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SYNTHESIS AND CHARACTERIZATION OF THE FOUR-COORDINATE AZIDONITROSYLBIS(TRIPHENYLPHOSPHINE)NICKEL

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Introduction:

Structures of four-coordinate diphosphine nickel complexes have been studied extensively because of their stereochemical flexibility. Examples are plentiful for both square planar and tetrahedral geometries; intermediate geometries are also known. A notable example is the dibromobis(diphenylbenzylphosphine) nickel(II) complex which crystallizes with both the tetrahedral and the square planar forms in the same lattice (4). The structure of the title complex (Fig. 1) has been reported by Enemark (3) and exhibits distorted, pseudo tetrahedral geometry (P–Ni–P angle 120°; (N_3)–Ni–NO angle 129°; NiP_2–NiN_2 dihedral angle 84.1°) with bent azide (Ni–N–N angle 129°, d[Ni–N_3] = 2.108 Å) and bent nitrosyl (Ni–N–O angle 153°, d[Ni–NO] = 1.686Å).

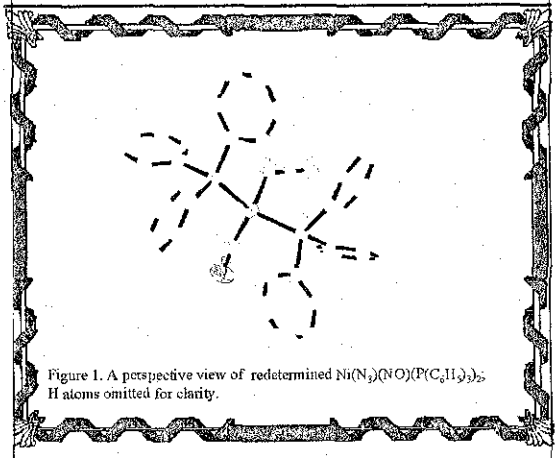

Figure 1. A perspective view of redetermined $Ni(N_3)(NO)(P(C_6H_5)_3)_2$. H atoms omitted for clarity.

While the reported structure has a low discrepency index the distances within the azide ligand are suspect. The author noted the unusual pattern of oriented elongated atomic displacement parameters, visible (Fig. 2), and suggested a chloronitrosyl (bistriphenylphosphine)nickel impurity (starting material for the azido synthesis) cocrystallized with the azido complex leading to the unusually short N–N distance shown (Fig. 2). A cursory look at the atomic displacement parameters of other azido structures in the literature indicates that this or similar problems are present in many azido structures. A search for metal bound azide structures in the Cambridge Structure Database found only 270 structure reports and only 22 structure reports for four-coordinate nickel bound to azide. As the structure databases are used for experimental data to calibrate computational methods and both nitrosyl and azide are receiving increased attention due to biochemical relevance we feel it is useful to improve this structure.

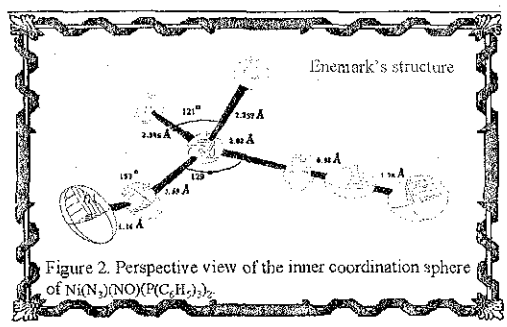

Figure 2. Perspective view of the inner coordination sphere of $Ni(N_3)(NO)(P(C_6H_5)_3)_2$.

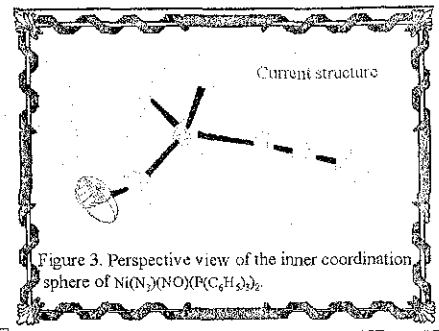

Figure 3. Perspective view of the inner coordination sphere of $Ni(N_3)(NO)(P(C_6H_5)_3)_2$.

Synthesis Procedure :

All syntheses (1,5) were carried out under an inert atmosphere using Schlenk techniques and reagent grade starting materials:

Synthesis of dibromobis(triphenylphosphine)nickel(II)

$$NiBr_2{\cdot}3H_2O + 2P(C_6H_5)_3 \xrightarrow{\text{2-propanol}} NiBr_2(P(C_6H_5)_3)_2\downarrow + 3H_2O$$

Synthesis of bromonitrosylbis(triphenylphosphine)nickel(II)

$$NiBr_2(P(C_6H_5)_3)_2 + NaNO_2 + P(C_6H_5)_3 \xrightarrow{THF} NiBr(NO)(P(C_6H_5)_3)_2 + NaBr\downarrow + OP(C_6H_5)_3$$

Synthesis of azidonitrosylbis(triphenylphosphine)nickel(II)

$$NiBr(NO)(P(C_6H_5)_3)_2 + NaN_3 \xrightarrow{MeOH} Ni(N_3)(NO)(P(C_6H_5)_3)_2 + NaBr\downarrow$$

Results, Discussion and Conclusions:

The compound has been redetermined based on a high quality x-ray data set collected on a KappaCCD diffractrometer. The compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The structure consists of discrete $Ni(N_3)(NO)(P(C_6H_5)_3)_2$ molecules with *pseudo tetrahedral coordination geometry* about the Ni atom (Fig. 3).

On refinement the atoms of the azide group were not well behaved. Examination of an electron density difference map revealed the strongest peak in a position appropriate for a bromo substituent. Inclusion of the bromine atom with the constraint that the occupancies of the bromo and azido groups sum to unity gave an acceptable refinement. The final refinement showed about 12% bromo and 88% azido substituent. Data collected on two additional crystals also showed about 12% bromo complex. Apparent contact distances between Br and N1–N2 are 0.50 and 0.68 Å, respectively, making it necessary to model these three atoms as isotropic atoms. Refinement converged with $R_1 = 0.047$ and an essentially featureless electron density difference map.

The P–Ni–P angle is 120.9°, the N_3–Ni–NO angle is 130.6(9)°, and the dihedral angle between the P–Ni–P and N_3–Ni–NO planes is 84.7(3)°. The distances of Ni–N_3 2.008 Å, Ni–NO = 1.692 Å, N1–N2 = 1.150 Å and N2–N3 = 1.157 Å, and the azide ligand is nonlinearly coordinated to the Ni atom and asymmetrically related to the two phosphine ligands as found previously.

Table 1

Distances (Å)	Angles (°)
Ni–P1 2.244(8)	P1–Ni–P2 120.90
Ni–P2 2.289(1)	P1–Ni–N1 103.01
Ni–N1 2.008(3)	P1–Ni–N4 101.22
Ni–N4 1.692(9)	P2–Ni–N1 94.58
N1–N2 1.150(5)	*P2–Ni–N4 109.91*
N2–N3 1.157(8)	N1–Ni–N4 129.13
N4–O1 1.129(0)	Ni–N1–N2 126.58
	Ni–N4–O1 152.72
	N1–N2–N3 173.71

NiP_2–NiN_2 dihedral angle 84.73°

The current discrepency index is lower than the previous determination, the thermal parameters of the azido nitrogen atoms have been controlled to reasonable shape, and the distances in the azido group (Table 1) are reasonable. However, the problem of obtaining pure crystals of the azido complex is not solved. We are exploring additional strategies to obtain pure complex for further characterization.

Crystal Data	Enemark's Structure	Current Structure
Crystal system:	Monoclinic	Monoclinic
Space group:	*$P2_1/c$ (No 14)*	*$P2_1/c$ (No.14)*
Unit cell a =	13.691(6) Å	13.597(5) Å
b =	19.211(10) Å	19.098(8) Å
c =	12.582(5) Å	12.562(4) Å
β =	98.13(5) °	98.59(5) °
V =	3276.03 Å^3	3221.89 Å^3
Z =	4	4
Temperature=	296 K	298 K
d_{calc} =	1.33 Mg m^{-3}	1.35 Mg m^{-3}
Radiation type=	MoKα	MoKα
R_1 =	0.053	0.047

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