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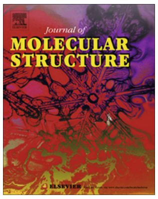

Theoretical study of the electron-donating effects of thiourea ligands in catalysis

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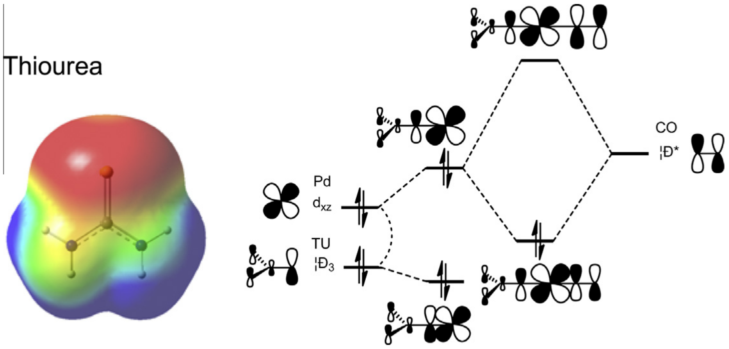
HIGHLIGHTS

- Explained why thiourea and its derivatives often act as strong electron-donating ligands in palladium-catalyzed reactions.
- A new p–d–π interaction model is proposed to explain the intensity of d–π interaction between metal and π-acid ligand.
- The molecular orbitals of thiourea and its derivatives are clarified to the coordination model of thiourea with metals.

GRAPHICAL ABSTRACT

Thiourea and its derivatives often act as strong electron-donating ligands in palladium-catalyzed reactions. Density functional theory calculations were performed to investigate the electronic effects of thiourea ligands in palladium complexes, and a new p–d–π interaction model is proposed.



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ABSTRACT

Thiourea and its derivatives often act as strong electron-donating ligands in palladium-catalyzed reactions. Density functional theory calculations were performed to investigate the electronic effects of thiourea ligands in palladium complexes, and a p–d–π interaction model is proposed. In this model, a Pd(d)—S(p) interaction is responsible for the increased binding of π acceptor ligands such as CO and olefins, which are present in important intermediates in Pd-catalyzed reactions. This d–p interaction is a four-electron, two-orbital interaction; it raises the energy of the Pd(d_{yz}) orbital, bringing it closer to the π^* orbital of the CO or olefin ligand, and increases back donation. Thiourea-ligated transition metals are therefore favorable for the binding of acidic π ligands.

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Introduction

Thiourea is a small molecule with a delocalized thioamide group, formed by replacing the oxygen atom in urea with a sulfur atom. The structure and properties of thiourea have been extensively studied experimentally and theoretically [1]. Thiourea-ligated transition-metal complexes were first reported in 1894 [2], followed by their crystal structures [3]. However, because of the strong coordinative and adsorptive properties of the sulfur atom, thiourea was categorized as a catalyst poison for a long time, preventing thiourea being used to its full potential [4]. In a

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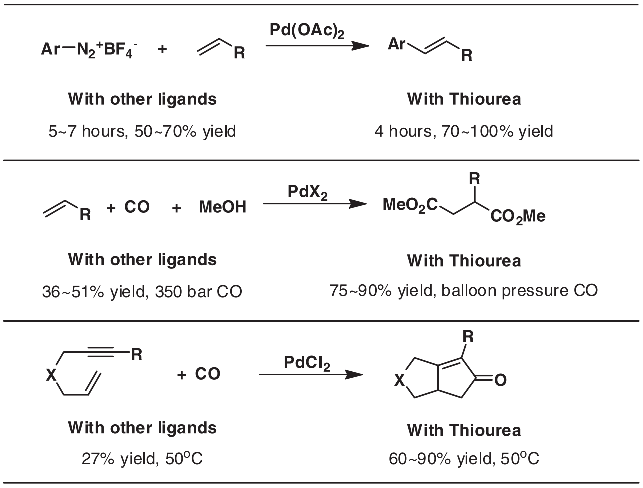
conceptual breakthrough in 1968 by Chiusoli et al. [5], thiourea and its derivatives were used as ligands in transition-metal-catalyzed organic synthesis.

In the past two decades, palladium-catalyzed cross-coupling reactions have emerged as versatile synthetic methods for the formation of C—C bonds [6]. In these reactions, phosphine ligands are used to stabilize palladium catalysts and reactive intermediates [7]. Although much has been achieved using palladium-catalyzed cross-coupling reactions with phosphine ligands, the air-sensitivity of some phosphine ligands hamper further applications [8]. Recently, Yang and coworkers demonstrated that thioureas, which are air- and water-stable ligands, work efficiently in Pd-catalyzed carbonylation [9], methoxycarbonylation [10], Heck, Suzuki, and Suzuki carbonylative reactions [11], Pauson–Khand reactions [12], and others [13] (Scheme 1). Further contributions to palladium/thiourea-catalyzed transformations have been made by Yang et al. [14], Gabriele et al. [15], Zhang and Allen [16], and Yang et al. [17] and their coworkers. When thioureas were used as ligands, these Pd-catalyzed reactions gave moderate to high product yields under mild conditions, such as low reaction temperatures (ca. 50–100 °C) and reduced reaction pressures in transformations involving a gas (i.e., carbon monoxide). The question is: how do thiourea ligands promote Pd-catalyzed reactions?

From a mechanistic point of view, olefin-, alkyne-, or carbonyl-insertion steps are commonly involved and are the rate-determining steps in these transformations [18]. Thioureas facilitate palladium-catalyzed reactions, so such ligands may play an essential role in the key step; this could be confirmed by theoretical calculations.

Although both theoretical and experimental [1] studies of the electronic structures of thioureas have been reported, to the best of our knowledge, the interactions between thioureas and transition metals have not been fully investigated. Furthermore, the explanation for the high activities of thioureas in transition-metal-catalyzed organic transformations is still unknown. Recently, we reported that in Pd/thiourea-catalyzed carbonylation, the thiourea could play a key role in two elementary steps, namely binding of the CO/π acceptors and the subsequent insertion step [18]. The binding of CO or another π acceptor to Pd(II) is usually thermodynamically unfavorable. Enhancement of the binding ability therefore generally speeds up the overall reaction. In this study, we used density functional theory (DFT) calculations to describe the mechanism by which thioureas enhance the binding abilities of π acceptors to Pd(II).



Scheme 1. Examples of the thiourea-promoted palladium-catalyzed coupling reactions.

It is known that thioureas have three possible coordination modes, namely coordination through N, S, and π-CS. Sautet and Lemaire showed that in Rh-catalyzed *trans* hydrogenation of ketones, no minimum for coordination through N was found, and coordination through S was favored over coordination through the π system by 9.0 kcal/mol [19]. They attributed this preference to the higher orbital energy of sulfur's lone-pair compared with the π orbital of the π system.

In Curran's infrared spectroscopic investigation of thiourea–metal complexes [3a], large shifts of the absorption maxima to high frequencies were associated with N—C—N antisymmetric stretching vibrations, indicating that the thiourea had an appreciable $^{+}N{=}C{-}S^{-}$ character (Scheme 2). Olah and Prakash [1g] explored the mono-, di-, and tri-protonation of thiourea under superacid conditions, using ^{13}C and ^{15}N NMR spectroscopies and theoretical calculations. S-protonated products were the preferred form. Their DFT calculations revealed that the S-protonated form is 20 kcal mol^{-1} more stable than the N-protonated form. These results indicate that the S atom in thiourea bears a partial negative charge.

Computational method

All the calculations were carried out with the GAUSSIAN 09 program [20]. Each structure was fully optimized by using the M06 [21] functional with the following basis set: the Stuttgart–Dresden effective core potential SDD with associated basis set [22] for the Pd atom, and standard basis set 6-311+G(d) for other atoms. Harmonic vibrational frequency calculations were performed for each structure to confirm a local minimum, and were used to give thermal corrections.

The reported molecular orbital (MO) energies were evaluated at the RHF/6-311G(d) level of theory to avoid poor estimates of the ionization potentials of small molecules provided by Kohn–Sham orbitals. A large basis set also gives better estimates of unoccupied orbital eigenvalues [23].

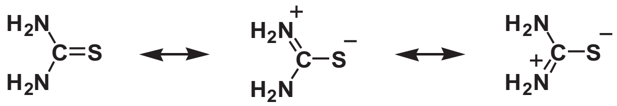
The electrostatic potential and natural population analysis (NPA) of the charges on thiourea and thioformaldehyde were calculated by the RHF method using the cc-pVTZ basis set, which gives more accurate values.

Results and discussion

The fully optimized geometry of unsubstituted thiourea is planar [1g,1h]. The MOs of thiourea can therefore be viewed as a combination of the orbitals from a thiocarbonyl and two NH_2 moieties.

The calculated orbital energies of thioformaldehyde are shown in Fig. 1 (left). The lowest unoccupied molecular orbital (LUMO) with the symmetry of B2 in C2v point group, which is consisted with the p_x orbital of carbon and the p_x orbital of sulfur, is the C═S π antibonding orbital, whereas the p_y orbital on sulfur dominates the highest occupied molecular orbital (HOMO) of thioformaldehyde with the symmetry of B1. The energy level of C═S π bonding orbital with B2 symmetry is 1.91 eV lower than that of the HOMO. The energy of the A1 symmetry sp hybrid lone-pair orbital on the sulfur is much lower.

For thiourea (Fig. 1, right), the in-phase and out-of-phase mixing of two atomic nitrogen p_x orbitals gives two new MOs, π_2



Scheme 2. Resonance structures of thiourea.

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