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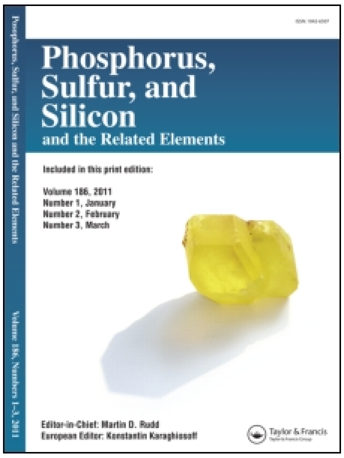

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Metal Complexes of Dithiatetrazocines

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METAL COMPLEXES OF DITHIATETRAZOCINES

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ABSTRACT Dithiatetrazocines of the type 1,5-$E_2N_4S_2$ (E=Me_2NC, R_2P) form the transition metal complexes $M(PR_3)_2(1,5\text{-}E_2N_4S_2)$ (M=Pt, Pd, Ni) which involve an η^2- S, S′ interaction with the metal. A reversible elimination of R_3P from these mononuclear complexes gives the binuclear complexes $[M(PR_3)(1,5\text{-}E_2N_4S_2)]_2$. These complexes have been shown by ^{31}P NMR to undergo a fluxional process involving a [1, 3] metallotropic shift. Mononuclear metal complexes may also be prepared from the novel dianion 1,5-$Ph_4P_2N_4S_2^{2-}$ and the appropriate metal dihalide complex.

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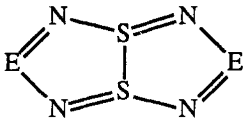
INTRODUCTION

The dithiatetrazocines are a class of eight-membered heterocyclic rings , **1**, which often possess a weak sulfur-sulfur cross-ring bond.[1] The σ and σ* orbitals of this weak S-S interaction have been shown to have an isolobal correspondence with the π and π* orbitals of an electron deficient alkene.[2]



1

(E=Me_2NC, R_2P)

This paper describes the synthesis and structural characterization of mono- and binuclear metal complexes of **1**. An alternative synthesis of the mononuclear complexes through the dianion of **1** (E=PPh_2) is also reported.

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SYNTHESIS

The addition of various dithiatetrazocines to zero-valent platinum and palladium complexes in toluene yields the mononuclear complexes of **1**.[3]

$$\mathrm{Pt(PPh_3)_2(C_2H_4)} \quad + \quad \mathrm{1,5\text{-}E_2N_4S_2} \xrightarrow{-\mathrm{C_2H_4}} \mathrm{Pt(PPh_3)_2(1,5\text{-}E_2N_4S_2)}$$

2a : E=Me_2NC
2b : E=Ph_2P
2c : E=Me_2P
2d : E=Et_2P

$$\mathrm{Pd(PPh_2R)_4} \quad + \quad \mathrm{1,5\text{-}E_2N_4S_2} \xrightarrow{-\,\mathrm{2PPh_2R}} \mathrm{Pd(PPh_2R)_2(1,5\text{-}E_2N_4S_2)}$$

3a : E=Ph_2P, R=Ph
3b : E=Ph_2P, R=Me
3c : E=Et_2P, R=Me

The mononuclear complexes undergo a reversible elimination of one phosphine resulting in the formation of binuclear complexes either upon heating or spontaneously in solution.[4]

$$\mathrm{2\ M(PPh_2R)_2(1,5\text{-}R'_4P_2N_4S_2)} \xrightleftharpoons[+2\,\mathrm{PPh_2R}]{-2\,\mathrm{PPh_2R}} \mathrm{[M(PPh_2R)(1,5\text{-}R'_4P_2N_4S_2)]_2}$$

4a : M=Pt, R=R′=Ph
4b : M=Pt, R=Ph, R′=Et
4c : M=Pd, R=R′=Ph
4d : M=Pd, R=Me, R′=Ph
4e : M=Pd, R=Me, R′=Et

The monomeric complex, **2a**, apparently does not form an analogous binuclear complex.

STRUCTURES

Pertinent structural features of a monomeric complex, $Pt(PPh_3)_2(1,5\text{-}Ph_4P_2N_4S_2)$, **2b**, and a binuclear complex, $[Pt(PPh_3)(1,5\text{-}Ph_4P_2N_4S_2)]_2$, **4a**, are given in Figures 1 and 2.

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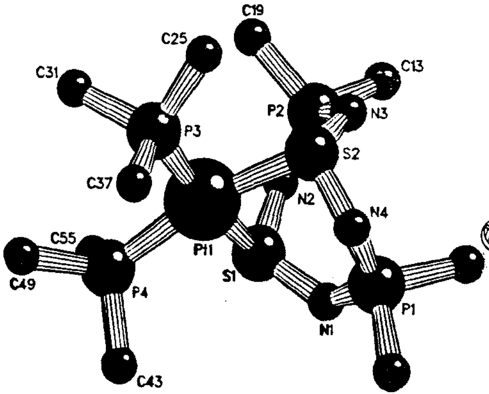
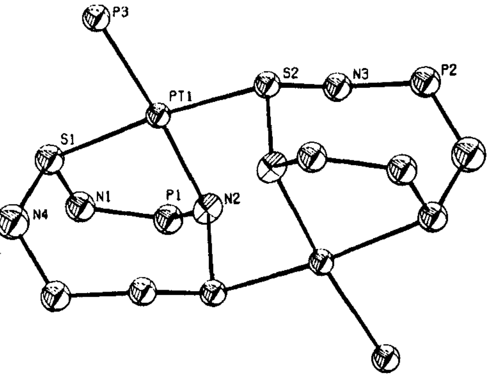


d(Pt1-S2) = 2.408(4)Å
d(Pt2-S2) = 2.341(4)
<S1Pt1S2 = 86.36(13)°
<P3Pt1P4 = 99.25(14)°

FIGURE 1 Structure of **2b**



d(Pt1-S1) = 2.344(3)Å
d(Pt1-S2) = 2.342(3)
d(Pt1-N2) = 2.089(7)
<S1Pt1N2 = 83.4(2)°

FIGURE 2 Structure of **4a**

For **2b** the geometry about Pt is approximately square planar with the heterocyclic ring exhibiting η^2- S, S′ coordination, while in **4a** the same ring acts as a chelating (N,S) ligand towards one platinum and as a bridging ligand through sulfur to the other metal atom.

FLUXIONAL BEHAVIOR OF BINUCLEAR COMPLEXES

The ^{31}P NMR spectrum of **4a** at -60°C shows two broad, equally intense, singlets due to the inequivalent heterocyclic Ph_2P groups (as well as a signal for the Ph_3P ligand). These signals broaden and collapse to a singlet at +35°C which corresponds to an interconversion barrier of 10.2 ± 0.2 kcal mol^{-1}. For this fluxional process a [1,3]-metallotropic shift involving a pendular movement of Pt(1) from N(2) to N(3A) and, concomitantly, Pt(1A) from N(3) to N(2A) is proposed (Figure 3). The complex **4b** also exhibits similar fluxional behavior while the Pd complexes appear to have much lower interconversion barriers.

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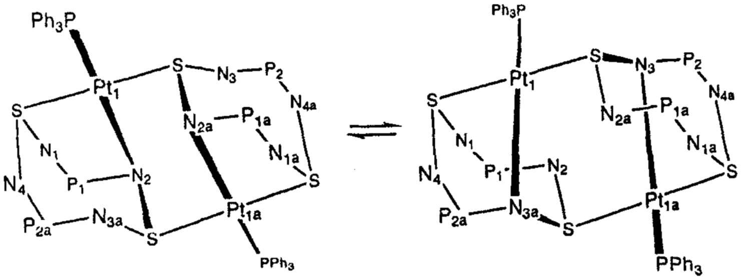

FIGURE 3 Proposed Mechanism for the [1,3]-Metallotropic Rearrangement of **4a**

DIANIONS OF DIPHOSPHADITHIATETRAZOCINES : AN ALTERNATIVE SYNTHESIS OF MONONUCLEAR COMPLEXES

The treatment of 1,5-$Ph_4P_2N_4S_2$ with two molar equivalents of superhydride, in THF, results in the formation of a yellow precipitate whose subsequent treatment with metal dichloride complexes yields the monomeric metal complexes.

$$\text{1,5-}Ph_4P_2N_4S_2 \quad + \quad 2LiBEt_3H \longrightarrow \text{"[1,5-}Ph_4P_2N_4S_2]Li_2\text{"}$$

$$\Big\downarrow L_2MCl_2$$

$$ML_2(\text{1,5-}Ph_4P_2N_4S_2)$$

2b : M=Pt, L=PPh_3
5a : M=Pt, L=PEt_3
5b : M=Ni, L_2=diphos

Compound **5b** represents the first example of a nickel complex of **1**, which cannot be prepared by the Ni(0) route.

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