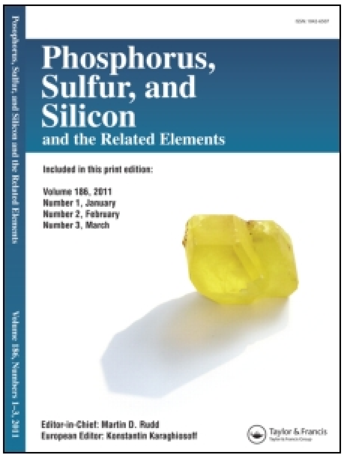

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COORDINATION CHEMISTRY OF DITHIAZOLYL RADICALS

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COORDINATION CHEMISTRY OF DITHIAZOLYL RADICALS

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*Reaction of benzo-1,2,3-dithiazolyl, **1**, with Pt(PPh$_3$)$_4$ has been shown to produce the aminothiolate complex (amt)Pt(PPh$_3$)$_2$ [amt = HNC$_6$H$_4$S], via oxidative addition of **1** to Pt(PPh$_3$)$_2$ followed by S-abstraction by PPh$_3$. Semi-empirical calculations (AM1 and EHT) have been used to probe the oxidative addition step of this reaction. These studies clearly reveal that close approach of **1** to Pt(PR$_3$)$_2$ induces electron transfer from Pt(PR$_3$)$_2$ to **1** with concomitant ring opening at the S—N bond and coordination to the metal centre. The SOMO of this complex retains the π^* character of the dithiazolyl ring.*

Keywords: Dithiazolyl; extended Hückel; oxidative addition

The reaction of 1,2,3,5-dithiadiazolyl radicals, RCNSSN, with zero-valent platinum/palladium complexes has been shown to occur via cleavage of the S—S bond and oxidative addition to the metal centre to give a monometallic intermediate.[1,2] Subsequent studies showed this to be the kinetic product, the thermodynamic product being a trimetallic species,[2] or a monometallic species formed via chalcogen abstraction.[3]

Recently we investigated the coordination chemistry of the isoelectronic benzo-1,2,3-dithiazolyl radical[4] (**1**) toward Pt(PPh$_3$)$_4$. This reaction was proposed to proceed via cleavage of the S—N bond and S-abstraction to yield the 5-membered metallocycle (**2**) (Scheme 1) which was characterized by x-ray diffraction.

Here we report the results of semi-empirical calculations into the mechanism of the oxidative addition of the benzo-1,2,3-dithiazolyl radical to Pt(PR$_3$)$_4$.

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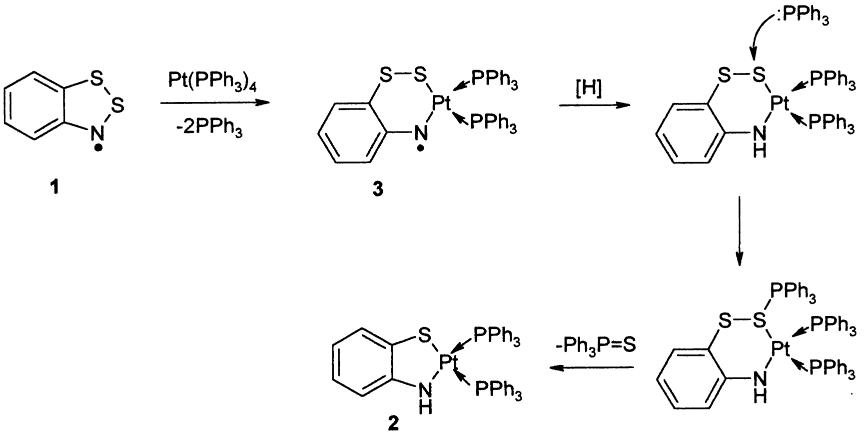

SCHEME 1

RESULTS AND DISCUSSION

Previous calculations[4] have shown that insertion of Pt(PMe$_3$)$_2$ into the S—N bond of **1** is thermodynamically preferred over insertion into the S—S bond yielding **3** as an intermediate (Figure 1). In order to investigate this process in more detail we have modeled the interaction of **1** with Pt(PH$_3$)$_2$. A series of calculations were carried out where the C$\cdots$Pt separation was gradually decreased from 10.0 to 3.0 Å. At each step the C—S—S angle was varied to provide a potential energy surface. Figure 2 shows the energy profile for the interaction between C_6H_4SNS and Pt(PH$_3$)$_2$; each step on the profile corresponds to the minimum energy geometry at a given Pt$\cdots$C separation.

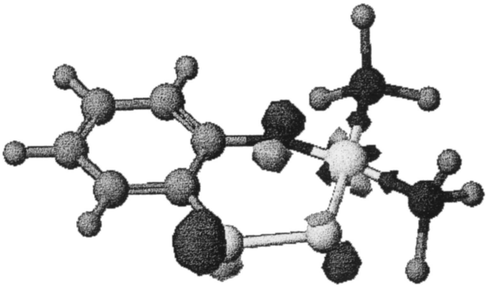

FIGURE 1 Geometry optimised structure of **3**. Selected bond lengths: Pt—N 1.764; Pt—S(1) 2.222; S(1)—S(2) 1.186; S(1)—C(1) 1.614; C(1)—C(2) 1.462; C(2)—N 1.309 Å.

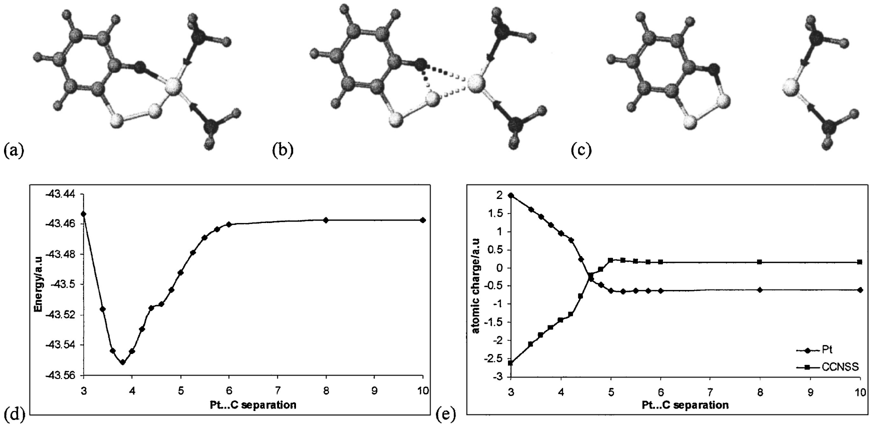

FIGURE 2 (a) Pt$\cdots$C = 3.8 Å, C—S—S = 108°; (b) Pt$\cdots$C = 4.6 Å, C—S—S = 94°; (c) Pt$\cdots$C = 6 Å, C—S—S = 90°; Variation in (d) total energy and (e) charge on heterocyclic ring and Pt atom as a function of separation between Pt and heterocyclic ring.

At a Pt$\cdots$C separation of 6 Å (or greater) (Pt$\cdots$S = 3.45 Å, Pt$\cdots$N = 3.98 Å), the two species can be considered as non-interacting **1** and $Pt(PH_3)_2$ (Figure 2c). On decreasing the Pt$\cdots$C separation to 4.6 Å (Pt$\cdots$S = 2.05 Å, Pt$\cdots$N = 2.64 Å), there is a gradual decrease in potential energy. Between 4.6 and 4.4 Å, there is evidence for a transition state in which the S—N bond is broken and the Pt$\cdots$S and Pt$\cdots$N bonds are formed. This is also the region in which transfer of electron density from $Pt(PH_3)_2$ to **1** occurs. Figure 2e shows a transfer of ca. 2 electrons from Pt to the dithiazolyl ring on passing through this transition state. This charge transfer leads to ring-opening of the heterocycle, with the C—S—S angle increasing from ~90° to ~110° to accommodate the increase in ring size. As the Pt$\cdots$C separation continues to decrease, Pt$\cdots$S and Pt$\cdots$N bond formation occurs. At a Pt$\cdots$C separation of 3.8 Å an energy minimum is achieved with a Pt—S bond distance of 1.49 Å and a Pt—N bond distance of 1.92 Å.

An examination of the region between 5.5 to 4.6 Å (shortly before S—N bond cleavage) identifies two potential energy minima corresponding to the dithiazolyl ring being "closed" and "open." At larger Pt$\cdots$C distances, the ring "closed" form is more stable whereas at shorter Pt$\cdots$C distances, the ring-open form becomes more stable and the S—N bond is broken. This ring-opening process appears to occur concomitantly with the electron transfer process.

The SOMO of **3** using both AM1 and EHT is a π^* orbital predominantly of S-character.

EXPERIMENTAL

Semi-empirical calculations were performed using extended Hückel theory with a STO-6G basis set implemented through Quantum Cache (v. 5.0, Fujitsu Co.). Geometry optimizations were performed using MOPAC/AM1 which is parameterized for Pt.

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