A New type of Intramolecular H···H···H Interaction involving N–H···H(Ir)···H–N Atoms. Crystal and Molecular Structure of $[IrH(\eta^1\text{-}SC_5H_4NH)_2(\eta^2\text{-}SC_5H_4N)(PCy_3)]BF_4\cdot 0.72CH_2Cl_2$

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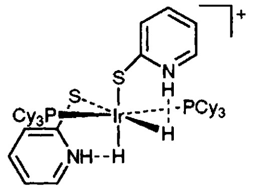
The iridium complexes, $[IrH(\eta^1\text{-}SC_5H_4NH)_2(\eta^2\text{-}SC_5H_4N)(PCy_3)](BF_4)$, **1**, and $[IrH(\eta^1\text{-}SC_5H_4NH)_2(\eta^1\text{-}SC_5H_4NH)_2(PCy_3)](BF_4)_2$, **2**, [Cy = cyclohexyl] in the solid state and in CD_2Cl_2 solution contain a new type of intramolecular H···H···H interaction contained in ten-membered bicyclic rings S–C–N–H···H(Ir)···H–N–C–S defined by the two 2-pyridiniumthiolate ligands coordinated in a monodentate fashion *via* sulfur to an iridium atom.

Recently, Lee *et al.*[1] and we[2] have independently discovered complexes that contain novel intramolecular H···H interactions of the type O–H···H–Ir and N–H···H–Ir respectively. The H···H distances in these complexes are in the range of 1.6–1.8 Å. These types of compounds are thought to be intermediates in the base catalysed heterolytic splitting of dihydrogen.[3] The iridium complex $[Ir\{H(\eta^1\text{-}SC_5H_4NH)\}_2(PCy_3)_2](BF_4)$, **3**, contains in CH_2Cl_2 solution two intramolecular Ir–H···H–N interactions in six-membered rings Ir–H···H–N–C–S, defined by the 2-pyridiniumthiolate ligands† coordinated in a monodentate fashion *via* sulfur to iridium. We also demonstrated[2] that this hydrogen–hydrogen interaction can be disrupted by introducing a competing hydrogen bond acceptor. Here we report the isolation and characterization of two new iridium complexes $[IrH(\eta^1\text{-}SC_5H_4NH)_2(\eta^2\text{-}SC_5H_4N)(PCy_3)](BF_4)$, **1**, and $[IrH(\eta^1\text{-}SC_5H_4NH)_2(\eta^1\text{-}SC_5H_4NH)_2(PCy_3)](BF_4)_2$, **2**, containing the novel intramolecular hydrogen–hydrogen interactions involving three hydrogen atoms to form a N–H···H(Ir)···H–N unit.

$IrH_5(PCy_3)_2$ (100 mg) was heated under reflux with 3.5 equiv. of protonated 2-mercaptopyridine $HSC_5H_4N\cdot HBF_4$ (92 mg) in $CHCl_3$ for 24 h to give a clear yellow solution. Concentration of the solution followed by addition of 2:1 *n*-hexane:diethyl ether yielded the yellow microcrystalline, air-stable complex $[IrH(\eta^1\text{-}SC_5H_4NH)_2(\eta^2\text{-}SC_5H_4N)(PCy_3)](BF_4)$, **1**, analytically pure and in good yield (82 mg, 70%). Complex **1** can also be prepared by treating complex **2** (see below) with 3 equiv. of NEt_3 in CH_2Cl_2 at 30 °C for 20 min. Removal of solvents followed by addition of 2:1 hexane–diethyl ether yields a yellow crystalline solid. The crystal structure of **1**‡ as deduced from a X-ray diffraction study at 173 K reveals an iridium atom in a distorted octahedral environment (Fig. 1). It is surrounded by a PCy_3 group, two 2-pyridiniumthiolate ligands bound *via* sulfur atoms S(2) and S(3), and a chelating 2-pyridinethiolate ligand. The hydride ligand H(1ir) *trans* to the chelating sulfur S(1) completes the octahedral geometry around the Ir centre. The Ir–H hydrogen atom H(1ir) is placed in the calculated position at 1.60(5) Å from the Ir atom in an area of positive electron density. The X-ray structure shows that the N–H groups of the 2-pyridiniumthiolate ligands are located close to the position occupied by the Ir–H hydride. In this arrangement the average H···H distance in the N–H···H(Ir)···H–N unit is calculated to be 1.9 ± 0.2 Å. The presence of the hydride is also inferred from the *trans*-influence directed at the sulfur atom S(1). The Ir–S(1) bond [2.486(2) Å] which is *trans* to the Ir–H bond is significantly longer than the other two Ir–S bonds in the molecule [Ir–S(2) 2.355(2), Ir–S(3) 2.351(2) Å]. The H–N–C–S–Ir–S–C–N–H unit is planar (mean deviation from plane 0.04 Å), and the dihedral angle between this plane and the plane containing the Ir atom and the three sulfur atoms [S(1), S(2) and S(3)] is 30°.



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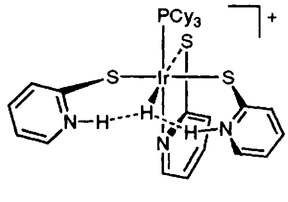
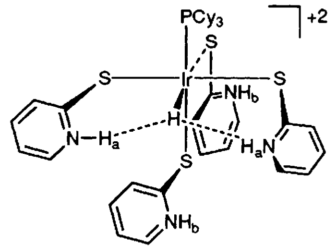


1



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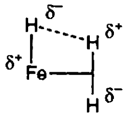
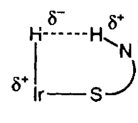


A



B

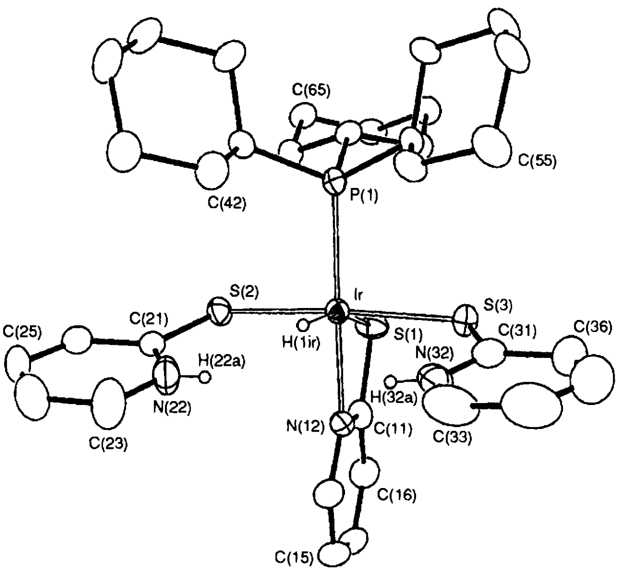


Fig. 1 A thermal ellipsoid plot of the cation **1** showing the relative positions of the hydrogen atoms H(22A), H(1ir) and H(32a) involved in the H···H···H interaction. The hydrogen atom H(1ir) is placed in the calculated position while those of the N–H bonds are in the refined positions. Selected bond lengths (Å) and bond angles (°) are: Ir–P(1) 2.309(2), Ir–S(1) 2.486(2), Ir–S(2) 2.355(2), Ir–S(3) 2.351(2), Ir–N(12) 2.122(5), N(12)–Ir–P(1) 172.1(1), S(3)–Ir–S(2) 169.7(1), S(1)–Ir–S(2) 85.3(1), S(1)–Ir–S(3) 84.8(1), P(1)–Ir–S(1) 105.8(1), P(1)–Ir–S(2) 91.8(1), P(1)–Ir–S(3) 93.8(1), N(12)–Ir–S(1) 66.4(1), N(12)–Ir–S(2) 86.3(2), N(12)–Ir–S(3) 86.9(2).

Additional evidence for the N–H···H(Ir)···H–N interaction comes from the ^1H NMR data for **1** in CD_2Cl_2 solution. The two hydrogen bonded NH protons in **1** appear at δ 12.7 as a broad singlet with a minimum T_1 of 0.215 s (relaxation rate 4.65 s^{-1}) at 400 MHz, 213 K. Each of these protons is near to two dipolar nuclei; the ^{14}N nucleus and a hydride. When the relaxation contribution (1.8 s^{-1}) of the ^{14}N at about 0.95 Å is subtracted from the relaxation rate of N–H, the calculated[5] IrH–HN distance is 1.80 ± 0.05 Å. Similarly, the hydride resonance centred at δ −18.4 is a doublet [$^2J_{PH}$ 17.3 Hz] with a minimum T_1 of 0.165 s (400 MHz, 183 K). When the relaxation contribution of the cyclohexyl proton (0.4 s^{-1}) at about 2.3 Å is subtracted from the hydride relaxation rate (6.1 s^{-1}), the calculated hydride–HN distance is 1.81 ± 0.05 Å. Therefore, the H···H distance in the N–H···H(Ir)···H–N unit of **1** in CD_2Cl_2 is about 1.80 ± 0.03 Å, which is similar to the distance calculated from the X-ray structure (1.9 ± 0.2 Å). The presence of H···H···H contact in solution was also confirmed by an NOE difference experiment; selective irradiation of hydride resonance leads to 12% enhancement of the NH peak.

$IrH_5(PCy_3)_2$ (50 mg) was stirred with $HSC_5H_4N{\cdot}HBF_4$ (53 mg) in CH_2Cl_2 for 0.5 h to give a clear yellow solution. Removal of solvent followed by washing with hexanes yielded analytically pure complex **2** (55 mg, 76%). The structure of this complex was characterized by ^1H NMR and confirmed by a preliminary X-ray crystallographic study.§ Evidence for the N–H···H(Ir)···H–N interactions in solution was obtained from the ^1H NMR experiment. The Ir–H hydride resonance appears as a doublet centred at δ −18.5 due to coupling to PCy_3 in the *cis* position [$^2J_{PH}$ 16.8 Hz] and integrates to one hydrogen atom. The resonances due to N–H protons H_a and H_b appear as broad singlets at δ 12.5 and 13.1, respectively, and each resonance integrates to two hydrogen atoms. Below 233 K, the IrH, NH_a and NH_b resonances broaden considerably and the resonance due to NH_b splits into two separate peaks centred at δ 13.3 and 13.2. At this temperature the T_1 values (at 400 MHz) of IrH, NH_a and NH_b are 0.217, 0.250 and 0.524 s (the average of 0.520 and 0.527 s measured for the split peaks of NH_b resonance), respectively. The large T_1 value (0.524 s) of the resonance at δ 13.1 suggests that this proton is not associated in the H···H···H interaction, while the resonance at δ 12.5 which has a T_1 value (0.250 s) comparable to that of Ir–H (0.217 s) is the one that is involved in the intramolecular H···H···H interaction. The Ir–H hydrogen atom is near to two dipolar nuclei, namely the two NH_a hydrogen atoms. The calculated IrH–H_aN distances on the basis of a minimum T_1 value of 0.217 s for IrH is 1.86 ± 0.05 Å. Similarly, each of the NH_a protons are also near to two dipolar nuclei; the ^{14}N nucleus at about 0.95 Å (relaxation rate contribution of 1.8 s^{-1}) and the hydride which must therefore be at 1.88 ± 0.05 Å. An NOE difference experiment has also confirmed the presence of N–H_a···H(Ir)···H_a–N type hydrogen–hydrogen interaction in solution of **2**; irradiation of the hydride resonance at room temperature resulted in 4.3% enhancement of the NH_a peak at δ 12.5, while no enhancement was observed for the NH_b resonance at δ 13.1. There is no observable coupling between H_a and Ir–H.

The non-bonding H···H distance of 1.86 ± 0.01 Å between one of the hydrogen atoms of the dihydrogen ligand and a *cis*-hydride in $Fe(H)_2(\eta^2\text{-}H_2)(PEtPh_2)_3$[6] falls in the range of H···H distances of 1.75–1.90 Å in complexes **1**, **2** and **3**. Theoretical studies have attributed the short H···H contact and the unusual tilt of the η^2-H_2 ligand observed in this iron complex to either an attractive *cis*-effect[6,7] in which there is a covalent overlap between the filled Fe–H σ-orbital and an empty H–H σ*, or to a dipole–dipole interaction[8] between a polarised η^2–H_2 ligand and the *cis*-hydride as shown in **A**. One could argue that a similar attractive covalent '*cis*-effect', or polarization and alignment of Ir–H and N–H bonds occur in the above studied iridium complexes as shown in **B**, and that they are responsible for these unusual types of intramolecular H···H interactions.

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Footnotes

† 2-Pyridiniumthiolate ligand is also referred to as 1*H*-pyridine-2-thionato; see ref. 4.

‡ *Crystal data* for **1** (crystallised from CH_2Cl_2–pentane): M = 954.05, monoclinic, space group $P2_1/n$, a = 12.486(6), b = 16.552(4), c = 19.535(4) Å, β = 103.79(2), V = 3921(2) Å^3, Z = 4, T = 173 K, D_c = 1.616 g cm^{-3}, F(000) = 1913, μ = 3.751 mm^{-1}, λ = 0.71073 Å, crystal dimensions 0.36 × 0.41 × 0.18 mm, 9401 reflections with $I > 2\sigma(I)$ converged at R = 0.0470, wR = 0.0926 after a semi-empirical absorption correction. The hydrogen atom on the iridium, H(1ir), was isotropically refined with an Ir–H distance fixed at 1.60(5) Å. Calculations were performed by using SHELXTL-PC and SHELXL-93.[9] A difference electron density contour map in the plane containing H(22a), H(32a) and H(1ir) atoms, experimental details of the treatment of the Ir–H atom, H(1ir), in the X-ray structure refinement, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ The details of the single crystal X-ray structural data of **2** will be published elsewhere.

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