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The Synthesis and Characterization of $Ni[P(OPh)_3]_2(SN_3)\cdot 2H_2O$, Sulfur trinitride)bis(triphenylphosphite)nickel(II) Dihydrate

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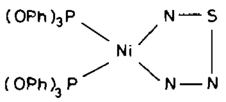
The platinum(0) compound, $Pt(P(Ph)_3)_4$, reacts with tetrasulfur tetranitride, S_4N_4, to yield $(P(Ph)_3)_2Pt(S_4N_4)$ *via* coordinative addition of S_4N_4 to the reactive intermediate $Pt(P(Ph)_3)_2$. The same starting materials under different reaction conditions yield $(P(Ph)_3)_2$ $Pt(S_2N_2)$ *via* oxidative addition [1]. Although a few nickel(II) compounds with sulfur–nitrogen ligands have been reported, reactions of zerovalent nickel compounds with S_4N_4 or $S_4N_4H_4$ have not been studied. In this communication we report the synthesis and characterization of $Ni[P(OPh)_3]_2(SN_3)\cdot 2H_2O$, prepared by the reaction of tetrasulfur tetranitride and tetrakis(triphenylphosphite)nickel(0).

The absorption spectra of this diamagnetic compound in acetone at room temperature exhibits three bands at 550 nm (ϵ = 80 mol^{-1} cm), 380 nm (ϵ = 145), and 325 nm (ϵ = 289) respectively, possibly due to electronic transitions $^1A_{1g} \rightarrow {}^1A_{2g}$; $^1A_{1g} \rightarrow {}^1B_{1g}$; and $^1A_{1g} \rightarrow {}^1E_g$. These three spin-allowed electronic transitions are typical of the square planar d^8 configuration [2]. Hence, we believe $Ni[P(OPh)_3]_2(SN_3)$ to be a bivalent square planar nickel(II) compound formed by an oxidative addition of a S_4N_4 fragment to a zerovalent reactive intermediate $Ni[P(OPh)_3]_2$ [3] *i.e.*

$$\begin{tikzcd} Ni[P(OPh)_3]_4 \arrow[r, phantom, "\rightleftarrows"] & Ni[P(OPh)_3]_2 \arrow[d, "S_4N_4"] \\ & Ni[P(OPh)_3]_2(SN_3) + ? \end{tikzcd}$$

S_4N_4 is known to yield the ligand S_3N when it reacts with palladium(II) chloride in methanol [4]. So it is reasonable that a fragment SN_3 might also be formed in the reaction ($S_4N_4 \rightleftarrows SN_3 + S_3N$). The material $Ni[P(OPh)_3]_2(SN_3)$ is the first example of a compound containing SN_3 fragment. It was isolated in approximately 50% yield. We were unable to characterize the species present in the filtrate. It is possible that in addition to the fragment SN_3, the other S_4N_4 fragment formed may be S_3N as found in the case of the reaction of palladium(II) chloride. Since S_4N_4 does not possess N–N bonding [5], the presence of the ligand SN_3^{2-} is unexpected but not surprising. In the first step of the oxidative addition, S_4N_4 might be reduced to $S_4N_4^{2-}$ which then undergoes fragmentation. Both polarographic [6] and e.s.r. [7] studies indicate the possible existence of the anion $S_4N_4^{2-}$. Although S_4N_4 does not exhibit N–N bonding, the anion $S_4N_4^{2-}$ might have an electronic structure which can give rise to the ligand $(N\text{–}S\text{–}N\text{–}N)^{2-}$ on fragmentation. No structural information can be obtained from the infrared spectra of the material. However, since this is a bivalent nickel(II) square planar complex, the following structure is highly likely.



Experimental

Tetrakis(triphenylphosphite)nickel(0) was prepared by the sodium tetrahydroborate reduction of a reaction mixture containing triphenylphosphite and nickel(II) nitrate hexahydrate [8]. Tetrasulfur tetranitride was prepared using a literature method [9]. The absorption spectra in acetone at ambient temperature were recorded using a Cary 14 recording spectrophotometer. All materials used were of reagent grade and further purification was not necessary. The procedure for the preparation of $Ni[P(OPh)_3]_2(SN_3)\cdot 2H_2O$ is: Tetrakis(triphenylphosphite)nickel(0) (0.65 g, 0.05 mmol) was dissolved in a minimum volume of benzene and 0.092 g (0.05 mmol) of S_4N_4 was added to it while stirring. The mixture was stirred for an hour and filtered. The brown filtrate was kept undisturbed at room temperature for several days (up to one week) until deep brown crystals appeared. The crystals were filtered off, washed with pentane, and dried in vacuum. Yield, 0.20 g (53% based on $Ni[P(oph)_3]_4$), m.p. 247–250 °C (dec.) *Anal.* calculated for $C_{36}H_{30}N_3O_6P_2SNi\cdot 2H_2O$: 54.77; H, 4.35; N, 5.32; S, 4.05. Found: C, 54.22; H, 4.70; N, 5.76; S, 3.92.

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