

# Rhodium and Iridium Complexes Derived from *trans*-[MCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (M = Rh, Ir) and Pyridine-2-thiolate or 4,6-Dimethylpyrimidine-2-thiolate Ligands: *S*-Monodentate Coordination versus *S,N*-Chelation and *S,N*-Bridging; Reactivity of *trans*-[Ir('Spy')(CO)(PPh<sub>3</sub>)<sub>2</sub>] and *trans*-[Ir('SpymMe<sub>2</sub>')(CO)(PPh<sub>3</sub>)<sub>2</sub>] towards Acid

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Treatment of *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] with the sodium salts of the *S,N*-hybrid ligands, pyridine-2-thiol ('pySH') and 4,6-dimethylpyrimidine-2-thiol ('Me<sub>2</sub>pymSH'), produced *trans*-[Ir('Spy')(CO)(PPh<sub>3</sub>)<sub>2</sub>] (**1**) and *trans*-[Ir('SpymMe<sub>2</sub>')(CO)(PPh<sub>3</sub>)<sub>2</sub>] (**2**), containing *S*-monodentate thiolato ligands. In contrast, the reactions between *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] and the two bifunctional thiolate ligands yielded the PPh<sub>3</sub>-loss products [Rh(μ-'Spy'-κN,κS)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (**3**) and [Rh('SpymMe<sub>2</sub>'-κN,κS)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (**4**), whose structures in the solid state were determined by single-crystal X-ray diffraction. In binuclear complex **3**, the bridging pyridine-2-thiolate ligands are bound to the adjacent metal centers through their N and S atoms in a head-to-tail manner. The crystal structure of **4** consists of mononuclear molecules possessing four-membered Rh–S–C–N chelate rings with the sulfur atom *trans* to the CO ligand. In solution, both **3** and **4** display temperature-dependent dynamic behavior. Reaction of **2** with trifluoroacetic acid resulted in protonation of the iridium atom and

ring closure to form the monocationic chelate complex [IrH('SpymMe<sub>2</sub>'-κN,κS)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, which was isolated and characterized by X-ray crystallography as the hydrogen bis(trifluoroacetate) salt [IrH('SpymMe<sub>2</sub>'-κN,κS)(CO)(PPh<sub>3</sub>)<sub>2</sub>][H(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>] (**5a**). Protonation of both the iridium and one pyrimidine nitrogen atom was observed in the analogous reaction of **2** with HBF<sub>4</sub>, which afforded the 4,6-dimethylpyrimidinium-2-thiolato chelate complex [IrH(2-SC<sub>4</sub>HNN(H)Me<sub>2</sub>-4,6-κN,κS)(CO)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> as a mixture of two isomers, having the hydride ligand either *trans* to S (**5c**) or *trans* to N (**5d**). The complex [IrH('Spy')<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] (**6**) resulted from oxidative addition of pyridine-2-thiol to **1** or reaction of *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] with an excess of the 'pySH' ligand. Complex **6** reacted with HBF<sub>4</sub> in CHCl<sub>3</sub> with cleavage of one Ir–S bond and protonation at the metal center to produce the ionic chelate complex [IrH('Spy'-κN,κS)(CO)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>) (**7**) which was also fully characterized by X-ray analysis.

## Introduction

Our recent interest has focused on the chelation of bidentate *P,N* and *P,O* ligands, in particular with respect to the reactivity of their transition metal complexes towards Brønsted acids.<sup>[1,2,3]</sup> In this context, two ring-opened iridium(III) compounds, [IrHCl<sub>2</sub>(CO)(PPh<sub>3</sub>)(PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>N(Me)H-2)]<sup>[2]</sup> and [IrHCl<sub>2</sub>(CO)(PPh<sub>3</sub>)(PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OH-2)]<sup>[3]</sup> resulting from reaction of their parent iridium(I) chelate complexes *trans*-[Ir(CO)(PPh<sub>3</sub>)(PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>E-2)] (E = NMe, O) with hydrogen chloride, have been shown to exist as mixtures of Ir–PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>EH-2 rotamers which are stabilized by intramolecular –N(Me)H⋯Cl(Ir) and –OH⋯H(Ir)⋯Cl hydrogen bonding. Following these studies, we have turned our attention to iridium and rhodium complexes derived from the requisite Vaska-type precursors *trans*-[MCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] and bifunctional ligands having soft *S*

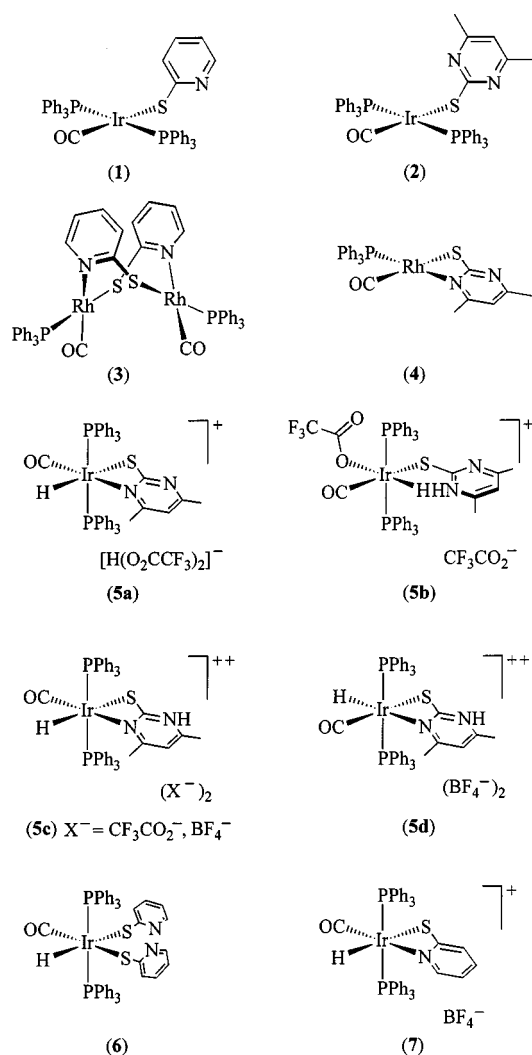
and hard *N* ends, such as pyridine-2-thiol, NC<sub>5</sub>H<sub>4</sub>SH-2 ('pySH'), and 4,6-dimethylpyrimidine-2-thiol, 4,6-Me<sub>2</sub>C<sub>4</sub>HN<sub>2</sub>-SH-2 ('Me<sub>2</sub>pymSH'), respectively.

Both the ligands and their conjugate bases are ubiquitous *S,N* donors that form a wide variety of complexes with p-, d-, and also f-block metals.<sup>[4–8]</sup> The published work concerning the chemistry of relevant coordination compounds of the platinum group metals rhodium and iridium in their lower oxidation states is dominated by di- and trinuclear complexes with *S,N*-bridging thiolates, derived from bimetallic olefin and carbonyl precursors, such as [M<sub>2</sub>(μ-Cl)<sub>2</sub>(di-olefin)<sub>2</sub>] (M = Rh,<sup>[9a–9c,10a]</sup> Ir<sup>[9d,10a]</sup>) or [Rh<sub>2</sub>(μ-Cl)<sub>2</sub>(CO)<sub>4</sub>].<sup>[11]</sup>

The compounds reported in this paper (Scheme 1) were synthesized with the principal objectives of (i) investigating the coordination properties of the two *S,N* donors in Vaska-type environments and (ii) elucidating the reactivity of the resulting complexes towards Brønsted acids. Because of the basicity of the pyridine and pyrimidine heterocycles, and owing to the pronounced basic character of the metal ion in coordinatively unsaturated d<sup>8</sup> complexes, protonation of four-coordinate Rh<sup>I</sup> and, specifically, Ir<sup>I</sup> compounds [MX(CO)L<sub>2</sub>] bearing *S*-monodentate 'Spy' or 'SpymMe<sub>2</sub>' ligands by strong acids was expected to occur both at the

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metal center and the nitrogen atom. The resulting products could exhibit intramolecular N–H···H–M hydrogen bonding, as it has been previously demonstrated that pyridine-2-thiol, if coordinated as a monodentate  $\text{HN}^+\text{C}_5\text{H}_4\text{S}^-$  zwitterion, has a distinct propensity to behave as a weakly acidic N–H donor toward weakly basic  $\text{Ir}^{\text{III}}\text{--H}$  acceptor functions.<sup>[12]</sup> In this connection, the behavior towards protic acids of two related  $\text{Rh}^{\text{I}}$  and  $\text{Ir}^{\text{I}}$  complexes  $[\text{M}(\text{S}_2\text{NC}_7\text{H}_4)(\text{CO})(\text{PPh}_3)]$  with *S*-monodentate benzothiazole-2-thiolate ligands is worth mentioning: Protonation of the rhodium derivative with  $\text{HBF}_4$  takes place at the noncoordinated nitrogen atom giving  $[\text{Rh}(\text{S}_2\text{N}(\text{H})\text{C}_7\text{H}_4)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ ,<sup>[9e,9f]</sup> in contrast to the iridium homologue where protonation occurs at the metal center with production of the hydrido-iridium(III) complex  $[\text{IrH}(\text{S}_2\text{NC}_7\text{H}_4)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ .<sup>[9f]</sup>



Scheme 1

## Results and Discussion

### Syntheses and Solid-State Structures of $\text{Rh}^{\text{I}}$ and $\text{Ir}^{\text{I}}$ Thiolates

The *S*-monodentate pyridine-2- and 4,6-dimethylpyridine-2-thiolato derivatives  $\text{trans}[\text{Ir}(\text{'Spy})(\text{CO})(\text{PPh}_3)_2]$

(1) and  $\text{trans}[\text{Ir}(\text{'SpmMe}_2)(\text{CO})(\text{PPh}_3)_2]$  (2) were formed smoothly by combining the sodium salts of the respective thiols and Vaska's complex,  $\text{trans}[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ , in a 1:1 stoichiometry in THF at room temperature. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the two compounds consist of singlets ( $\delta = 23.1$  for 1 and 19.4 for 2), indicating the expected pairs of equivalent phosphane ligands (Scheme 1).

Under the conditions chosen for the preparation of 1, the rhodium(I) complex  $\text{trans}[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$  and sodium pyridine-2-thiolate underwent  $\text{Cl}^-/\text{'pyS}^-$  exchange accompanied by elimination of a phosphane ligand to give the binuclear  $\text{PPh}_3$ -loss product  $[\{\text{Rh}(\mu\text{'Spy})(\text{CO})(\text{PPh}_3)\}_2]$  (3). Prior to this work, a highly fluxional complex of identical composition was reported to result from solution equilibration of  $[\text{Rh}_2(\mu\text{'Spy})_2(\text{CO})_3(\text{PPh}_3)]$ , affording  $[\{\text{Rh}(\mu\text{'Spy})(\text{CO})_2\}_2]$  together with  $[\{\text{Rh}(\mu\text{'Spy})(\text{CO})(\text{PPh}_3)\}_2]$ .<sup>[9b]</sup> From the  $^{31}\text{P}\{^1\text{H}\}$  NMR data observed at the slow exchange limit, an unspecified ground-state structure with equivalent  $\text{PPh}_3$  ligands *trans* to the sulfur atoms was tentatively inferred for this dirhodium compound.<sup>[9b]</sup> Complex 3 is also fluxional in solution (see below) and adopts a solid-state structure consisting of bimetallic molecules in which both pyridine-2-thiolate ligands bridge two *cis* coordination sites of the metal centers through their S and N atoms, the pairs of Rh–N and Rh–S bonds being *trans* to the CO and  $\text{PPh}_3$  ligands, respectively (Figure 1). The coordination planes of the two metal centers are inclined to each other at an angle of  $34.9^\circ$ . In addition, the donor atoms coordinated to Rh(1) and Rh(2) are staggered, the torsion angles being  $-46.4$  and  $-51.3^\circ$  for the N(1)–Rh(1)···Rh(2)–N(2) and C(1)–Rh(1)···Rh(2)–C(2) fragments, and  $134.7$  and  $137.7^\circ$  for S(1)–Rh(1)···Rh(2)–S(2) and P(1)–Rh(1)···Rh(2)–P(2), respectively. The molecular structure of 3 thus closely resembles those of the related tetracarbonyl and thiazoline-2-thiolato-bridged species  $[\{\text{Rh}(\mu\text{'Spy}-\kappa\text{N},\kappa\text{S})(\text{CO})_2\}_2]$ <sup>[9b]</sup> and  $[\{\text{Rh}(\mu\text{-S}_2\text{NC}_3\text{H}_4-\kappa\text{N},\kappa\text{S})(\text{L})(\text{L}')\}_2]$  (L, L' = COD;<sup>[10a]</sup> CO,  $\text{PMe}_3$ ;<sup>[10b]</sup> CO,  $\text{PPh}_3$ <sup>[10b]</sup>), similarly containing twisted nonparallel metal coordination planes, linked in a head-to-tail fashion by the nitrogen and mercapto sulfur atoms of two *N*-heterocyclic thiolate bridges. The Rh(1)···Rh(2) separation,  $3.1952(5)$  Å, is shorter than that of  $3.2435(3)$  Å in  $[\{\text{Rh}(\mu\text{-S}_2\text{NC}_3\text{H}_4-\kappa\text{N},\kappa\text{S})(\text{CO})(\text{PPh}_3)\}_2]$ <sup>[10b]</sup> and presumably reflects the observation that the tilt of the coordination planes in 3,  $34.9^\circ$ , is somewhat closer to parallel than the  $38.5^\circ$  observed in the latter compound. All metal-to-ligand bond lengths (Figure 1) are as expected as compared to those of structurally analogous dirhodium derivatives.<sup>[9b,10a,10b]</sup>

Surprisingly, treatment of  $\text{trans}[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$  with 4,6-dimethylpyrimidine-2-thiolate did not afford any *S,N*-linked or *S*-bridged binuclear product, but resulted in formation of the unusual four-membered Rh–S–C–N metallaheterocycle  $[\text{Rh}(\text{'SpmMe}_2-\kappa\text{N},\kappa\text{S})(\text{CO})(\text{PPh}_3)]$  (4). The X-ray structure analysis of this complex showed the presence of molecules with a slightly distorted planar coordination geometry (Figure 2), as evidenced (i) from the sum

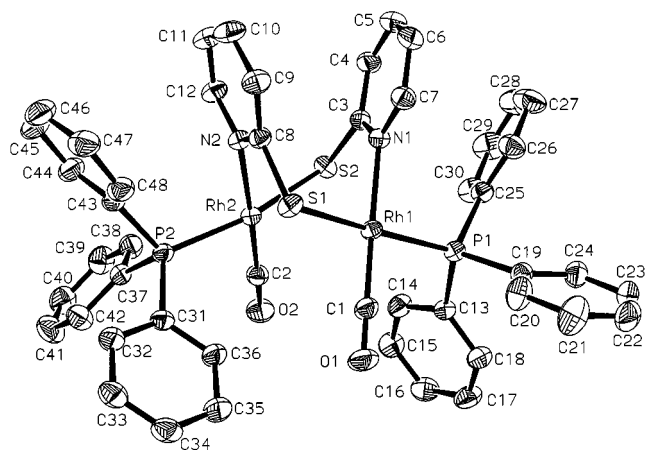
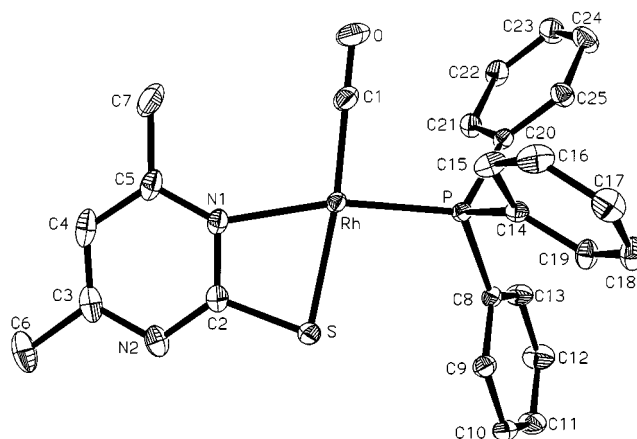


Figure 1. Molecular structure of  $[\{\text{Rh}(\mu\text{-}'\text{Spy}\text{-}\kappa\text{N},\kappa\text{S})(\text{CO})(\text{PPh}_3)_2\}_2]$  (**3**); selected interatomic distances [Å] and angles [°]: Rh(1)---Rh(2) 3.1952(5), Rh(1)–S(1) 2.3929(8), Rh(1)–P(1) 2.2871(7), Rh(1)–N(1) 2.122(2), Rh(1)–C(1) 1.807(3), Rh(2)–S(2) 2.4053(7), Rh(2)–P(2) 2.2768(7), Rh(2)–N(2) 2.118(2), Rh(2)–C(2) 1.828(3), S(1)–C(8) 1.749(3), S(2)–C(3) 1.749(3), N(1)–C(3) 1.353(3), N(2)–C(8) 1.359(3), S(1)–Rh(1)–P(1) 169.98(3), S(1)–Rh(1)–N(1) 88.35(6), S(1)–Rh(1)–C(1) 90.22(9), P(1)–Rh(1)–N(1) 92.53(6), P(1)–Rh(1)–C(1) 88.40(9), S(2)–Rh(2)–P(2) 165.96(3), S(2)–Rh(2)–N(2) 87.93(6), S(2)–Rh(2)–C(2) 91.01(9), P(2)–Rh(2)–N(2) 91.36(6), P(2)–Rh(2)–C(2) 88.58(9), Rh(1)–S(1)–C(8) 105.62(9), Rh(2)–N(2)–C(8) 119.6(2), S(1)–C(8)–N(2) 117.6(2), Rh(2)–S(2)–C(3) 107.90(9), Rh(1)–N(1)–C(3) 120.0(2), S(2)–C(3)–N(1) 119.6(2).

of the of the four interligand *cis* angles, 354.08°, and (ii) from the angles between the normals to the planes defined by the P–Rh–C(1) and N(1)–Rh–S, or the C(1)–Rh–N(1) and P–Rh–S fragments, which are 3.94° and 4.06°, respectively. The four-membered chelate ring exhibits a bend along the N(1)⋯S vector of 4.31°, i.e., it adopts a very flat folded conformation. Considerable ring strain is evident from the small chelate bite angle of only 69.03(7)°. The metal-to-nitrogen bond in **4**, 2.128(2) Å, is somewhat longer than the two Rh–N distances observed for **3**, 2.118(2) and 2.122(2) Å, in spite of being *trans* to the PPh<sub>3</sub> ligand which has a weaker *trans* influence than the carbonyl ligand *trans* to the nitrogen atoms in **3**. By contrast, the length of the Rh–S bond opposite to the CO ligand with its strong *trans* influence in **4**, 2.371(1) Å, is slightly shorter than the Rh–S distances in **3**, 2.3929(8) and 2.4053(7) Å, where the mercapto groups are coordinated *trans* to the PPh<sub>3</sub> ligand. The small N(1)–Rh–S bite angle (see above) and the acute valence angle at the sulfur atom in **4**, 80.89(9)°, emphasize the strain within the small chelate ring, since an increase of the Rh–S bond length, accompanied by a shortening of the Rh–N linkage, would result in further unfavorable compression of the Rh–S–C angle.

### Structures of Rhodium Complexes **3** and **4** in Solution

The structures adopted by two rhodium(I) thiolates in solution diverge considerably from those in the solid state, scrambling of the phosphane ligands and rearrangement processes arising from facile interconversion of the coordination modes of the two *S,N*-bonded thiolates being common phenomena.



the possibility that both mechanisms are operative. Note, however, that the exchange of  $\text{PPh}_3$  ligands observed at higher temperatures, i.e., the intermediacy of the formally three-coordinate  $\{\text{Rh}(\text{'SpymMe}_2\text{'-}\kappa\text{N},\kappa\text{S})(\text{CO})\}$ , is more readily reconciled with the interconversion of species having either the sulfur or the nitrogen atom *trans* to the phosphorus atom than with ligand scrambling according to Equation (1), for which loss of chelation with intermediate formation of *S*-monodentate  $\{\text{Rh}(\text{'SpymMe}_2\text{'-}\kappa\text{S})(\text{CO})(\text{PPh}_3)\}$  is the sole prerequisite.

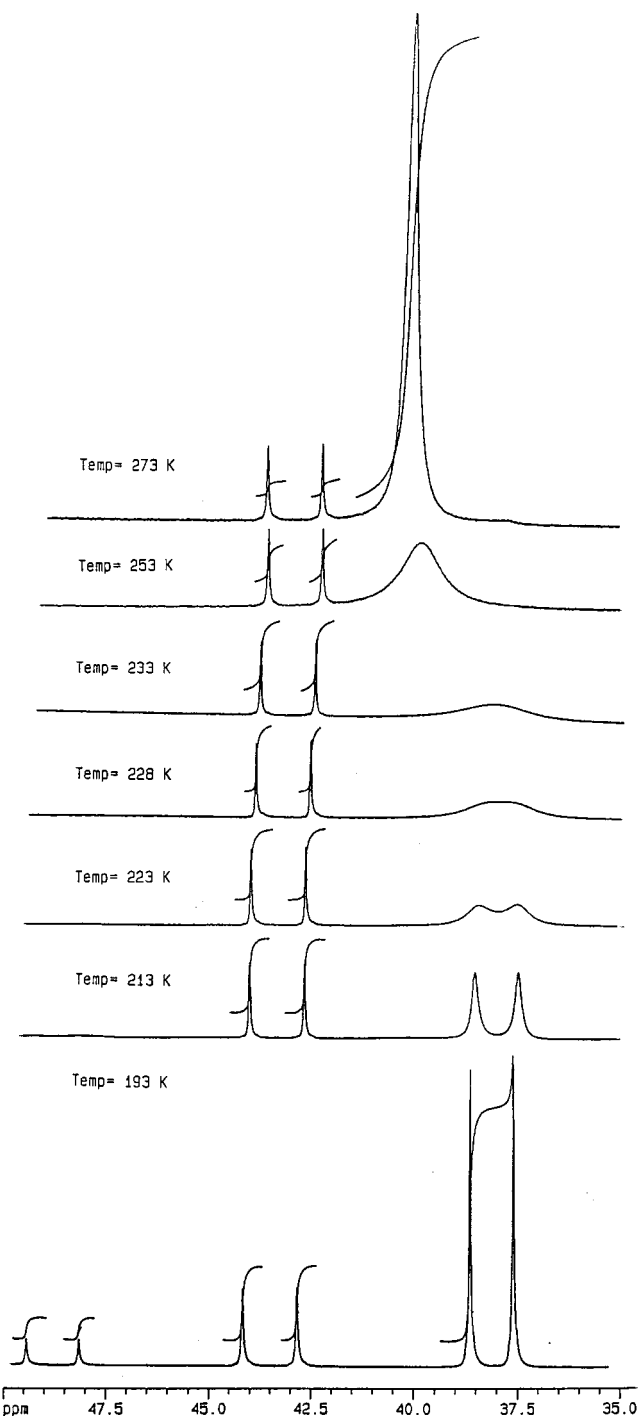
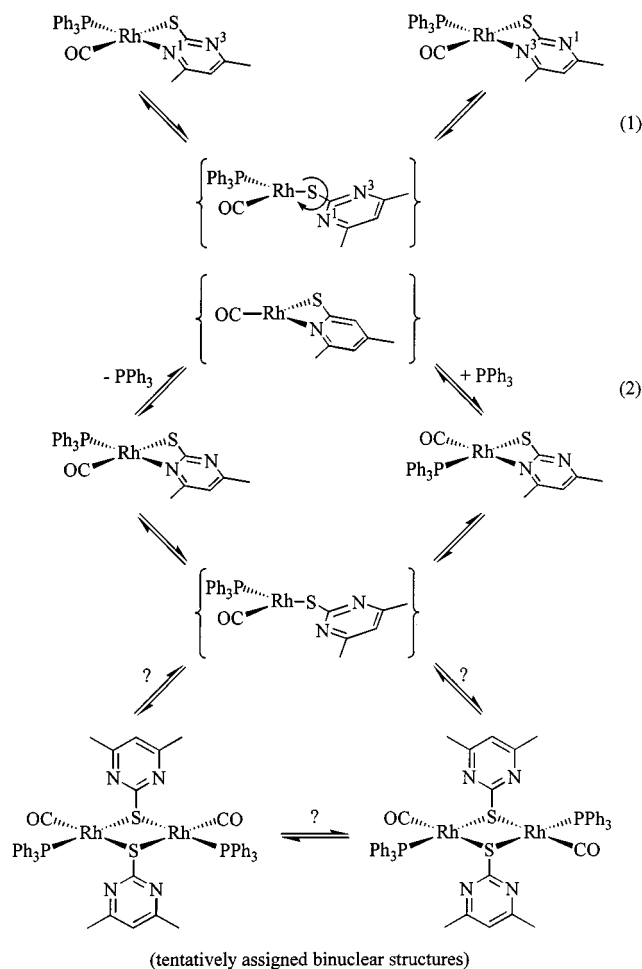


Figure 3. Temperature-dependent  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of  $[\text{Rh}(\text{'SpymMe}_2\text{'-}\kappa\text{N},\kappa\text{S})(\text{CO})(\text{PPh}_3)]$  (**4**);  $\text{CD}_2\text{Cl}_2$  solutions



Scheme 2. Structures believed to account for the dynamic behavior of  $[\text{Rh}(\text{'SpymMe}_2\text{'-}\kappa\text{N},\kappa\text{S})(\text{CO})(\text{PPh}_3)]$  (**4**) in solution

Complex **4** is not the only species present in solution at lower temperatures, since the temperature-dependent emergence of the  $^{31}\text{P}$  doublet arising from **4** is accompanied by the appearance of additional Rh-coupled resonances which are *not* observed for freshly prepared samples at ambient temperature, but show up as sharp doublets centered at  $\delta = 43.1$  ( $J = 161$  Hz) and  $48.4$  ( $J = 157$  Hz) when the solution is first cooled to  $0^\circ\text{C}$  and then to  $-80^\circ\text{C}$  (Figure 3). These shift values and coupling constants closely resemble those of the *cis*-(*P,P*) and *trans*-(*P,P*) forms of a number of thiolato-*S*-bridged dirhodium complexes  $[\{\text{Rh}(\mu\text{-SAr})(\text{CO})(\text{PPh}_3)\}_2]$ :  $\delta \approx 43$  (*cis*),  $45$  (*trans*);  $^1J(\text{Rh},\text{P}) \approx 160$  Hz.<sup>[13]</sup> For this reason, the low-field resonance at  $\delta = 48.4$  emerging below  $-60^\circ\text{C}$  is tentatively attributed to a thiolato-*S*-bridged binuclear isomer of **4** with the two phosphane ligands in *trans* positions, the signal located at  $\delta = 43.1$  correspondingly being assigned to the isomeric *cis* form. Both species can arise from **4** by loss of chelation (vide supra) followed by dimerization and, vice versa, may be cleaved to reform the monomer either with the Rh–N or the Rh–S bond *trans* to the  $\text{PPh}_3$  ligand. Once formed, the resonance centered at  $\delta = 43.1$  persists as a sharp doublet on raising the temperature, which shows that the associ-



ated molecules are nonfluxional on the NMR time scale and interconvert with those of **4** only very slowly, if at all.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the dirhodium complex **3**, recorded in CD<sub>2</sub>Cl<sub>2</sub> at –80 °C, displays two sharp doublets at δ = 37.0 [<sup>1</sup>J(Rh,P) = 132 Hz] and 41.7 [<sup>1</sup>J(Rh,P) = 162 Hz] with relative intensities 9 and 1, respectively. The latter signal obviously corresponds to the low-temperature resonance {δ = 42.1, <sup>1</sup>J(Rh,P) = 162 Hz; [D<sub>6</sub>]acetone, –60 °C} previously assigned to the structurally uncharacterized PPh<sub>3</sub>-disubstituted complex [{Rh(μ-‘Spy’)(CO)(PPh<sub>3</sub>)}<sub>2</sub>] which Oro and co-workers observed in acetone solution as a rearrangement product of [Rh<sub>2</sub>(μ-‘Spy’)<sub>2</sub>(CO)<sub>3</sub>(PPh<sub>3</sub>)].<sup>[9b]</sup> In line with the tentative spectral assignments made above, we attribute the less intense doublet exhibited by **3** in dichloromethane at δ = 41.7 to a thiolato-*S*-bridged *cis*-(*P,P*)-isomeric form of **3**, viz. [{Rh(μ-‘Spy’-κS)(CO)(PPh<sub>3</sub>)}<sub>2</sub>]. The more intense doublet at δ = 37.0 is then thought to arise from the *S,N*-bridged dirhodium complex **3** itself. It should be emphasized that in the structurally similar, albeit nonfluxional, thiazoline-2-thiolato-bridged complex [{Rh(μ-S<sub>2</sub>NC<sub>3</sub>H<sub>4</sub>-κN,κS)(CO)(PPh<sub>3</sub>)}<sub>2</sub>], the <sup>31</sup>P nuclei resonate at δ = 39.8 although their coupling to the rhodium nucleus (164 Hz) is larger.<sup>[10b]</sup> On raising the temperature to –40 °C, the slow exchange limit signal attributed to **3** collapses reversibly into a time-averaged signal which remains broad and shifts upfield to δ ≈ 25 if the solution is warmed to ca. 35 °C, thereby indicating a chemical exchange process but providing no further information. Reversible broadening of the doublet assigned to the *S*-bridged dimer [{Rh(μ-‘Spy’-κS)(CO)(PPh<sub>3</sub>)}<sub>2</sub>] on warming and cooling the solution likewise points to some unknown dynamic behavior of the associated molecules, which in this respect are clearly different from the rigid species giving rise to the sharp doublet at δ = 41.3 in the temperature-dependent <sup>31</sup>P{<sup>1</sup>H} spectra of **4** (Figure 3). Facile interconversion of binuclear structures bridged by pyridine-2-thiolato ligands in different bonding modes is well documented<sup>[9b,9c]</sup> but seems to be less feasible for structures involving the sterically more demanding 4,6-dimethylpyrimidine-2-thiolate system.

### Protonation of Iridium Complexes 1 and 2

Treatment of **1** or **2** with hydrogen chloride in CH<sub>2</sub>Cl<sub>2</sub> results in protolytic cleavage of the Ir–S bond and oxidative addition of HCl to give the long-known complex [IrHCl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>].<sup>[14]</sup> While only uncharacterized mixtures of products were isolated from reactions between **1** and HBF<sub>4</sub> or CF<sub>3</sub>CO<sub>2</sub>H, clean protonation of the iridium atom was observed to occur if **2** was combined with excess trifluoroacetic acid in dichloromethane. The resulting product, formally a 1:2 adduct between **1** and CF<sub>3</sub>CO<sub>2</sub>H, was characterized by X-ray diffraction as the hydrogen bis(trifluoroacetate) salt of a monopositive hydrido-iridium(III) complex, [IrH(‘SpymMe<sub>2</sub>’-κN,κS)(CO)(PPh<sub>3</sub>)<sub>2</sub>][H(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>], containing the pyrimidine-2-thiolate ligand in a chelating coordination mode (Scheme 1, **5a**; Figure 4), rather than the hoped-for trifluoroacetate-coordinated [IrH-{OC(O)CF<sub>3</sub>}(2-SC<sub>4</sub>HNN(H)Me<sub>2</sub>-4,6)(CO)(PPh<sub>3</sub>)<sub>2</sub>]-

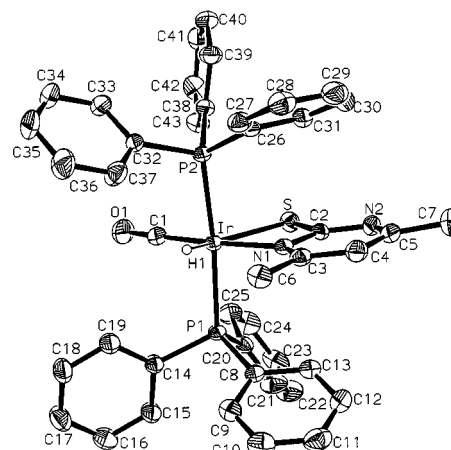


Figure 4. Molecular structure of [IrH(‘SpymMe<sub>2</sub>’-κN,κS)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (cation of **5a**); selected bond lengths [Å] and angles [°]: Ir–S 2.481(2), Ir–P(1) 2.367(1), Ir–P(2) 2.367(1), Ir–N(1) 2.080(5), Ir–C(1) 1.858(8), Ir–H(1) 1.31(6), S–C(2) 1.727(7), N(1)–C(2) 1.360(8), N(2)–C(2) 1.320(8); P(1)–Ir–P(2) 173.02(6), N(1)–Ir–C(1) 174.5(3), S–Ir–P(1) 94.57(6), S–Ir–P(2) 92.31(6), S–Ir–N(1) 66.7(1), S–Ir–C(1) 108.0(2), P(1)–Ir–N(1) 91.5(1), P(1)–Ir–C(1) 90.5(2), P(2)–Ir–N(1) 90.1(1), P(2)–Ir–C(1) 88.5(2), S–Ir–H(1) 154(3), P(1)–Ir–H(1) 94(3), P(2)–Ir–H(1) 79(3), N(1)–Ir–H(1) 89(3), C(1)–Ir–H(1) 96(3), Ir–S–C(2) 79.5(2), Ir–N(1)–C(2) 104.3(4), S–C(2)–N(1) 109.5(5)

O<sub>2</sub>CCF<sub>3</sub> (Scheme 1, **5b**), featuring intramolecular hydrogen bonding<sup>[12]</sup> between the Ir–H fragment and the N–H bond of a monodentate zwitterionic pyrimidinium-2-thiolate ligand. The sulfur atom of the four-membered Ir–S–C–N heterocycle is *trans* with respect to Ir–H, the metal-bound pyrimidine nitrogen atom being *trans* to the carbonyl group. The highly strained chelate ring [bite angle S–Ir–N(1), 66.7(1)°] exhibits a bend along the N(1)⋯S vector of 3.41°. As a consequence of the pronounced weakening of the *trans* influence of the hydride ligand, the Ir–S distance, 2.481(2) Å, is much longer than the metal–sulfur bond in chelate complex **4** [2.371(1) Å], resulting in the valence angle at the sulfur atom shrinking from 80.89(9)° in molecule **4** to 79.5(2)° in cation **5a**<sup>+</sup>. The [H(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>]<sup>–</sup> ion encountered in structure **5a** is precedented, typical examples are the alkali metal salts M[H(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>], where M = K, Rb, or Cs,<sup>[15]</sup> and the trifluoroacetic acid tetrahydrate which adopts the ionic structure [H<sub>5</sub>O<sub>2</sub>][H(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>]·6H<sub>2</sub>O.<sup>[16]</sup> The geometry, optimized for the “best”<sup>[17]</sup> hydrogen bond in the [H(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>]<sup>–</sup> anion of **5a** (O–H, 0.82 Å; H⋯O, 1.71 Å; O⋯O, 2.53 Å, OHO, 170.7°), is quite normal and compares well with those of earlier determinations. The planes defined by the two carboxylate fragments are twisted about the O–H⋯O bond, such that the angle between them is 71.9°.

Although the hydrogen bis(trifluoroacetate) anion is known to be stabilized by short and strong hydrogen bonds,<sup>[16b]</sup> it is somewhat surprising that in the crystal structure analysis, the second molecule of CF<sub>3</sub>CO<sub>2</sub>H (*p*K<sub>a</sub> = 0.18) consumed in the protonation of **2** binds to the CF<sub>3</sub>CO<sub>2</sub><sup>–</sup> counterion rather than the basic pyrimidine nitrogen atom of the [IrH(‘SpymMe<sub>2</sub>’-κN,κS)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cation formed in the first step.<sup>[18]</sup> It

is difficult to ascertain whether this bonding situation is restricted to the solid state or whether and to what extent the  $[\text{H}(\text{O}_2\text{CCF}_3)_2]^-$  ion persists in solution. Proton NMR spectra of  $\text{CD}_2\text{Cl}_2$  solutions of **5a** did contain a sharp singlet at  $\delta = 15.0$ , indicative of hydroxy protons involved in hydrogen-bonding, but otherwise remained inconclusive as the complex could not be isolated completely free from lattice water (see Experimental Section) which rapidly exchanges with the acid. Using  $\text{HBF}_4$  to protonate compound **2** led to formation of the tetrafluoroborate  $[\text{IrH}(\text{Spy}'\text{-}\kappa\text{N},\kappa\text{S})(\text{CO})(\text{PPh}_3)_2]\text{BF}_4 \cdot \text{HBF}_4$  as a formal analogue of the trifluoroacetate **5a**. In contrast with the latter, the cation of the  $\text{BF}_4^-$  salt exists as two isomers which differ in the bonding of the hydride ligand, which may be *trans* to the S atom,  $\delta(\text{IrH}) = -14.46$  (t), or *trans* to the N atom,  $\delta(\text{IrH}) = -16.57$  (t).<sup>[19]</sup> Based on the relative peak areas of these hydride signals and the associated methyl singlets at  $\delta = 1.88$  and  $2.45$  (IrH *trans* to S) and  $\delta = 2.17$  and  $2.40$  (IrH *trans* to N), the isomer ratio *trans*-(H,S)/*trans*-(H,N) can be estimated as 67:33, in good agreement with the  $^{31}\text{P}$  spectra containing singlets at  $\delta = 8.2$  and  $9.0$  with relative intensities 60:40. Dichloromethane solutions of the tetrafluoroborate also displayed a concentration-dependent, broadened proton resonance in the range  $8 < \delta < 13$ , attributable to a nitrogen-bonded proton engaged in further hydrogen bonding, presumably to  $\text{BF}_4^-$ . Hence, the two isomeric tetrafluoroborates are tentatively assigned structures **5c** and **5d** with *N*-protonated 4,6-dimethylpyrimidin-2-thiolato chelate ligands.

Pyridine-2-thiol oxidatively adds to *trans*- $[\text{Ir}(\text{Spy}')(\text{CO})(\text{PPh}_3)_2]$  (**1**), forming  $[\text{IrH}(\text{Spy}')_2(\text{CO})(\text{PPh}_3)_2]$  (**6**). This complex is more directly prepared by reaction of *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$  with an excess of the 'pySH' ligand in the presence of triphenylphosphane to prevent  $\text{PPh}_3$  dissociation. The *trans*-(P,P)-*cis*-(S,S) coordination geometry shown for **6** in Scheme 1 is suggested by spectral data. In particular, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum displays a singlet ( $\delta = 7.61$ ), and the proton NMR spectrum contains an IrH triplet which shows equal *cis* coupling (10.8 Hz) to the two equivalent  $^{31}\text{P}$  nuclei and is shifted to much lower frequencies ( $\delta = -13.54$ ) than appear to be diagnostic of the presence of *trans*-H–Ir–CO units ( $\delta \approx -9$ ) in carbonylhydrido complexes of the general type  $[\text{IrH}(\text{X})(\text{Y})(\text{CO})(\text{PR}_3)_2]$ .<sup>[21–23]</sup> Iridium complex **6** reacts with  $\text{HBF}_4$  in  $\text{CHCl}_3$  solution by cleavage of one Ir–S bond and protonation at the metal center to form the ionic chelate complex  $[\text{IrH}(\text{Spy}'\text{-}\kappa\text{N},\kappa\text{S})(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$  (**7**). The cation of this compound is isoelectronic with  $[\text{OsH}(\text{Spy}'\text{-}\kappa\text{N},\kappa\text{S})(\text{CO})(\text{PPh}_3)_2]$  which was previously isolated as a mixture of two *trans*-(P,P) isomers having the hydrido ligand *trans* to the N atom or *trans* to the S atom.<sup>[5a][20a]</sup> The X-ray structure analysis of **7** showed that  $[\text{IrH}(\text{Spy}'\text{-}\kappa\text{N},\kappa\text{S})(\text{CO})(\text{PPh}_3)_2]^+$  exists in the *trans*-(P,P)-*trans*-(H,S) form (Figure 5). Bond lengths and angles within the near-planar four-membered ring (bend along  $\text{N}\cdots\text{S}$  vector,  $2.20^\circ$ ) are similar to those found for pyrimidine-2-thiolato derivat-

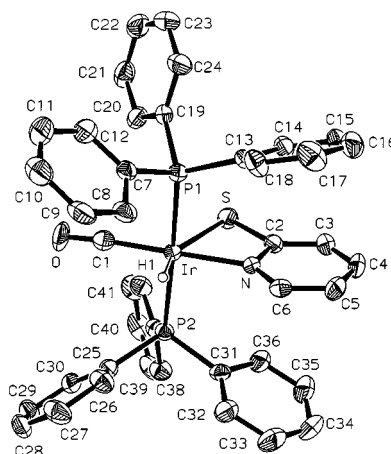


Figure 5. Molecular structure of  $[\text{IrH}(\text{Spy}'\text{-}\kappa\text{N},\kappa\text{S})(\text{CO})(\text{PPh}_3)_2]^+$  (cation of **7**); selected bond lengths [Å] and angles  $^\circ$ : Ir–S 2.508(2), Ir–P(1) 2.371(1), Ir–P(2) 2.357(1), Ir–N 2.069(5), Ir–C(1) 1.853(8), Ir–H(1) 1.49(7), S–C(2) 1.725(6), N–C(2) 1.351(8); P(1)–Ir–P(2) 174.16(6), N–Ir–C(1) 177.9(3), S–Ir–P(1) 92.56(6), S–Ir–P(2) 93.14(6), S–Ir–N 66.3(1), S–Ir–C(1) 111.7(3), P(1)–Ir–N 90.3(1), P(1)–Ir–C(1) 90.4(2), P(2)–Ir–N 90.9(1), P(2)–Ir–C(1) 88.6(2), S–Ir–H(1) 154(2), P(1)–Ir–H(1) 84(2), P(2)–Ir–H(1) 91(2), N–Ir–H(1) 88(2), C(1)–Ir–H(1) 94(3), Ir–S–C(2) 78.7(2), Ir–N–C(2) 105.1(4), S–C(2)–N 110.0(5)

ive **5**: Ir–S 2.507(2) Å; Ir–N 2.069(5) Å; S–Ir–N 66.3(1) $^\circ$ ; Ir–S–C(2) 78.7(2) $^\circ$ .

While treatment of the osmium(II) complex  $[\text{OsH}(\text{Spy}'\text{-}\kappa\text{N},\kappa\text{S})(\text{CO})(\text{PPh}_3)_2]$  with  $\text{HBF}_4$  resulted in the formation of the highly acidic, yet stable, dihydrogen derivative  $[\text{Os}(\text{H}_2)(\text{Spy}'\text{-}\kappa\text{N},\kappa\text{S})(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ ,<sup>[20]</sup> no similar transformation was observed on attempted protonation of **7**. Previously, a model for predicting the properties of dihydrogen complexes  $[\text{M}(\text{H}_2)\text{L}_5]$  was described,<sup>[24]</sup> based on estimated electrochemical potentials  $E_{1/2}(\text{d}^5/\text{d}^6)$  calculated by use of Lever's ligand additivity approach<sup>[25]</sup> for six-coordinate complexes. It was concluded that dihydrogen complexes  $[\text{M}(\text{H}_2)\text{L}_5]$  that are stable with respect to loss of  $\text{H}_2$  at ambient temperature will correspond to hypothetical dinitrogen complexes  $[\text{M}(\text{N}_2)\text{L}_5]$  with potentials  $E_{1/2}(\text{d}^5/\text{d}^6)$  of about 2 V versus NHE if the  $\text{H}_2$  ligand is *trans* to a  $\sigma$  donor on a Group 7, 8, or 9 metal ion; on the other hand, dinitrogen complexes with potentials above 2 V will have corresponding  $[\text{M}(\text{H}_2)\text{L}_5]$  species that lose dihydrogen irreversibly at 20–25  $^\circ\text{C}$ , possibly with the exception of  $[\text{Ir}^{\text{III}}(\text{H}_2)\text{L}_5]^{n+}$  where stable metal– $\text{H}_2$  bonding appears feasible up to potentials  $E_{1/2}([\text{Ir}^{\text{IV}}(\text{H}_2)\text{L}_5]^{n+}/[\text{Ir}^{\text{III}}(\text{H}_2)\text{L}_5]^{(n-1)+})$  of ca. 2.2 V.<sup>[24]</sup> By use of the sum of additive electrochemical ligand parameters,  $\Sigma E_L$ , as proposed by Lever ( $E_L = 0.99$  V for CO, 0.68 V for  $\text{N}_2$ , and 0.39 V for  $\text{PPh}_3$ )<sup>[25a]</sup> and Morris ( $E_L = -0.28$  V for chelating 'Spy'),<sup>[20b]</sup> and the linear correlation  $E_{1/2} = 0.7\Sigma E_L + 1.3$ , suggested by Morris for the  $\text{Ir}^{\text{IV}}/\text{Ir}^{\text{III}}$  redox couple,<sup>[24]</sup> the  $E_{1/2}(\text{d}^5/\text{d}^6)$  value for a hypothetical dinitrogen-containing dication  $[\text{Ir}(\text{N}_2)(\text{Spy}'\text{-}\kappa\text{N},\kappa\text{S})(\text{CO})(\text{PPh}_3)_2]^{2+}$  is estimated at ca. 2.8 V, far beyond the limit where stable bonding of  $\text{H}_2$  could be expected for a dipositive dihydrogen species  $[\text{Ir}(\text{H}_2)(\text{Spy}'\text{-}\kappa\text{N},\kappa\text{S})(\text{CO})(\text{PPh}_3)_2]^{2+}$ !

## Conclusion

This work has shown that the Vaska-type complexes *trans*-[MCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (M = Rh, Ir) react with bifunctional anionic pyridine- and 4,6-dimethylpyrimidine-2-thiolates to yield products whose nature is sensitive to the metal center and the steric requirements of the ligands. With iridium(I), both 'Spy<sup>−</sup>' and 'SpymMe<sub>2</sub><sup>−</sup>' act as *S*-monodentates to give the complexes, *trans*-[Ir('Spy')(CO)(PPh<sub>3</sub>)<sub>2</sub>] (**1**) and *trans*-[Ir('SpymMe<sub>2</sub>')(CO)(PPh<sub>3</sub>)<sub>2</sub>] (**2**), which result from simple anion exchange. In similar reactions, *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] undergoes loss of both the chloride ion and one PPh<sub>3</sub> ligand, affording derivatives in which the two anionic *S,N* donors act as bidentate bridging or chelate ligands. With 'Spy<sup>−</sup>' as an entering ligand we see the formation of bimetallic [{Rh(μ-'Spy'-κ*N*,*S*)(CO)(PPh<sub>3</sub>)<sub>2</sub>}] (**3**) where the two pyridine-2-thiolate moieties act as *S,N* bridges in the head-to-tail arrangement frequently encountered<sup>[9b,10]</sup> for heterocyclic ligands with *N*–C–*S* donor sets. The sterically more demanding 4,6-dimethylpyrimidine-2-thiolate system, on the other hand, does not give any related doubly *S,N*-bridged binuclear product with nearly parallel heterocyclic rings but rather acts as a chelate ligand towards Rh<sup>I</sup>, producing the unusual four-membered ring complex [Rh('SpymMe<sub>2</sub>'-κ*N*,κ*S*)(CO)(PPh<sub>3</sub>)<sub>3</sub>] (**4**). Because of facile interconversion of the bonding modes of the *S,N*-coordinated ligands, the structures adopted by **3** and **4** in the solid state are not maintained in solution but show temperature-dependent dynamic behavior.

Reaction of iridium complexes bearing *S*-bonded 'Spy' and 'SpymMe<sub>2</sub>' ligands with strong acids (CF<sub>3</sub>CO<sub>2</sub>H, HBF<sub>4</sub>) results in protonation of only the metal center, except for the *trans*-(*H,S*) and *trans*-(*H,N*) isomers of [IrH(2-SC<sub>4</sub>HNN(H)Me<sub>2</sub>-4,6-κ*N*,κ*S*)(CO)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> where NMR spectroscopy suggests that protonation at the noncoordinated nitrogen atom of the pyrimidine heterocycle also occurs. There was no indication of reactions leading to products displaying "nonclassical" intramolecular IrH⋯HN hydrogen bonding. The failure to isolate such derivatives within the family of complexes studied here is accounted for by the ease of the 'Spy' and 'SpymMe<sub>2</sub>' ligands to act as *S,N* donor chelates in spite of their small bite angles. This prevents the formation of hydrido-iridium derivatives containing *S*-monodentate thiolate ligands with "dangling" pyridyl or pyrimidinyl substituents, which would allow a sufficiently close approach of the ring nitrogen atoms to the Ir–H bond.

## Experimental Section

**General Remarks:** All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents prior to use. – IR: Mattson Polaris. – NMR: Bruker DPX 300 (300.1 MHz for <sup>1</sup>H, 121.5 MHz for <sup>31</sup>P)

at 20 ± 2 °C (if not stated otherwise) with TMS as internal or with H<sub>3</sub>PO<sub>4</sub> as external standard (downfield positive). – The starting complexes *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>[26]</sup> and *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>[27]</sup> were prepared by literature methods; the ligands pyridine-2-thiol and 4,6-dimethylpyrimidine-2-thiol were used as obtained commercially.

***trans*-[Ir('Spy')(CO)(PPh<sub>3</sub>)<sub>2</sub>] (**1**):** A solution of pyridine-2-thiol (170.1 mg, 1.53 mmol) in THF (10 mL) was treated with sodium hydride (36.8 mg, 1.54 mmol) at room temperature for 1 h and then added to a suspension of *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (1.002 g, 1.28 mmol) in THF (25 mL). The dark red mixture was stirred for 1 h at ambient conditions and then concentrated to dryness. The residue was taken up in toluene (60 mL) and the solution was filtered through a layer of sea sand/Celite. Concentration of the filtrate to 5 mL and careful addition of pentane (60 mL) caused the precipitation of a yellow-orange powder which was recrystallized from dichloromethane to give the product complex as orange crystals; yield 880 mg (80%). – IR (KBr):  $\tilde{\nu}$  = 1924 (CO) cm<sup>−1</sup>. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 6.08 (d, *J* = 8.1 Hz, 1 H, C<sub>5</sub>H<sub>4</sub>N), 6.28 (d, *J* = 8.4 Hz, 1 H, C<sub>5</sub>H<sub>4</sub>N), 6.42 ("t", *J* = 13.2 Hz, 1 H, C<sub>5</sub>H<sub>4</sub>N), 6.62 ("t", *J* = 13.2 Hz, 1 H, C<sub>5</sub>H<sub>4</sub>N), 7.3–7.4 (m, 18 H, C<sub>6</sub>H<sub>5</sub>), ca. 7.6 (m, 12 H, C<sub>6</sub>H<sub>5</sub>). – <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 21.3. – C<sub>42</sub>H<sub>34</sub>IrNOP<sub>2</sub>S (855.0): calcd. C 59.00, H 4.01, N 1.64, S 3.75; found C 59.15, H 4.00, N 1.53, S 3.93.

***trans*-[Ir('SpymMe<sub>2</sub>')(CO)(PPh<sub>3</sub>)<sub>2</sub>] (**2**):** 4,6-Dimethylpyrimidine-2-thiol (85.4 mg, 0.61 mmol) was deprotonated by treatment with an equimolar amount of sodium methoxide in methanol (5 mL). The resulting solution was added dropwise to a stirred suspension of *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (44.2 mg, 0.56 mmol) in THF. After stirring for 3 h at ambient conditions, the solvent was removed in vacuo to leave a semisolid residue which was re-dissolved in benzene (25 mL). Filtration through sea sand/Celite followed by concentration of the filtrate to ca. 3 mL gave a clear solution from which the product was isolated by slow addition of pentane (50 mL); yield 420 mg (85%) as orange microcrystals. – IR (KBr):  $\tilde{\nu}$  = 1928 (CO) cm<sup>−1</sup>. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.73 (s, 6 H, CH<sub>3</sub>), 5.55 (s, 1 H, C<sub>4</sub>H), ca. 7.3 (m, 18 H, C<sub>6</sub>H<sub>5</sub>), ca. 7.5 (m, 12 H, C<sub>6</sub>H<sub>5</sub>). – <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 19.4. – C<sub>43</sub>H<sub>37</sub>IrN<sub>2</sub>O<sub>2</sub>S<sub>2</sub> (884.2): calcd. C 58.36, H 4.22, N 3.17, S 3.62; found C 58.50, H 4.25, N 3.08, S 3.39.

**[{Rh(μ-'Spy'-κ*N*,κ*S*)(CO)(PPh<sub>3</sub>)<sub>2</sub>}] (**3**):** A procedure analogous to that for **1** was employed, using *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (549.7 mg, 0.80 mmol) and sodium pyridine-2-thiolate (117.2 mg, 0.88 mmol) in THF (30 mL) at room temperature for 3 h. Crystallization of the product from dichloromethane/pentane furnished the orange complex as the compound [{Rh(μ-'Spy'-κ*N*,κ*S*)(CO)(PPh<sub>3</sub>)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>] (**3**·CH<sub>2</sub>Cl<sub>2</sub>); yield 360 mg (82%). – IR (KBr):  $\tilde{\nu}$  = 1937 (CO) cm<sup>−1</sup>. – <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, −40 °C):  $\delta$  = 5.65 ("t", *J* = 12.4 Hz, 2 H, C<sub>5</sub>H<sub>4</sub>N), 6.19 (d, *J* = 8.2 Hz, 2 H, C<sub>5</sub>H<sub>4</sub>N), 6.37 ("t", *J* = 10.2 Hz, 2 H, C<sub>5</sub>H<sub>4</sub>N), 6.55 (d, *J* = 5.1 Hz, 2 H, C<sub>5</sub>H<sub>4</sub>N), 7.1–7.3 (m, 18 H, C<sub>6</sub>H<sub>5</sub>), ca. 7.5 (m, 12 H, C<sub>6</sub>H<sub>5</sub>). – <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, −80 °C):  $\delta$  = 37.0 [d, <sup>1</sup>*J*(Rh,P) = 132 Hz]. – C<sub>48</sub>H<sub>38</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Rh<sub>2</sub>S<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (1092): calcd. C 53.91, H 3.69, N 2.57; found C 54.26, H 3.34, N 2.25.

**[Rh('SpymMe<sub>2</sub>'-κ*N*,κ*S*)(CO)(PPh<sub>3</sub>)] (**4**):** The yellow-orange complex was prepared as for **2** by allowing *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (590.4 mg, 0.85 mmol) to react with a 10% excess of methanolic sodium 4,6-dimethylpyrimidine-2-thiolate in THF (20 mL); yield 410 mg (91%). – IR (KBr):  $\tilde{\nu}$  = 1968 (CO) cm<sup>−1</sup>. – <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 1.89 (s, 6 H, CH<sub>3</sub>), 5.72 (s, 1 H, C<sub>4</sub>H), ca. 7.4 (m, 9 H, C<sub>6</sub>H<sub>5</sub>), ca. 7.7 (m, 6 H, C<sub>6</sub>H<sub>5</sub>). – <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, −80



$^{\circ}\text{C}$ ):  $\delta = 37.7$  [d,  $^1\text{J}(\text{Rh}, \text{P}) = 126$  Hz]. –  $\text{C}_{25}\text{H}_{22}\text{N}_2\text{OPRhS}$  (532.4): calcd. C 56.40, H 4.17, N 5.26, S 6.02; found C 56.84, H 4.22, N 5.28, S 5.92.

**[IrH('SpymMe<sub>2</sub>'-κN,κS)(CO)(PPh<sub>3</sub>)<sub>2</sub>][H(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>] (5a):** Complex **2** (144.6 mg, 0.16 mmol) was allowed to react with an excess of neat trifluoroacetic acid (40 μL, ca. 0.5 mmol) in dichloromethane (20 mL) at room temperature for 30 min. Slow concentration of the mixture caused the product to precipitate as bright yellow crystals containing 1 molecule of lattice water per formula unit (**5a**·H<sub>2</sub>O); yield 160 mg (88%). – IR (KBr):  $\tilde{\nu} = 1792$  (C=O), 2053 (CO), 2170 (IrH)  $\text{cm}^{-1}$ . –  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = -13.01$  [t,  $\text{cis-}^2\text{J}(\text{P}, \text{H}) = 10.5$  Hz, 1 H, IrH], 1.47, 2.20 (both s, 3 H each, both  $\text{CH}_3$ ), 6.28 (s, 1 H,  $\text{C}_4\text{H}$ ), ca. 7.4 (m, 18 H,  $\text{C}_6\text{H}_5$ ), ca. 7.7 (m, 12 H,  $\text{C}_6\text{H}_5$ ), 15.0 (s, OH). –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 8.2$  (s). –  $\text{C}_{47}\text{H}_{39}\text{F}_6\text{IrN}_2\text{O}_5\text{P}_2\text{S}\cdot\text{H}_2\text{O}$  (1130): calcd. C 49.95, H 3.66, N 2.48; found C 49.54, H 3.24, N 2.16.

**[IrH(2-SC<sub>4</sub>HNN(H)Me<sub>2</sub>-4,6-κN,κS)(CO)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (Mixture of Isomers 5c and 5d):** A solution of **2** (189.5 mg, 0.21 mmol) in dichloromethane (20 mL) was treated with  $\text{HBF}_4$  (30 μL, 54% in  $\text{Et}_2\text{O}$ ). The mixture was stirred for 2.5 h at ambient conditions and then concentrated to dryness. The residue was re-dissolved in  $\text{CH}_2\text{Cl}_2$  (8 mL) and the resulting solution was filtered and diluted with pentane (40 mL) to furnish the product as a light yellow microcrystalline precipitate containing solvent of crystallization; yield 190 mg (79%). – **5c**:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = -14.46$  [t,  $\text{cis-}^2\text{J}(\text{P}, \text{H}) = 9.9$  Hz, 1 H, IrH], 1.88, 2.45 (both s, 3 H each, both  $\text{CH}_3$ ), 7.05 (s, 1 H,  $\text{C}_4\text{H}$ ), ca. 7.6 (m,  $\text{C}_6\text{H}_5$ ). –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 8.2$  (s). – **5d**:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = -16.57$  [t,  $\text{cis-}^2\text{J}(\text{P}, \text{H}) = 10.8$  Hz, 1 H, IrH], 2.17, 2.40 (both s, 3 H each, both  $\text{CH}_3$ ), 7.03 (s, 1 H,  $\text{C}_4\text{H}$ ), ca. 7.6 (m,  $\text{C}_6\text{H}_5$ ). –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 9.0$  (s). – Isomeric distribution (from  $^1\text{H}$  NMR): **5c**, 67%; **5d**, 33%. –  $\text{C}_{43}\text{H}_{39}\text{B}_2\text{F}_8\text{IrN}_2\text{OP}_2\text{S}\cdot\text{CH}_2\text{Cl}_2$  (1145): calcd. C 46.17, H 3.61, N 2.45, S 2.79; found C 46.15, H 3.76, N 2.61, S 2.45.

**[IrH('Spy')<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] (6):** A 1:2 mixture of *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (480.4 mg, 0.62 mmol) and pyridine-2-thiol (140.2 mg, 1.26 mmol) was combined with excess triphenylphosphane (880 mg, 3.35 mmol) in benzene (80 mL). Stirring at room temperature for 24 h caused the product complex to separate from solution as a light yellow precipitate; yield 350 mg (58%). – IR (KBr):  $\tilde{\nu} = 2036$  (CO), 2177 (IrH)  $\text{cm}^{-1}$ . –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -13.54$  (t,  $\text{cis-}^2\text{J}(\text{P}, \text{H}) = 10.8$  Hz, 1 H, IrH), 5.87 (d,  $J = 7.2$  Hz, 2 H,  $\text{C}_5\text{H}_4\text{N}$ ), 6.48 ("t",  $J = 14.4$  Hz, 1 H,  $\text{C}_5\text{H}_4\text{N}$ ), 6.66 ("t",  $J = 14.3$  Hz, 1 H,  $\text{C}_5\text{H}_4\text{N}$ ), 6.94 ("t",  $J = 16.2$  Hz, 2 H,  $\text{C}_5\text{H}_4\text{N}$ ), 7.07 (d,  $J = 6.8$  Hz, 2 H,  $\text{C}_5\text{H}_4\text{N}$ ), 7.2–7.6 (m, 30 H,  $\text{C}_6\text{H}_5$ ). –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 7.6$  (s). –  $\text{C}_{47}\text{H}_{39}\text{IrN}_2\text{OP}_2\text{S}_2$  (966.1): calcd. C 58.43, H 4.07, N 2.90; found C 58.60, H 4.20, N 2.68.

**[IrH('Spy'-κN,κS)(CO)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>) (7):** A solution of **6** (170.1 mg, 0.18 mmol) in chloroform (10 mL) was stirred with  $\text{HBF}_4$  (0.3 mL, 54% in  $\text{Et}_2\text{O}$ ) at ambient conditions for 1 h. Dilution of the mixture with diethyl ether (70 mL) resulted in the precipitation of **7** (150 mg, 88%) as bright yellow crystals. – IR (KBr):  $\tilde{\nu} = 2047$  (CO), 2162 (IrH)  $\text{cm}^{-1}$ . –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -13.52$  (t,  $\text{cis-}^2\text{J}(\text{P}, \text{H}) = 11.0$  Hz, 1 H, IrH), 5.94 (d,  $J = 8.3$  Hz, 1 H,  $\text{C}_5\text{H}_4\text{N}$ ), 6.34 ("t",  $J = 14.9$  Hz, 1 H,  $\text{C}_5\text{H}_4\text{N}$ ), 6.93 ("t",  $J = 15.5$  Hz, 1 H,  $\text{C}_5\text{H}_4\text{N}$ ), 7.02 (d,  $J = 6.2$  Hz, 1 H,  $\text{C}_5\text{H}_4\text{N}$ ), 7.4–7.6 (m, 30 H,  $\text{C}_6\text{H}_5$ ). –  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 7.5$  (s). –  $\text{C}_{42}\text{H}_{35}\text{BF}_4\text{IrNOP}_2\text{S}$  (942.7): calcd. C 53.51, H 3.74, N 1.49, S 3.40; found C 53.17, H 3.73, N 1.59, S 3.40.

**X-ray Structure Determinations:** Single crystals of **3**· $\text{CH}_2\text{Cl}_2$  (size  $0.55 \times 0.43 \times 0.26$  mm), **4** (size  $0.45 \times 0.40 \times 0.24$  mm), **5a** (size  $0.38 \times 0.30 \times 0.13$  mm), and **7** (approximate size  $0.4 \times 0.2 \times 0.2$  mm) were grown from dichloromethane/pentane (**3**· $\text{CH}_2\text{Cl}_2$ , **4**), chloroform/diethyl ether (**7**), and by crystallizing the hydrate **5a**·H<sub>2</sub>O from dichloromethane. Diffraction measurements were made at  $-70 \pm 2$  °C (**4**) and  $20 \pm 2$  °C (**3**· $\text{CH}_2\text{Cl}_2$ , **5a**, **7**) on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71073$  Å): orientation matrices and unit cell parameters from the setting angles of 25 centered medium-angle reflections; collection of the diffraction intensities by  $\omega$  scans (data corrected for absorption by  $\psi$  scans; **3**· $\text{CH}_2\text{Cl}_2$ :  $T_{\min} = 0.61$ ,  $T_{\max} = 0.78$ ; **4**:  $T_{\min} = 0.69$ ,  $T_{\max} = 0.81$ ; **5a**:  $T_{\min} = 0.40$ ,  $T_{\max} = 0.70$ ; **7**:  $T_{\min} = 0.33$ ,  $T_{\max} = 0.54$ ). The structures were solved by direct methods employing the SIR-92<sup>[28]</sup> program system and subsequently refined by full-matrix least-squares procedures on  $F^2$  (SHELX-97<sup>[29]</sup>) with allowance for anisotropic thermal motion of all non-hydrogen atoms. The residual electron density remaining after refinement of the structural model resulting for **3**· $\text{CH}_2\text{Cl}_2$  suggested threefold rotational disorder of the solvate molecule about the Cl–C–Cl bisector, which was accounted for by assigning the particular chlorine positions split occupancies of 0.333 each. The  $\text{CF}_3$  groups of the hydrogen-bridged trifluoroacetate ions in structure **5** were found to be disordered over two sites with refined occupancies of 0.25:0.75 and 0.33:0.67, respectively. H atoms were included in the molecular models assuming ideal geometry and using appropriate riding models (IrH of **5a** and **7** located from final  $\Delta F$  maps). Some diffuse residual electron density near the inversion center of the triclinic unit cell of **5a** was modeled by assuming the presence of 1 molecule of lattice water originating from the synthesis and remaining after crystallization. – **3**· $\text{CH}_2\text{Cl}_2$ :  $\text{C}_{49}\text{H}_{40}\text{Cl}_2\text{N}_2\text{O}_2\text{P}_2\text{Rh}_2\text{S}_2$  (1092); triclinic,  $P\bar{1}$ ,  $a = 11.260(1)$ ,  $b = 13.436(1)$ ,  $c = 16.881(3)$  Å,  $\alpha = 78.87(1)^\circ$ ,  $\beta = 74.57(1)^\circ$ ,  $\gamma = 76.848(7)^\circ$ ,  $V = 2373.3(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $d_{\text{calcd.}} = 1.528$  g cm<sup>−3</sup>,  $\mu(\text{Mo-}K_\alpha) = 1.004$  mm<sup>−1</sup>;  $2.52^\circ \leq \Theta \leq 29.97^\circ$ , 14439 reflections ( $0 \leq h \leq +15$ ,  $-18 \leq k \leq +18$ ,  $-22 \leq l \leq +23$ ) collected, 13789 unique;  $wR = 0.096$  for all data and 586 parameters,  $R = 0.039$  for 10393 structure factors  $F_o > 4\sigma(F_o)$ . – **4**:  $\text{C}_{25}\text{H}_{22}\text{N}_2\text{OPRhS}$  (532.4); triclinic,  $P\bar{1}$ ,  $a = 9.254(7)$ ,  $b = 10.035(2)$ ,  $c = 13.0940(8)$  Å,  $\alpha = 93.05(1)^\circ$ ,  $\beta = 93.71(2)^\circ$ ,  $\gamma = 101.33(2)^\circ$ ,  $V = 1187.1(9)$  Å<sup>3</sup>,  $Z = 2$ ,  $d_{\text{calcd.}} = 1.489$  g cm<sup>−3</sup>,  $\mu(\text{Mo-}K_\alpha) = 0.894$  mm<sup>−1</sup>;  $2.51^\circ \leq \Theta \leq 30.08^\circ$ , 7187 reflections ( $-13 \leq h \leq +13$ ,  $-14 \leq k \leq +14$ ,  $0 \leq l \leq +18$ ) collected, 6908 unique;  $wR = 0.120$  for all data and 283 parameters,  $R = 0.029$  for 6215 structure factors  $F_o > 4\sigma(F_o)$ . – **5a**·H<sub>2</sub>O:  $\text{C}_{47}\text{H}_{41}\text{F}_6\text{IrN}_2\text{O}_6\text{P}_2\text{S}$  (1130); triclinic,  $P\bar{1}$ ,  $a = 11.771(1)$ ,  $b = 14.100(1)$ ,  $c = 15.573(1)$  Å,  $\alpha = 85.418(8)^\circ$ ,  $\beta = 83.124(9)^\circ$ ,  $\gamma = 69.235(9)^\circ$ ,  $V = 2397.4(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $d_{\text{calcd.}} = 1.565$  g cm<sup>−3</sup>,  $\mu(\text{Mo-}K_\alpha) = 2.967$  mm<sup>−1</sup>;  $2.64^\circ \leq \Theta \leq 25.97^\circ$ , 10526 reflections ( $-14 \leq h \leq +14$ ,  $-17 \leq k \leq +17$ ,  $-1 \leq l \leq +19$ ) collected, 9397 unique;  $wR = 0.115$  for all data and 612 parameters,  $R = 0.046$  for 7494 structure factors  $F_o > 4\sigma(F_o)$ . – **7**:  $\text{C}_{42}\text{H}_{35}\text{BF}_4\text{IrNOP}_2\text{S}$  (942.7); orthorhombic,  $Pbca$ ,  $a = 18.766(3)$ ,  $b = 18.104(1)$ ,  $c = 23.404(2)$  Å,  $V = 7951(1)$  Å<sup>3</sup>,  $Z = 8$ ,  $d_{\text{calcd.}} = 1.575$  g cm<sup>−3</sup>,  $\mu(\text{Mo-}K_\alpha) = 3.544$  mm<sup>−1</sup>;  $2.60^\circ \leq \Theta \leq 23.97^\circ$ , 7863 reflections ( $-1 \leq h \leq +21$ ,  $-1 \leq k \leq +20$ ,  $-26 \leq l \leq +2$ ) collected, 6215 unique;  $wR = 0.074$  for all data and 482 parameters,  $R = 0.033$  for 3830 structure factors  $F_o > 4\sigma(F_o)$ . – Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC-136220 (**7**), -136221 (**5a**·H<sub>2</sub>O), -136222 (**4**), and -136223 (**3**· $\text{CH}_2\text{Cl}_2$ ). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].



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- [17] H atom position generated by the HFIX 83 option of SHELX-97, see ref.<sup>[29]</sup>
- [18] Structure **5a** was initially refined as the 1:2 complex salt [IrH(2-SC<sub>4</sub>HNN(H)Me<sub>2</sub>-4,6-κN,κS)(CO)(PPh<sub>3</sub>)<sub>2</sub>](O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> (Scheme 1; **5c**; X<sup>−</sup> = CF<sub>3</sub>CO<sub>2</sub><sup>−</sup>) containing a dipositive cation with a pyridinium-2-thiolato ligand protonated at N(2). A subsequent validation check with the PLATON-99 program package (see ref.<sup>[30]</sup>), however, revealed an unusual short nonbonded contact distance of 2.53 Å between two carboxylate oxygen atoms of the two trifluoroacetate counterions located at general positions *x*<sub>1</sub>, *y*<sub>1</sub>, *z*<sub>1</sub> and −*x*<sub>2</sub> − 1, −*y*<sub>2</sub>, −*z*<sub>2</sub> + 1. Furthermore, checking of the derived structural model showed that the polar N(2)–H bond had no acceptor acting as a weak base towards the acidic pyrimidinium proton. To account for these problems, the 1:1 complex salt [IrH(‘SpmMe<sub>2</sub>’-κN,κS)(CO)-(PPh<sub>3</sub>)<sub>2</sub>][H(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>] with an O–H⋯O-bridged hydrogen bis-(trifluoroacetate) anion was taken as the basis for the final stages of refinement.
- [19] These isomer assignments are in accordance with trends in the <sup>1</sup>H NMR data reported by others (ref.<sup>[20b,21–23]</sup>) according to which the hydride resonance of the isomeric form having the hydride ligands *trans* to the more electronegative atom, e.g. N, appears at lower frequencies than that in which the M–H bond is *trans* to a less electronegative donor atom such as sulfur.
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