*Inorganica Chimica Acta,* 9 (1974) L2

## Letters

---

# Synthesis and Structural Characterization of an Unexpected σ-Phenyl-Nickel(II) Complex

P. DAPPORTO and L. SACCONI

*Istituto di Chimica Generale e Inorganica, Laboratorio C.N.R., 39 Via Nardi, Florence, Italy*

(Received May 2, 1974)

As has been reported, when $NiBr_2$ or $NiI_2$ are reacted with the tripod ligand $N(CH_2CH_2AsPh_2)_3$ ($NAs_3$) and $NaBPh_4$ in butanol, five-coordinate complexes of nickel(II) having the formula $[Ni(NAs_3)X]BPh_4$ are obtained.[1] If $NiCl_2$ is used, red crystals are formed which are air stable and soluble in polar organic solvents. The same product is obtained if the reaction mixture of $NiBr_2$ is boiled. That the compound is diamagnetic and shows one absorption band at 19,600 $cm^{-1}$ with a shoulder at 25,000 $cm^{-1}$ suggests the presence of five-coordinate nickel(II) species. Surprisingly the compound did not show the presence of halogen, and the obtained C, H, N, As and Ni analytical data could not be interpreted in a satisfactory way. The structure was subsequently solved by X-ray analysis.

The crystals are triclinic, space group $P\bar{1}$, with lattice constants $a$ = 18.132(3), $b$ = 13.377(2), and $c$ = 13.162(2) Å; $\alpha$ = 84.65(2), $\beta$ = 73.80(2), and $\gamma$ = 86.93(2)°; and $Z$ = 2. Intensity measurements were collected on a Philips diffractometer, and the structure determination and refinement were carried out using 3008 independent reflections with $I \geqslant 3\sigma(I)$ to an $R$ = 0.069.

The structure consists of $[Ni(NAs_3)(\sigma\text{-}C_6H_5)]^+$ cations and $BPh_4^-$ anions. The nickel atom is five-coordinate, linked to the four donor atoms of the ligand molecule and to a carbon atom of a free phenyl ring in an apical position. The geometry can be described as trigonal-bipyramidal (Fig. 1).

Bond lengths and angles about the nickel are: Ni–As(1), 2.32; Ni–As(2), 2.39; Ni–As(3), 2.30; Ni–N, 2.10; Ni–C, 1.87 Å (all $\sigma$ = 0.01 Å); As(1)–Ni–As(2), 113.8; As(1)–Ni–As(3), 122.3; As(2)–Ni–As(3), 122.6; As(1)–Ni–N, 87.6; As(1)–Ni–C, 92.6; As(2)–Ni–N, 84.9; As(2)–Ni–C, 101.1; As(3)–Ni–N, 85.9; As(3)–Ni–C, 88.3; N–Ni–C, 173.3° (all $\sigma$ = 0.2°).

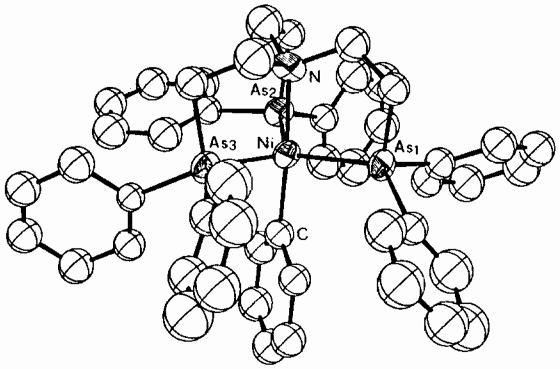

Fig. 1. Structure of $[Ni(NAs_3)(\sigma\text{-}C_6H_5)]^+$ cation.

The measured carbon–nickel σ-bond of 1.87 Å may be compared with the values of 1.88 and 1.91 Å calculated by using the covalent radius of 0.73 Å for a $sp^2$ carbon atom and the values of 1.15 [2] and 1.18 Å.[3] respectively, for the covalent radius of nickel(II). This measured Ni–C distance is similar also to that of 1.905 Å which was measured for the unique compound, $(\pi\text{-}C_5H_5)Ni(PPh_3)(\sigma\text{-}C_6H_5)$,[4] which has a phenyl group bound directly to a nickel (II) atom.

The few aryl-complexes described to date have been generally prepared by either the use of reagents containing metal–carbon σ-bond, as Li, Na, or Mg-aryl derivatives, or by oxidative addition of aryl-halo derivatives on nickel(0) complexes. The preparation of the title compound is the first reported synthesis of a σ-phenyl nickel derivative obtained by starting from a nickel(II) compound without the use of specific reagents capable of releasing phenyl groups.

1 L. Sacconi, I. Bertini and F. Mani, *Inorg. Chem.*, 7, 1417 (1968).
2 L. Pauling and M. L. Huggins, *Z. Krist.*, *87*, 205 (1934).
3 D. R. Fahey, *Organometal. Chem. Rev.*, 7, 245 (1972).
4 M. R. Churchill and T. A. O'Brien, *J. Chem. Soc.*, *A*, 2970 (1968).