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# Iridium assisted S–H and C–H activation of benzaldehyde thiosemicarbazones. Synthesis, structure and electrochemical properties of the resulting complexes

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ABSTRACT

Reaction of five **4-R**-benzaldehyde thiosemicarbazones (R = $OCH_3$, $CH_3$, H, Cl and $NO_2$) with $[Ir(PPh_3)_3Cl]$ in refluxing ethanol in the presence of a base ($NEt_3$) affords complexes of three different types, *viz.* **1-R**, **2-R** and **3-R**. In the **1-R** complexes the thiosemicarbazone is coordinated to iridium as a monoanionic bidentate N,S-donor forming a four-membered chelate ring. Two triphenylphosphines, a hydride and a chloride are also coordinated to the metal center. The **2-R** complexes are very similar in composition and stereochemistry to the corresponding **1-R** complexes, except that a second hydride is bound to iridium instead of the chloride. In the **3-R** complexes, the thiosemicarbazones are coordinated to iridium as dianionic tridentate C,N,S-donors forming two adjacent five-membered chelate rings. Two triphenylphosphines and a hydride are also coordinated to the metal center. Structures of the **1-$NO_2$**, **2-$NO_2$** and **3-$NO_2$** complexes have been determined by X-ray crystallography. Reaction of the same **4-R**-benzaldehyde thiosemicarbazones with $[Ir(PPh_3)_3Cl]$ in refluxing toluene in the presence of $NEt_3$ affords complexes of two types, *viz.* **3-R** and **4-R**. The **4-R** complexes are very similar in composition and stereochemistry to the corresponding **3-R** complexes, except that a chloride is bound to iridium instead of the hydride. Structure of the **4-$CH_3$** complex has been determined by X-ray crystallography. In all the complexes the two $PPh_3$ ligands are trans. All the complexes show intense MLCT transitions in the visible region. Cyclic voltammetry on the complexes shows an Ir(**III**)–Ir(**IV**) oxidation on the positive side of SCE followed by an oxidation of the coordinated thiosemicarbazone. A reduction of the coordinated thiosemicarbazone is also observed on the negative side of SCE.



## 1. Introduction

The chemistry of thiosemicarbazone complexes of the transition metal ions has been receiving significant current attention, largely because of the bioinorganic relevance of these complexes [1]. A large majority of the thiosemicarbazone complexes have found wide medicinal applications owing to their potentially beneficial biological (*viz.* antibacterial, antimalarial, antiviral and antitumor) activities [2]. Systematic studies on the binding of thiosemicarbazones to different transition metal ions are of considerable importance in this respect. However, we have been exploring the chemistry of platinum metal complexes of the thiosemicarbazones [3], with the primary objective of gaining a chemical control over the variable binding mode of these ligands, and the present work has emerged out of this exploration. The aim of the present study has been to scrutinize the interaction of a group of **4-R**-benzaldehyde thiosemicarbazones (**I**) with iridium. It may be relevant to mention here that though the chemistry of thiosemicarbazone complexes of many transition metals has been extensively studied [1], that of iridium appears to have remained practically unexplored [3d]. Upon their reaction with ruthenium and osmium the benzaldehyde thiosemicarbazones (**I**) have been observed to bind to the metal centers, via dissociation of the acidic proton, as monoanionic bidentate N,S-donors forming a rather unusual four-membered chelate ring (**II**) [3a,h–j]. Our investigations have revealed that in view of the geometry of these ligands (**I**) across the C=N bond, formation of the four-membered chelate ring (**II**) is most favorable and that of the five-membered chelate ring (**III**), which appears to be very likely for the thiosemicarbazones in general, is not possible because of the steric hindrance that develops between the phenyl ring of the benzaldehyde thiosemicarbazone and the metal center. It is worth noting here that we have not been able to find a single example of a structurally characterized complex of the benzaldehyde thiosemicarbazones (**I**), where the thiosemicarbazone is coordinated as in **III**. Five-membered chelate ring (**IV**) formation by the benzaldehyde

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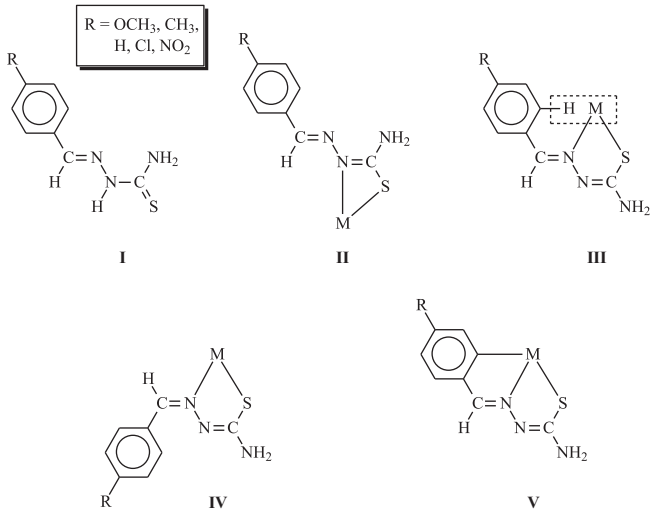
thiosemicarbazones (**I**) has been observed only in very few cases, which are associated with conformational change around the C=N bond [4]. Though five-membered chelate ring (**III**) formation by the benzaldehyde thiosemicarbazones (**I**) without any conformational change has been realized to be impossible, closeness of the phenyl ring to the metal center in **III** points to the possibility of its orthometallation (**V**) via C–H bond activation. Such C–H bond activation is of significant contemporary importance, with particular reference to metal mediated chemical transformations of organic molecules [5]. With the intention of inducing coordination mode **V** in the benzaldehyde thiosemicarbazone ligands (**I**), their reaction has been carried out with a reactive iridium complex, *viz.* $[Ir(PPh_3)_3Cl]$. This particular iridium complex has been chosen as the starting material because of its demonstrated ability to accommodate a tridentate ligand via oxidative addition and, more importantly, its proven efficiency to successfully mediate C–H bond activation of organic molecules [3d,6]. This simple strategy has indeed worked nicely, affording a group of organoiridium complexes, in addition to complexes of other types. This paper deals with the chemistry of all these complexes, with special reference to their formation, structure and electrochemical properties.




## 2. Experimental

### 2.1. Materials

Iridium trichloride was obtained from Arora Matthey, Kolkata, India. $[Ir(PPh_3)_3Cl]$ was prepared as before [6b]. Thiosemicarbazide and the five *para*-substituted benzaldehydes were purchased from SRL, Mumbai, India. The thiosemicarbazone ligands were prepared by reacting equimolar amounts of thiosemicarbazide and the respective *para*-substituted benzaldehyde in 1:1 ethanol–water mixture. Purification of acetonitrile and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were performed as reported in the literature [7]. All other chemicals and solvents were reagent grade commercial materials and were used as received.

### 2.2. Synthesis

#### 2.2.1. *1*-$NO_2$, *2*-$NO_2$ *and* *3*-$NO_2$

*para*-Nitrobenzaldehyde thiosemicarbazone (24 mg, 0.10 mmol) was dissolved in ethanol (50 mL) and triethylamine (20 mg, 0.20 mmol) was added to it. The solution was then purged with a stream of dinitrogen for 10 min and to it was added $[Ir(PPh_3)_3Cl]$ (100 mg, 0.10 mmol). The mixture was refluxed under a dinitrogen atmosphere for 24 h, whereby a red solution was obtained. Evaporation of this solution afforded a dark solid, which was subjected to purification by thin layer chromatography on a silica plate. With benzene as the eluant, two distinct red bands separated, which were extracted separately with acetonitrile. Evaporation of the first red fraction gave a 1:1 mixture (in the form of co-crystals) of **1**-$NO_2$ and **2**-$NO_2$ (Yield: 42%) and that of the second red fraction afforded **3**-$NO_2$ (Yield: 25%).

*Anal.* Calc. for **1**-$NO_2$ and **2**-$NO_2$: C, 55.11; H, 4.01; N, 5.84. Found: C, 55.43; H, 4.00; N, 5.88%. $^1$H NMR [8]: −23.32 (t, hydride, $J_{P-H}$ = 13.5); −20.88 (d of t, hydrides, $J_{P-H}$ = 16.0, $J_{H-H}$ = 7.0); −20.82 (d of t, hydrides, $J_{P-H}$ = 16.0, $J_{H-H}$ = 7.0); 4.63 (s, $NH_2$); 4.99 (s, $NH_2$); 7.05 (s, 1H); 7.19 (d, 2H, $J_{H-H}$ = 8.8); 7.21–7.84 (2H + 4$PPh_3^*$); 7.99 (d, 2H, $J_{H-H}$ = 8.8); 8.04 (d, 2H, $J_{H-H}$ = 8.8); 8.09 (s, 1H). *Anal.* Calc. for **3**-$NO_2$: C, 56.22; H, 3.94; N, 5.96. Found: C, 56.35; H, 3.92; N, 5.99%. $^1$H NMR: −14.26 (t, hydride, $J_{P-H}$ = 16.7); 4.46 (s, $NH_2$); 6.74 (d, 1H, $J_{H-H}$ = 8.3); 7.20–7.62 (1H + 2$PPh_3^*$); 7.32 (d, 1H, $J_{H-H}$ = 8.1); 7.49 (s, 1H).

#### 2.2.2. *2*-*R* *and* *3*-*R* ($R \neq NO_2$)

All the **2**-**R** and **3**-**R** ($R \neq NO_2$) complexes were synthesized by following the same above procedure using appropriate *para*-substituted benzaldehyde thiosemicarbazone (**I**, $R \neq NO_2$) instead of *para*-nitrobenzaldehyde thiosemicarbazone. A yellow solution was obtained from the synthetic reaction, which afforded a yellow solid upon evaporation. Purification was achieved by thin layer chromatography on a silica plate. With benzene as the eluant, two distinct yellow bands separated, which were extracted separately with acetonitrile. Evaporation of the first yellow fraction gave **2**-**R** (Yield: ∼40%) and that of the second yellow fraction afforded **3**-**R** (Yield: ∼25%).

*Anal.* Calc. for **2**-$OCH_3$: C, 58.30; H, 4.53; N, 4.53. Found: C, 58.71; H, 4.47; N, 4.59%. $^1$H NMR: −20.25 (d of t, hydride, $J_{P-H}$ = 16.0, $J_{H-H}$ = 6.5); −15.80 (d of t, hydride, $J_{P-H}$ = 16.0, $J_{H-H}$ = 6.5); 3.76 (s, $OCH_3$); 4.48 (s, $NH_2$); 7.21–7.29 (4H*); 7.30–7.65 (azomethine + 2$PPh_3^*$). *Anal.* Calc. for **3**-$OCH_3$: C, 58.43; H, 4.33; N, 4.54. Found: C, 58.91; H, 4.37; N, 4.56%. $^1$H NMR: −14.50 (t, hydride, $J_{P-H}$ = 16.5); 3.25 (s, $OCH_3$); 4.25 (s, $NH_2$); 6.12 (s, 1H); 6.09 (d, 1H, $J_{H-H}$ = 7.4); 6.63 (d, 1H, $J_{H-H}$ = 7.5); 6.81 (s, azomethine); 7.13–7.75 (2$PPh_3^*$).

*Anal.* Calc. for **2**-$CH_3$: C, 59.33; H, 4.61; N, 4.61. Found: C, 59.82; H, 4.53; N, 4.67%. $^1$H NMR: −19.33 (d of t, hydride, $J_{P-H}$ = 16.5, $J_{H-H}$ = 6.0); −15.27 (d of t, hydride, $J_{P-H}$ = 16.5, $J_{H-H}$ = 6.0); 1.99 (s, $CH_3$); 4.49 (s, $NH_2$); 7.05–7.15 (4H*); 7.29–7.66 (azomethine + 2$PPh_3^*$). *Anal.* Calc. for **3**-$CH_3$: C, 59.46; H, 4.40; N, 4.62. Found: C, 60.02; H, 4.44; N, 4.67%. $^1$H NMR: −14.21 (t, hydride, $J_{P-H}$ = 16.5); 1.78 (s, $CH_3$); 4.61 (s, $NH_2$); 6.52 (s, 1H); 6.65 (d, 1H, $J_{H-H}$ = 7.4); 6.96 (s, azomethine); 7.02 (d, 1H, $J_{H-H}$ = 8.2); 7.12–7.58 (2$PPh_3^*$).

*Anal.* Calc. for **2**-**H**: C, 58.92; H, 4.46; N, 4.69. Found: C, 59.37; H, 4.41; N, 4.62%. $^1$H NMR: −19.31 (d of t, hydride, $J_{P-H}$ = 18.0, $J_{H-H}$ = 6.0); −15.28 (d of t, hydride, $J_{P-H}$ = 16.5; $J_{H-H}$ = 6.0); 4.55 (s, $NH_2$); 7.07–7.11 (3H*); 7.13–7.16 (2H*); 7.18–7.68 (azomethine + 2$PPh_3^*$). *Anal.* Calc. for **3**-**H**: C, 59.05; H, 4.25; N, 4.70. Found: C, 59.39; H, 4.23; N, 4.69%. $^1$H NMR: −14.48 (t, hydride, $J_{P-H}$ = 18.0); 4.26 (s, $NH_2$); 6.05 (t, 1H, $J_{H-H}$ = 7.0); 6.43 (t, 1H, $J_{H-H}$ = 7.3); 6.59 (d, 1H, $J_{H-H}$ = 7.3); 6.64 (d, 1H, $J_{H-H}$ = 7.3); 6.71 (s, azomethine); 7.05–7.69 (2$PPh_3^*$).

*Anal.* Calc. for **2**-**Cl**: C, 56.73; H, 4.19; N, 4.51. Found: C, 57.11; H, 4.22; N, 4.55%. $^1$H NMR: −19.27 (d of t, hydride, $J_{P-H}$ = 16.5, $J_{H-H}$ = 6.0); −15.34 (d of t, hydride, $J_{P-H}$ = 18.0; $J_{H-H}$ = 6.0); 4.58 (s, $NH_2$); 7.05 (d, 2H, $J_{H-H}$ = 8.0); 7.16 (d, 2H, $J_{H-H}$ = 8.5); 7.20–7.67 (azomethine + 2$PPh_3^*$). *Anal.* Calc. for **3**-**Cl**: C, 56.85; H, 3.98; N, 4.52. Found: C, 57.29; H, 3.92; N, 4.56%. $^1$H NMR: −14.49 (t, hydride, $J_{P-H}$ = 18.0); 4.30 (s, $NH_2$); 6.46 (d, 1H, $J_{H-H}$ = 8.0); 6.51 (s,