cm^{-1}): 2320, 2295 *ν*(CN); 824 *ν*(PF). ^{1}H NMR (CD_2Cl_2, *δ*): 11.59 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H5), 7.53−7.34 (m, 30H, P*Ph*$_3$), 7.03 (apparent t, 7.5 Hz, 1H, H4), 6.90 (apparent t, 7.2 Hz, 1H, H3), 6.29 (d, $^3J_{HH}$ = 9.3 Hz, 1H, H2), 2.52 (s, 3H, SC*H*$_3$), 2.17 (s, 3H, C*H*$_3$CN), 1.99, (s, 3H, C*H*$_3$CN). ^{13}C NMR (CD_2Cl_2, *δ*): 224.4, (t, $^2J_{CP}$ = 4.5 Hz, C1), 180.9 (t, $^2J_{CP}$ = 7.5 Hz, C5), 155.4 (s, C3), 134.5 (t′, $^{3,5}J_{CP}$ = 10.6 Hz, *m*-PPh$_3$), 132.6 (s, *p*-PPh$_3$), 129.2 (t′, $^{2,4}J_{CP}$ = 12.0 Hz, *o*-PPh$_3$), 127.5 (s, C4), 127.4 (s, CH$_3$*C*N), 126.5 (s, CH$_3$*C*N), 125.3 (t′, $^{1,3}J_{CP}$ = 58.1 Hz, *i*-PPh$_3$), 123.6 (s, C2), 22.6 (s, S*C*H$_3$), 3.6 (s, *C*H$_3$CN), 3.3 (s, *C*H$_3$CN). ^{31}P NMR (CD_2Cl_2, *δ*): −2.45 (s, *P*Ph$_3$), −144.28 (sep, $^1J_{PF}$ = 711 Hz, *P*F$_6$). ^{19}F NMR (CD_2Cl_2, *δ*): −73.5 (d, $^1J_{FP}$ = 709 Hz, P*F*$_6$).

[Ir(C$_5$H$_4${NH=C(Me)S-1})(MeCN)(PPh$_3$)$_2$][PF$_6$]$_2$ (6a). 3 (100 mg, 0.100 mmol) was dissolved in dichloromethane (5 mL), and acetonitrile (52 *μ*L, 1.0 mmol) and then triflic acid (18 *μ*L, 0.20 mmol) were added. The solution instantly turned red upon the addition of the acid. After 15 min, ammonium hexafluorophosphate (96 mg, 0.59 mmol) dissolved in ethanol (5 mL) was added to the stirred solution. The solution turned green, and a green precipitate was formed. Further precipitation was effected by the removal of dichloromethane under reduced pressure, and dark-green crystals of pure **6a** were collected by filtration and washed with ethanol (2 × 3 mL, 100 mg, 81%). Anal. Calcd for $C_{45}H_{41}F_{12}IrN_2P_4S$: C, 45.57; H, 3.48; N, 2.36. Found: C, 45.55; H, 3.68; N, 2.38. MS (FAB$^+$, NBA). Calcd for $C_{45}H_{41}{}^{193}IrN_2P_3SF_6$ [M − (PF_6^-)]$^+$: *m*/*z* 1041.173 70. Found: *m*/*z* 1041.174 58. IR (cm^{-1}): 3289 *ν*(NH); 2325, 2295 *ν*(CN); 824 *ν*(PF). ^{1}H NMR (CD_2Cl_2, *δ*): 12.35 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H5), 10.23 (br s, 1H, N*H*), 7.36−7.58 (m, 30H, P*Ph*$_3$), 6.86 (d, $^3J_{HH}$ = 8.7 Hz, 1H, H2), 6.75 (apparent t, 8.1 Hz, 1H, H4), 6.55 (apparent t, 7.8 Hz, 1H, H3), 1.92 (s, 3H, C*H*$_3$CN), 1.87 (s, 3H, C*H*$_3$C(N)S). ^{13}C NMR (CD_2Cl_2, *δ*): 232.3 (s, C1), 210.9 (s, C5), 190.0 (s, C6), 170.2 (s, C3), 134.6 (t′, $^{3,5}J_{CP}$ = 9.0 Hz, *m*-PPh$_3$), 133.1 (s, *p*-PPh$_3$), 129.4 (t′, $^{2,4}J_{CP}$ = 10.6 Hz, *o*-PPh$_3$), 128.3 (s, CH$_3$*C*N), 127.2 (s, C4), 125.5 (s, C2), 123.5 (t′, $^{1,3}J_{CP}$ = 58.9 Hz, *i*-PPh$_3$), 21.9 (s, *C*H$_3$C(N)S), 3.0 (s, *C*H$_3$CN). ^{31}P NMR (CD_2Cl_2, *δ*): 12.18 (s, *P*Ph$_3$), −144.18 (sep, $^1J_{PF}$ = 711 Hz, *P*F$_6$). ^{19}F NMR (CD_2Cl_2, *δ*): −73.2 (d, $^1J_{FP}$ = 709 Hz, P*F*$_6$).

[Ir(C$_5$H$_4${NH=C(*p*-tolyl)S-1})(*p*-tolyl-CN)(PPh$_3$)$_2$][PF$_6$]$_2$ (6b). 6b was prepared by the same procedure as that used for **6a**, except that the acetonitrile was replaced by *p*-tolunitrile (117 mg, 1.00 mmol; yield = 107 mg, 80%). Anal. Calcd for $C_{57}H_{49}F_{12}IrN_2P_4S$·EtOH: C, 45.57; H, 3.48; N, 2.36. Found: C, 45.55; H, 3.68; N, 2.38 (NMR spectroscopy showed the presence of 1 mol equiv of EtOH of crystallization). The crystal for X-ray structural analysis was grown from dichloromethane/*n*-hexane and proven to be a dichloromethane solvate. IR (cm^{-1}): 3291 *ν*(NH); 2258 *ν*(CN); 824 *ν*(PF). ^{1}H NMR (CD_2Cl_2, *δ*): 12.87 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H5), 10.36 (br s, 1H, N*H*), 7.55−7.26 (m, 38H, P*Ph*$_3$ and tolyl C*H*), 7.22 (apparent t (partially obscured), H4), 6.91 (d, $^3J_{HH}$ = 8.7 Hz, 1H, H2), 6.65 (apparent t, 7.8 Hz, 1H, H3), 2.49 (s, 3H, tolyl C*H*$_3$), 2.44 (s, 3H, tolyl C*H*$_3$). ^{13}C NMR (CD_2Cl_2, *δ*): 229.8 (s, C1), 209.7 (s, C5), 185.6 (s, C6), 168.8 (s, C3), 147.0 (s, tolyl *C*CH$_3$), 146.5 (s, tolyl *C*CH$_3$), 134.1 (t′, $^{3,5}J_{CP}$ = 10.6 Hz, *m*-PPh$_3$), 133.9 (s, tolyl *C*H), 132.4 (s, *p*-PPh$_3$), 129.60 (s, tolyl *C*H), 129.58 (s, tolyl *C*H), 129.2 (t′, $^{2,4}J_{CP}$ = 11.3 Hz, *o*-PPh$_3$), 128.1 (s, tolyl *C*-C6 or tolyl *C*-CN), 128.0 (s, tolyl *C*H), 127.4 (s, C4), 126.6 (s, tolyl *C*-C6 or tolyl *C*-CN), 125.4 (s, C2), 123.0 (t′, $^{1,3}J_{CP}$ = 58.9 Hz, *i*-PPh$_3$), 104.5 (s, tolyl *C*N), 22.1 (s, tolyl *C*H$_3$), 21.7 (s, tolyl *C*H$_3$). ^{31}P NMR (CD_2Cl_2, *δ*): 11.68 (s, *P*Ph$_3$), −143.96 (sep, $^1J_{PF}$ = 713 Hz, *P*F$_6$). ^{19}F NMR (CD_2Cl_2, *δ*): −73.1 (d, $^1J_{FP}$ = 712 Hz, P*F*$_6$).

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Supporting Information Available: Crystal and refinement data as well as crystal data in CIF format for complexes **3** and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org. The atom coordinates can also be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax +44-1223-336-033; e-mail deposit@ccdc.cam.ac.uk, or http://www.ccdc.cam.ac.uk) as supplementary publication nos. CCDC 739119 and 739118, respectively.