Heterolytic and Homolytic Activation of Dihydrogen at an Unusual Iridium (II) Sulfide

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Received March 6, 2001

Two pathways are recognized for the activation of dihydrogen by metal catalysts, homolytic and heterolytic. Homolytic activation involves oxidative addition to metals usually in low oxidation states. Heterolytic activation, which occurs with no formal change in oxidation state, is associated with metals in higher oxidation states and gives rise to hydridic (H^-, usually attached to a metal) and protic (H^+) centers.[1] Heterolytic activation is especially important for metal sulfides, being central to three topical catalytic processes, nitrogen fixation,[2] hydrogen metabolism,[3] and fossil fuel desulfurization (HDS).[4] Soluble metal sulfido complexes are known to add H_2, leading to the formation of SH ligands.[5,6] In this report we describe the preparation of a very unusual metal sulfide that is of further interest because it reacts with 2 equiv of dihydrogen via *both* homolytic and heterolytic pathways.

We have previously generated reactive metal sulfides species via desulfurization of polysulfido precursors.[7] This approach is guided by the following concepts:

(i) for a given molecularity, the reactivity of MS_x species toward small molecule substrates correlates with M/S ratio,

(ii) metal polysulfides can be viewed as thermodynamically stable adducts of more reactive species with higher M/S ratios, and

(iii) the exothermic conversion[8] of $PR_3 + S$ into SPR_3 can drive the formation of reactive species from polysulfido precursors.

We have applied this approach to the generation of reactive sulfides of iridium, a metal known to be highly active for HDS.[4,9]

Our starting reagent was $(NBu_4)_3[Ir(S_6)_2(S_x)]$ (**1**; $x = 4$, 6), a mixture of two closely related octahedral complexes recently characterized by Albrecht-Schmitt and Ibers.[10] For present purposes, these two species behave indistinguishably. ^{31}P NMR measurements show that treatment of MeCN solutions of **1** with 20 equiv of PPh_3 gives ∼12 equiv of $SPPh_3$. Upon standing, the auburn reaction solution produced red-green pleochroic microcrystals of $Ir_2S_2(PPh_3)_4$ (**2**, yield: 40−60%). In this reaction the PPh_3 serves both to remove sulfur and to stabilize the resulting Ir−S species.

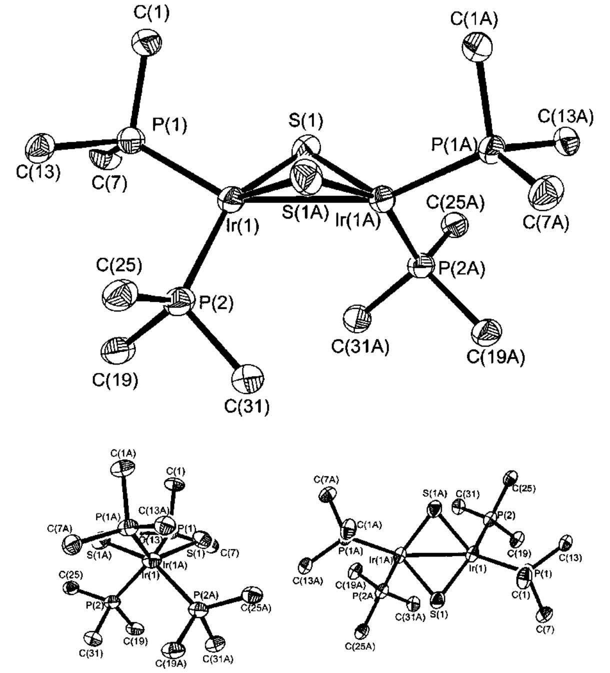

Figure 1. Structure of **2** with thermal ellipsoids set at 50% probability level. The structure of **3** is similar. Key parameters (Å, deg) for **2**: Ir(1)−Ir(1A), 2.7575(3); Ir(1)−S(1), 2.2706(13); Ir(1)−S(1A), 2.3106(12); Ir(1)−P(1), 2.2606(12); Ir(1)−P(2), 2.2705(13); S(1)−Ir(1)-S(1A), 95.70(5); Ir(1)−S(1)-Ir(1A), 74.01(4). Key parameters (Å, deg) for **3**: Ir(1)−Ir(1A), 2.7541(5); Ir(1)−S(1), 2.290(2); Ir(1)−S(1A), 2.362(2); Ir(1)−P(1), 2.267(2); Ir(1)−P(2), 2.2666(18); S(1)−Ir(1)-S(1A), 90.69(8); Ir(1)−S(1)-Ir(1A), 72.57(5). For **2**, **3**, **4**, respectively: P−Ir−Ir−P dihedral angles: 69.9, 56, 44.2°; for S−Ir−Ir−S, 136.4, 123.8, 103°.

Crystallographic analysis of **2** reveals a bitetrahedral structure with a pair of μ-S atoms (Figure 1).[11] Sulfides of Ir^{II} (or Rh^{II}) are unprecedented and tetrahedral complexes of Ir are very rare.[12] In **2,** the Ir−Ir separation of 2.75 Å is consistent with Ir−Ir bonding, as is its diamagnetism. The distortion of the IrP_2S_2 units from tetrahedral symmetry is ascribed to steric interactions between the pair of quasi-axial PPh_3 ligands. ^{31}P NMR spectrum of **2** consists of a single resonance (δ16) even at −90 °C; the dynamic process is proposed to involve a flattened (D_{2h}) Ir_2S_2 butterfly intermediate.

Compound **2** bears an obvious relationship to $Ir_2(\mu\text{-S})(\mu\text{-SH})(\mu\text{-H})H_2(PPh_3)_4$ (**4**), prepared previously by the addition of H_2S to $[IrH_2(PPh_3)_2(Me_2CO)_2]^+$ followed by deprotonation. Mueting and Pignolet showed that **4** exists as a pair of isomers that differ with respect to the stereochemistry at μ-S*H* (^1H NMR: δ 0.39, −0.9).[13] Consistent with its structural similarity to **4**, **2** (toluene

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(11) **2**: $C_{72}H_{6}0Ir_2P_4S_2.(MeCN)_2$, green monoclinic *C*2/*c*; 0.44 mm × 0.32 mm × 0.30 mm; $a = 22.3333(11)$ Å, $b = 13.1125(7)$ Å, $c = 24.0252(12)$ Å; $\alpha = \gamma = 90°$, $\beta = 112.6350(10)°$; $V = 6581.0(6)$ Å^3; $Z = 4$. 193 K; λ(Mo Kα), $1.83 = \Theta = 28.71°$; 21290 reflns. [R(int) = 0.0540] reflns (7956 unique); R1, wR2 [$I > 2\sigma(I)$] = 0.0376, 0.0791. **3**: $C_{72}H_{60}Ir_2P_4S_2.(Me_2CO)_2$, black monoclinic *C*2/*c*; 0.02 mm × 0.17 mm × 0.16 mm; $a = 23.3048(13)$ Å, $b = 13.1143(7)$ Å, $c = 24.1374(13)$ Å; $\alpha = \gamma = 90°$, $\beta = 114.4350(10)°$; $V= 6716.3(6)$ Å^3; $Z = 4$. 193(2) K.; λ(Mo Kα), $1.83 = \Theta < 22.50°$; 19787 reflns [R(int) = 0.0775] (4395 unique); R1, wR2 [$I > 2\sigma(I)$] = 0.0312, 0.0547.

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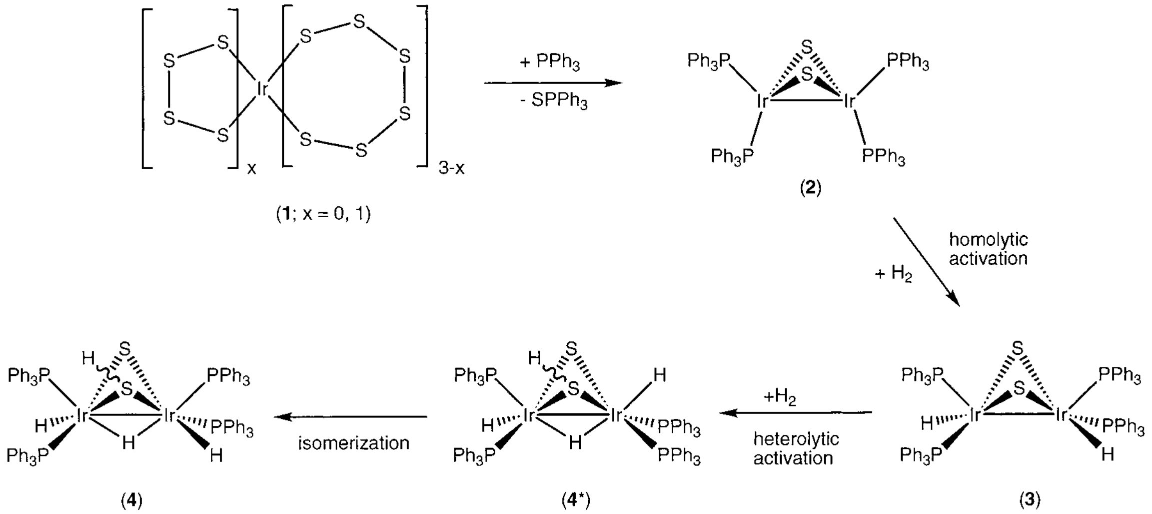
Scheme 1



solution) absorbs 2 equiv of H_2 (1 atm, min, 25 °C) to give **4** in quantitative yield (see Scheme 1).

The availability of **2** and **4** provided a unique opportunity to examine the sequence of the heterolytic (resulting in both Ir−H and S−H bonds) versus homolytic (resulting in two Ir−H bonds) processes. We first confirmed that **2** and **4** do not react. Toluene-d_8 solutions of **2** absorb 1 equiv of H_2 at 25 °C to give olive green **3**. Crystallographic and NMR analysis of **3**-d_2 reveal a C_2-symmetric species $[Ir^{III}(D)(PPh_3)_2]_2(\mu\text{-}S)_2$; the terminal deuterium atoms were located crystallographically. Compounds **2**, **3**, and **4** are structurally very similar, the most significant difference being the PIrIr′P′ and SIrIr′S′ torsional angles which decrease with higher coordination numbers (Figure 1). ^1H NMR spectra in the hydride region for **3** feature a broadened triplet at −60 °C and a quintet at +70 °C. The ^{31}P NMR spectrum of **3** features a pair of singlets (−80 °C) that coalesce near room temperature. It is known that $J(P,P')$ can be small for *cis*-phosphines;[14] the values of $J(Ir\mathit{H},P)$ are normal however. Overall, the DNMR results can be explained by a rapid intermetallic hydride exchange. In warm (40 °C) DMF solutions **3** loses H_2 to reform **2**. Extrapolating from this observation, a new synthesis of **2** involves the reaction of $IrCl(PPh_3)_3$ and NaSH in DMF at 40 °C.

Since **3** results from homolytic activation of hydrogen, that is, $(Ir^{II})_2(S)_2 + H_2 \rightarrow (HIr^{III})_2(S)_2$, the conversion **3** into **4** must be heterolytic in character. Labeling studies show, however, that this transformation is complex. The products from the addition of H_2 to **3**-d_2 and of D_2 to **3** were indistinguishable, with SH:IrH ratio of ~1:3, with a negligible equilibrium isotope effect.[5] Thus, while the conversion of **3** into **4** is formally heterolytic (with no change in formal oxidation state), the pathway must allow exchange between the Ir*H* and S*H* centers (eq 1).

$$\underset{\mathbf{3}\text{-}d_2}{Ir_2(\mu\text{-}S)_2(D)_2(PPh_3)_4} + H_2 \rightarrow \underset{\mathbf{4}\text{-}d_2}{Ir_2(\mu\text{-}S)(\mu\text{-}SD_{0.5}H_{0.5})(\mu\text{-}D_{0.5}H_{0.5})(D_{0.5}H_{0.5})_2(PPh_3)_4} \quad (1)$$

Low-temperature (−20 °C) ^1H NMR measurements revealed a short-lived intermediate (**4***) in the conversion of **3** to **4** (the conversion of **2** into **3** occurs with no detectable intermediates). Under optimized conditions, **4*** comprises ~20% of the mixture. Like **4**, **4*** consists of a pair of isomers each with nonequivalent SH and IrH units (other isomers than shown are possible). We propose that the isomerization of **4*** into **4** proceeds via the opening of one μ-H linkage followed by pseudorotation of the five-coordinate Ir center. Under an excess of H_2, the conversions of **3** into **4*** and of **4*** into **4** are first-order in the diiridium compounds, with rate constants (25 °C) of 3.0×10^{-5} and 6.50×10^{-5} s^{-1} atm^{-1}, respectively, assuming $P(H_2) \sim 1$ atm. When **4***-d_2 is generated via **3**-d_2 + H_2, the hydrogen is distributed roughly equally over all sites, indicating that isotopic scrambling is a very low energy process.

In summary, the new species $Ir_2S_2(PPh_3)_4$, a unique Ir(II) sulfide, exhibits unusual reactivity. This complex binds 2 equiv of H_2, via an initial homolytic process followed by heterolytic activation. The high reactivity of **2** and **3** toward H_2 suggests that they will prove to be broadly reactive toward other reagents.

Acknowledgment. This research was supported by NSF and DOE. We thank Scott Wilson for assistance with X-ray crystallography.

Supporting Information Available: Atomic coordinates, bond distances and angles, thermal parameters for compounds **2** and **3** (PDF). X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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