Preparation of a series of dinuclear Ir(III) and Ir(II) complexes containing bridging thiolate ligands

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Abstract

Reactions of [Cp*IrCl(μ-Cl)$_2$IrCp*Cl] (Cp* = η^5-C$_5$Me$_5$) with RSH in CH$_2$Cl$_2$ at room temperature afforded two types of thiolate-bridged dinuclear Ir(III) complexes, [Cp*IrCl(μ-SR)$_2$IrCp*Cl] (2; R = Pr^i, Cy, CH$_2$Ph; Cy = cyclohexyl) or [Cp*Ir(μ-SEt)$_3$IrCp*]Cl, depending upon the nature of the substituent R. Reduction of 2 (R = Pr^i (2a), Cy) with excess Na–Hg in THF resulted in the formation of the dinuclear Ir(II) complexes [Cp*Ir(μ-SR)$_2$IrCp*] (3). X-ray diffraction studies were undertaken for 2a and 3b (R = Cy) to determine their detailed structures. 2a: C$_{26}$H$_{44}$Cl$_2$S$_2$Ir$_2$, space group C2/c, a = 21.255(8), b = 8.606(6), c = 17.788(6) Å, β = 118.39(2)°, Z = 4. 3b: C$_{32}$H$_{52}$S$_2$Ir$_2$, space group P2/n, a = 8.912(6), b = 11.224(6), c = 16.496(6) Å, β = 97.78(4)°, Z = 2. Complexes 3 reacted with CF$_3$COOH to give the cationic Ir(III) complexes having a bridging hydride ligand [Cp*Ir(μ-H)(μ-SR)$_2$IrCp*][OCOCF$_3$]. © 1997 Elsevier Science S.A.

Keywords: Crystal structures; Iridium complexes; Thiolate bridged complexes; Dinuclear complexes

1. Introduction

Recent studies in this laboratory on a series of diruthenium complexes [Cp*Ru(μ-SPr^i)$_2$RuCp*] (1), [Cp*Ru(μ-SPr^i)$_3$-RuCp*] and [Cp*RuCl(μ-SPr^i)$_2$RuCp*(H$_2$O)][OTf] (Cp* = η^5-C$_5$Me$_5$, OTf = OSO$_2$CF$_3$) [1] have shown that the thiolate-bridged dinuclear Ru(II) and/or Ru(III) sites in these complexes facilitate unique transformations of a range of substrates such as terminal alkynes [2], alkyl halides, H$_2$ [3] and hydrazines [4]. The presence of the firmly bound thiolate bridges in these complexes results in the retention of the bimetallic core throughout these stoichiometric or catalytic reactions.

For exploring further the intriguing reactivities displayed at the thiolate-bridged bimetallic sites, we have recently extended the chemistry of these diruthenium complexes to that of the related diiridium complexes. In this paper, we report the isolation and characterization of a new class of thiolate-bridged Ir(III) and Ir(II) complexes, [Cp*IrCl(μ-SR)$_2$IrCp*Cl] (2) and [Cp*Ir(μ-SR)$_2$IrCp*] (3), along with some reactivities of 3. In a recent communication [5],

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we have reported that 3a (R = Pr^i) reacts with S$_8$ to form the diiridium complex containing a novel nonasulfido bridge [Cp*Ir(μ-S$_9$)(μ-SPr^i)$_2$IrCp*]. It is to be noted that this reaction observed for the Ir complex 3a presents a sharp contrast to that of the Ru complex 1 with S$_8$, which gives a disulfide-bridged complex [Cp*Ru(μ-S$_2$)(μ-SPr^i)$_2$-RuCp*] exclusively [6].

2. Experimental

2.1. General

All manipulations were performed under a nitrogen atmosphere. Complex [Cp*IrCl(μ-Cl)$_2$IrCp*Cl] (4) was prepared according to the published method [7]. Thiols and CF$_3$COOH were commercially obtained and degassed prior to use. ¹H NMR spectra were recorded on a JEOL EX-270 spectrometer, while IR spectra were obtained on a Shimadzu 8100M spectrometer. For the ¹H NMR data, the signals arising from the cyclohexyl (Cy) protons are omitted. Elemental analyses were carried out using a Perkin-Elmer 2400II CHN analyzer.

2.2. Preparation of [Cp*IrCl(μ-SPr^i)$_2$IrCp*Cl] (2a)

Into a suspension of 4 (2.02 g, 2.54 mmol) in CH$_2$Cl$_2$ (40 cm³) was added Pr^{i}SH (0.65 cm³, 7.0 mmol), and the mixture

was stirred at room temperature for 12 h. The volatile materials were removed in vacuo and the residue was extracted with THF. Addition of hexane to the concentrated extract afforded **2a** as a yellow–orange crystalline solid (1.61 g, 72%). ^{1}H NMR (CDCl$_3$): δ 1.05 (d, J = 6.6 Hz, 12H, SCH*Me*$_2$), 1.54 (s, 30H, Cp*), 3.81 (sep, J = 6.6 Hz, 2H, SC*H*Me$_2$). *Anal.* Found: C, 35.60; H, 5.09. Calc. for C$_{26}$H$_{44}$Cl$_2$S$_2$Ir$_2$: C, 35.65; H, 5.06%.

2.3. Preparation of [Cp*IrCl(μ-SCy)$_2$IrCp*Cl] (2b)

This complex was isolated as a yellow–orange crystalline solid in 62% yield from **4** (300 mg, 0.377 mmol) and CySH (0.20 cm^3, 1.6 mmol) by the same method as that used to obtain **2a**. ^{1}H NMR (CDCl$_3$): δ 1.54 (s, 30H, Cp*). *Anal.* Found: C, 40.17; H, 5.61. Calc. for C$_{32}$H$_{52}$Cl$_2$S$_2$Ir$_2$: C, 40.19; H, 5.48%.

2.4. Preparation of [Cp*IrCl(μ-SCH$_2$Ph)$_2$IrCp*Cl] (2c)

This complex was also obtained as a yellow–orange crystalline solid in 78% yield from **4** (400 mg, 0.502 mmol) and PhCH$_2$SH (0.18 cm^3, 1.5 mmol) by the method described above. ^{1}H NMR (CDCl$_3$): δ 1.38 (s, 30H, Cp*), 3.92 (s, 4H, SCH$_2$Ph), 7.13–7.46 (m, 10H, SCH$_2$*Ph*). *Anal.* Found: C, 42.19; H, 4.60. Calc. for C$_{34}$H$_{44}$Cl$_2$S$_2$Ir$_2$: C, 42.01; H, 4.56%.

2.5. Preparation of [Cp*Ir(μ-SEt)$_3$IrCp*]Cl (5)

After EtSH (0.15 cm^3, 2.0 mmol) was added to a suspension of **4** (405 mg, 0.508 mmol) in CH$_2$Cl$_2$ (10 cm^3), the mixture was stirred at room temperature for 6 h. The resultant mixture was dried up in vacuo and the residue was extracted with CH$_2$Cl$_2$. Addition of hexane to the concentrated extract gave **5**·CH$_2$Cl$_2$ as a yellow crystalline solid (313 mg, 64%). ^{1}H NMR (CDCl$_3$): δ 1.27 (t, J = 7.6 Hz, 9H, SCH$_2$C*H*$_3$), 1.78 (s, 30H, Cp*), 2.60 (q, J = 7.6 Hz, 6H, SC*H*$_2$CH$_3$). *Anal.* Found: C, 33.39; H, 5.04. Calc. for C$_{27}$H$_{47}$Cl$_3$S$_3$Ir$_2$: C, 33.83; H, 4.94%.

2.6. Preparation of [Cp*Ir(μ-SPr^i)$_2$IrCp*] (3a)

Onto Na–Hg (0.5%, 4.58 g, 1.0 mmol) and **2a** (300 mg, 0.342 mmol) was added THF (7 cm^3), and the mixture was stirred at room temperature for 6 h. The reddish brown solution was collected by decantation and then evaporated to dryness in vacuo. The resulting solid was extracted with hexane and the extract was dried up again. Crystallization of the residue from toluene–MeCN afforded **3a** as dark red crystals (188 mg, 68%). ^{1}H NMR (C$_6$D$_6$): δ 1.29 and 1.30 (d, J = 6.7 Hz, 6H each, SCH*Me*$_2$), 2.02 (s, 30H, Cp*), 2.20 and 2.83 (sep, J = 6.7 Hz, 1H each, SC*H*Me$_2$). *Anal.* Found: C, 38.69; H, 5.56. Calc. for C$_{26}$H$_{44}$S$_2$Ir$_2$: C, 38.78; H, 5.51%.

2.7. Preparation of [Cp*Ir(μ-SCy)$_2$IrCp*] (3b)

This complex was obtained analogously from **2b** (300 mg, 0.288 mmol) and Na–Hg (0.3%, 13.56 g, 1.8 mmol) in 66% yield. ^{1}H NMR (C$_6$D$_6$): δ 2.07 (s, 30H, Cp*). *Anal.* Found: C, 43.55; H, 5.97. Calc. for C$_{32}$H$_{52}$S$_2$Ir$_2$: C, 43.41; H, 5.92%.

2.8. Preparation of [Cp*Ir(μ-H)(μ-SPr^i)$_2$IrCp*][OCOCF$_3$] (6a)

Into a solution of **3a** (102 mg, 0.127 mmol) in ether (7 cm^3) was added CF$_3$COOH (0.010 cm^3, 0.13 mmol) at −35°C, and the mixture was gradually warmed to room temperature with stirring. After 1 h, a yellow solid which deposited was filtered off and dried in vacuo. Recrystallization of the residue from THF–hexane afforded **6a** as red needles (69 mg, 59%). ^{1}H NMR (CDCl$_3$): δ − 16.98 (s, 1H, IrHIr), 1.05 and 1.23 (d, J = 6.7 Hz, 6H each, SCH*Me*$_2$), 2.00 and 2.19 (sep, J = 6.7 Hz, 1H each, SC*H*Me$_2$), 2.17 (s, 30H, Cp*). IR (KBr disk): 1698 cm^{-1} (ν(C=O)). *Anal.* Found: C, 36.60; H, 4.98. Calc. for C$_{28}$H$_{45}$O$_2$F$_3$S$_2$Ir$_2$: C, 36.59; H, 4.93%.

2.9. Preparation of [Cp*Ir(μ-H)(μ-SCy)$_2$IrCp*][OCOCF$_3$] (6b)

This complex was isolated as orange crystals in 37% yield from **3b** (80 mg, 0.090 mmol) and CF$_3$COOH (0.008 cm^3, 0.1 mmol) by the same method as that used to obtain **6a**. ^{1}H NMR (CDCl$_3$): δ − 16.95 (s, 1H, IrHIr), 2.16 (s, 30H, Cp*). IR (KBr disk): 1696 cm^{-1} (ν(C=O)). *Anal.* Found: C, 39.70; H, 5.35. Calc. for C$_{34}$H$_{53}$O$_2$F$_3$S$_2$Ir$_2$: C, 40.86; H, 5.35%.

2.10. X-ray crystallography of 2a and 3b

Single crystals of **2a** and **3b** were mounted in glass capillaries under Ar and transferred to a Rigaku AFC7R diffractometer equipped with a graphite-monochromated Mo Kα source (λ = 0.7107 Å). Cell constants and orientation matrices were derived from a least-squares fit of 25 machine-centered reflections with 39 < 2θ < 40°. The data collection was performed at room temperature. The intensities of three check reflections were measured every 150 reflections, which revealed no significant decay throughout the data collection for both compounds. Intensity data were corrected for Lorentz–polarization effects and for absorption (ψ-scans). Structure solution and refinements were carried out using the teXsan program package [8]. Coordinates of the non-hydrogen atoms were determined by the combination of Patterson methods and subsequent Fourier maps [9], and refined anisotropically by using full-matrix least-squares techniques, while hydrogen atoms were placed at the calculated positions (d(C–H) = 0.95 Å) and included at the final stages of refinements with fixed parameters, where hydrogen atoms were given the displacement factors (B_{eq}) 1.2 times greater than

Table 1
Details of X-ray crystallography for 2a and 3b

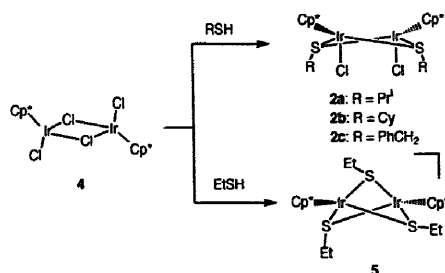|	2a	3b
Crystal data		
Formula	$C_{26}H_{44}Cl_2S_2Ir_2$	$C_{32}H_{52}S_2Ir_2$
FW	876.1	885.3
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2/n$
Crystal size (mm)	$0.10 \times 0.20 \times 0.50$	$0.20 \times 0.35 \times 0.40$
a (Å)	21.255(8)	8.912(6)
b (Å)	8.606(6)	11.224(6)
c (Å)	17.788(6)	16.496(6)
β (°)	118.39(2)	97.78(4)
V (Å³)	2862(2)	1634(1)
Z	4	2
D_{calc} (g cm⁻³)	2.033	1.798
μ(Mo Kα) (cm⁻¹)	96.60	83.00
Data collection		
2θ max. (°)	55	55
Scan method	ω–2θ	ω–2θ
Scan speed (° min⁻¹)	16	16
Unique reflections	3502	3961
Transmission factors	0.36–1.00	0.43–1.00
Solution and refinements		
No. reflections used	2674	2791
($I > 3\sigma(I)$)		
No. variables	145	163
Weighting scheme	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
R	0.040	0.030
R_w	0.032	0.024
Max. residual (e Å⁻³)	2.36	0.81

that of the associated atom. Important data for X-ray crystallography of 2a and 3b are listed in Table 1.

3. Results and discussion

3.1. Reactions of [Cp*IrCl(μ-Cl)₂IrCp*Cl] (4) with RSH

When 4 suspended in CH_2Cl_2 was treated with RSH at room temperature, two types of thiolate-bridged diiridium complexes were isolated from the reaction mixtures depending on the nature of R, viz. doubly bridged complexes [Cp*IrCl(μ-SR)₂IrCp*Cl] (2a: R = Pr^i; 2b: R = Cy; 2c: R = PhCH₂) or a triply bridged complex [Cp*Ir(μ-SEt)₃-IrCp*]Cl (5) (Scheme 1). A more bulkythiol, Bu^{t}SH, did not react with 4 even at 50°C in ClCH₂CH₂Cl. For the anterior diiridium complexes 2, the structure has been determined unambiguously by a single crystal X-ray diffraction study of 2a (vide infra), while the latter complex 5 has been characterized by analysis and spectroscopically.

Although several thiolate-bridged diiridium complexes are known (vide infra), those containing Ir(III) centers are still rare. In related work, reactions of 4 with lead or silver fluorothiolates have been reported previously [10], forming either mononuclear complexes [Cp*Ir(SR$_f$)₂] (R$_f$ = C$_6$F$_5$,

Scheme 1.

C_6F_4H-p) or dinuclear complexes such as [Cp*Ir(μ-SR$_f$)₃-IrCp*]Cl (R$_f$ = C₆H₄F-p, CF₃) and [Cp*Ir(SCF₃)(μ-SCF₃)₂-IrCp*(SCF₃)]. Furthermore, rhodium complexes with bridging fluorothiolate ligands [Cp*Rh(μ-SR$_f$)₃RhCp*] $^+$ (R$_f$ = C₆F₅, C₆H₄F-p, C₆H₄F-p) have analogously been isolated and fully characterized [10], while well-defined [Cp*RhCl(μ-SMe)₂RhCp*Cl] (7) and [Cp*Rh(μ-SMe)₃-RhCp*] $^+$ (8) have been known for some time [11].

3.2. Structures of diiridium complexes 2 and 5

The single-crystal X-ray analysis has disclosed unequivocally that 2a consists of two Cp*IrCl units connected by two SPr^i bridges. Important interatomic distances and angles in 2a are listed in Table 2, while the ORTEP drawing is shown in Fig. 1. The molecule has a crystallographically imposed C_2 axis passing through the center of the Ir₂S₂ plane and thus the two Cp* ligands as well as the two Cl ligands occupy the mutually *cis* positions. The Ir₂S₂ plane is puckered only slightly with a dihedral angle of 173° along the S–S vector and the two Pr^i groups in the thiolate ligands adopt the *syn* configuration both oriented toward the direction opposite to the sterically encumbered Cp* ligands. The Ir–Ir distance at 3.665(2) Å clearly suggests the absence of any bonding interaction between these two metal centers, which is almost comparable to the Ir(III)–Ir(III) separations of 3.568(1) and

Table 2
Selected interatomic distances and angles in 2a and 3b

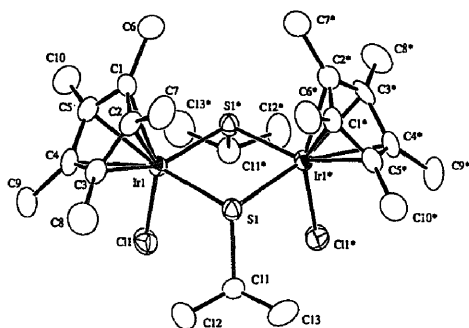|	2a	3b
Distances (Å)		
Ir(1)–Ir(1)*	3.665(2)	2.699(1)
Ir(1)–S(1)	2.391(2)	2.305(2)
Ir(1)*–S(1)	2.400(2)	2.311(2)
Ir(1)–Cl(1)	2.391(3)	
Ir(1)–C	2.163(9)–2.225(9)	2.155(6)–2.201(7)
S(1)–C	1.849(9)	1.833(6)
Angles (°)		
S(1)–Ir(1)–S(1)*	79.89(8)	88.77(8)
Ir(1)–S(1)–Ir(1)*	99.82(8)	71.56(5)
Cl(1)–Ir(1)–S(1)	93.85(9)	
Cl(1)–Ir(1)–S(1)*	92.40(9)	
Ir(1)*–Ir(1)–S(1)		54.32(5)
Ir(1)*–Ir(1)–S(1)*		54.13(5)

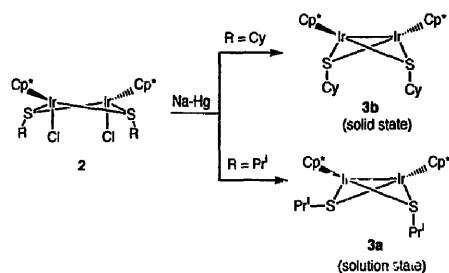Fig. 1. The X-ray structure of 2a. The thermal ellipsoids are drawn at the 50% probability level.

3.769(1) Å found in [Cp*(Me₃P)Ir(μ-S)₂IrCp*] [12] and 4 [13], as well as the Ir(III)–Ir(I) distance in [(cod)IrCl-(SC₆F₅)(μ-SC₆F₅)₂Ir(cod)] (3.660(1) Å) [14] ². These structural features are in good agreement with those reported for the closely related Rh complex 7 [11]. Structures of the Ru complexes [Cp*RuCl(μ-SR)₂RuCp*Cl] (R = Et [16], Prⁱ [1]) correlate well to that of 2a except for the presence of an Ru–Ru single bond in these diamagnetic Ru(III) complexes; the Ru–Ru distances in the SEt and SPrⁱ complexes being 2.850(2) and 2.853(2) Å, respectively.

The ¹H NMR spectrum of 2a is consistent with its X-ray structure, which shows one singlet assignable to the Cp* methyl protons along with one pair of doublet and septet due to the Prⁱ groups. From ¹H NMR criteria, it is conceivable that 2b and 2c have structures similar to that of 2a. Thus the spectrum of 2c indicates that two Cp* ligands as well as two CH₂Ph groups are equivalent, while that of 2b also showed the Cp* resonance as only one singlet, although complicated Cy resonances hampered characterization of the Cy orientation. As for the triply bridged complex 5, the ¹H NMR spectrum has disclosed the presence of the Cp* and SEt ligands in the ratio of 2:3. Equivalence of both of the two Cp* and the three SEt groups suggests a structure analogous to that of the Rh complex 8, having an approximate C₃ symmetry around the Ir–Ir vector with respect to the three SR groups (Scheme 1).

3.3. Reduction of 2 with Na–Hg to give [Cp*Ir(μ-SR)₂IrCp*] (3)

Treatment of 2a and 2b with excess Na–Hg (0.3–0.5%) in THF at room temperature gave dark red diiridium complexes 3a (R = Prⁱ) and 3b (R = Cy) (Scheme 2). An X-ray diffraction study has been undertaken by using a single crystal of 3b, the result of which is depicted in Fig. 2. Selected bond distances and angles are summarized in Table 2.

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² In contrast, non-bonding Ir–Ir distances in the thiolate-bridged dimeric Ir(I) complexes are significantly shorter and fall in the range e.g. 2.94–3.22 Å. See Refs. [14] and [15].
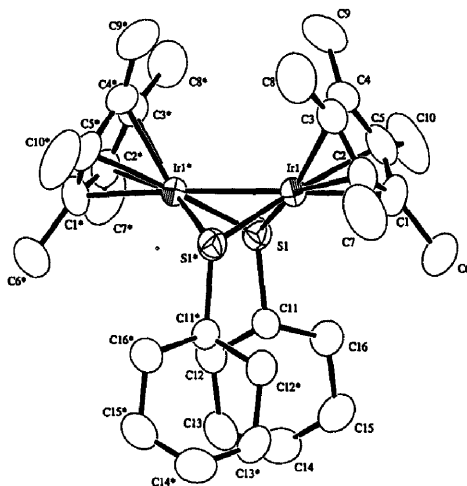

Scheme 2.

Fig. 2. The X-ray structure of 3b. The thermal ellipsoids are drawn at the 50% probability level.

Complex 3b has an expected dimeric structure, for which one half of the molecule relates to the other by a crystallographically imposed C₂ axis. The Ir–Ir distance of 2.699(1) Å is much shorter than that in 2a (3.665(2) Å), indicating the presence of the Ir–Ir single bond. This accounts well for the diamagnetic nature of 3 containing two d⁷ metal centers and the bond length observed for 3b is comparable to those in other thiolate-bridged Ir(II) complexes such as [{IrH(CO)[P(OMe)₃]}₂(μ-SBuⁱ)₂] (2.673(1) Å) (9) [15a], [{IrCl(cod)}₂(μ-SPh)₂] (2.800(1) Å) [15b], [{Ir(CO)(PMe₂Ph)}₂(μ-SBuⁱ)₂] (2.702(1) Å) [17] and [{P(OMe)₃}(CO)IrMe(μ-SBuⁱ)₂IrI(CO){P(OMe)₃}] (2.791(7) Å) [18]. Owing to the much shorter Ir–Ir contact than that in 2a, 3b has a bent Ir₂S₂ framework (dihedral angle along the S–S vector: 110° in 3b versus 173° in 2a) and a smaller Ir–S–Ir angle (71.56(5)° in 3b versus 99.82(8)° in 2a). The Cy groups of the thiolate ligands exhibit a *syn*-axial configuration with respect to the Ir₂S₂ ring.

However, the ¹H NMR spectrum of 3a shows two sets of doublet and septet with the same intensities arising from two inequivalent Prⁱ groups, in addition to only one singlet assign-

able to the Cp* methyl groups. This suggests that, at least in solution, the *anti* structure is plausible for 3a as illustrated in Scheme 2 [3]. The structure of 3b in solution is uncertain from the ^{1}H NMR criteria owing to the unresolvable complicated feature of the Cy resonances. As for the solid state structures of the four other Ir(II) complexes cited above, the *syn*-equatorial configuration of the two thiolate bridges has been demonstrated for only 9 and the other three compounds have been shown to consist of two *anti* thiolate ligands.

3.4. Reactions of 3 with CF₃COOH forming [Cp*Ir(μ-H)(μ-SR)₂IrCp*][OCOCF₃] (6)

Complex 3a reacted readily with 1 equiv. of CF₃COOH in ether to give the ionic Ir(III) complex 6a (R = Pr^i) in moderate yield (Eq. (1)).

$$\text{(1)}$$
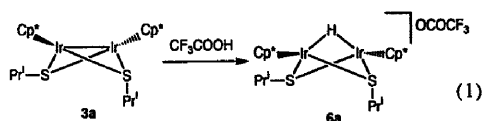
In the ^{1}H NMR spectrum of 6a, a singlet apparently assignable to the hydride proton appeared at -16.98 ppm. Furthermore, two Cp* ligands were recorded as one singlet, while two Pr^i groups resonated as two pairs of doublet and septet with the same intensities. These spectral data are indicative of a dimeric structure containing one hydride and two thiolate ligands which all bridge two Cp*Ir moieties symmetrically, where two Pr^i groups adopt an *anti* configuration [4]. The reaction of 3b with CF₃COOH under similar conditions resulted in the formation of the analogous complex 6b (R = Cy) but the configuration of the two Cy groups is uncertain.

4. Supplementary material

Tables listing atom coordinates, anisotropic temperature factors of non-hydrogen atoms, extensive bond distances and

angles, and observed and calculated structure factors, and figures illustrating a whole view of the molecules with full atom-numbering scheme for 2a and 3b are available from authors Y.M. or M.H. upon request.

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[3] Since the ^{1}H NMR spectra recorded at various temperatures are essentially unaltered and the *anti* configuration has been elucidated unambiguously for the Rh analogue [Cp*Rh(μ-SPr^i)₂RhCp*] in both the solid and solution state, it is likely that 3a also adopts the *anti* configuration in the solid form.

[4] The structure proposed here for 6a has been confirmed quite recently by the preliminary X-ray diffraction study of [Cp*Ir(μ-H)(μ-SPr^i)₂-IrCp*][OSO₂CF₃], which will be reported elsewhere.