

**Preliminary communication**

**INSERTION OF CARBON MONOXIDE INTO A NICKEL—CARBON BOND.  
 X-RAY STRUCTURE OF [TRIS(2-DIPHENYLPHOSPHINOETHYL)AMINE-  
 NICKELACETYL] TETRAPHENYLBORATE**

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**Summary**

Carbon monoxide reacts with  $[\text{NiCH}_3(\text{np}_3)]\text{BPh}_4$  ( $\text{np}_3 = \text{tris}(2\text{-diphenylphosphinoethyl)amine}$ ) with the formation of  $[\text{NiCOCH}_3(\text{np}_3)]\text{BPh}_4$ , the crystal structure of which has been determined by X-ray diffraction.

Insertion of carbon monoxide into transition metal—carbon  $\sigma$ -bonds to give acyl derivatives usually involves the action of a phosphine, arsine or carbon monoxide ligand on organometal carbonyl derivatives [1]. The insertion of carbon monoxide into metal complexes which do not contain carbon monoxide as a ligand is relatively rare, and only platinum and palladium derivatives are known to undergo this reaction [2]. No acyl nickel derivative has previously been made [3], either by carbonylation of stable nickel—carbon  $\sigma$ -bonds or by oxidative addition of aroyl chlorides to nickel(0) complexes [4].

We have found that carbon monoxide reacts readily at room temperature and normal pressure with the cationic five coordinate complex  $[\text{NiCH}_3(\text{np}_3)]\text{BPh}_4$  in tetrahydrofuran to give the acetyl compound  $[\text{NiCOCH}_3(\text{np}_3)]\text{BPh}_4$ . This compound, which crystallizes with 2.5 molecules of tetrahydrofuran, decomposes in air. (Found: C, 74.51; H, 6.62; N, 1.12; P, 7.12; Ni, 4.63.  $\text{C}_{78}\text{H}_{85}\text{NP}_3\text{NiO}_{3.5}\text{B}$  calcd.: C, 74.66; H, 6.83; N, 1.12; P, 7.38; Ni, 4.68 %). The IR spectrum in Nujol mull or  $\text{CH}_2\text{Cl}_2$  solution shows a band at  $1660\text{ cm}^{-1}$  characteristic of transition metal acyl derivatives.

A complete X-ray structural analysis has been carried out on the compound. The crystals are triclinic, space group  $P\bar{1}$ ,  $a$  18.168(4),  $b$  17.537(4),  $c$  10.789(3) Å,  $\alpha$  95.62(4),  $\beta$  100.88(4),  $\gamma$  95.80(4);  $Z$  2. The intensities of 1208 independent reflections with  $I \geq 3\sigma(I)$  were measured on a Philips PW 1100 automatic diffractometer. The structure was solved by the heavy atom technique and refined

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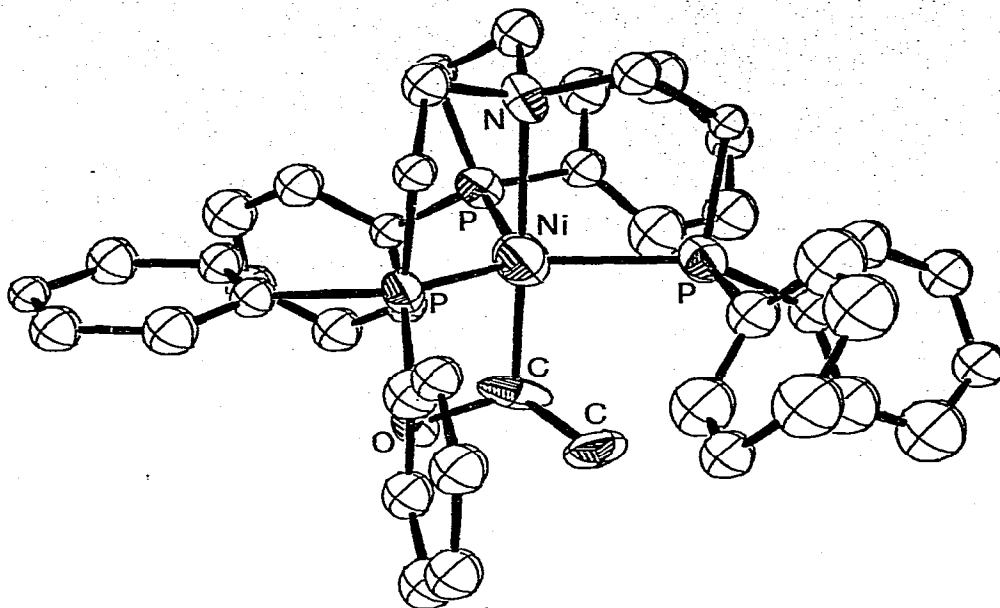


Fig. 1. The structure of  $[\text{NiCOCH}_3(\text{np}_3)]^+$ .

by a full-matrix least squares program. The final conventional  $R$  factor is 9.8. The rather high  $R$  value is due in part to decomposition of the crystal during the data collection and in part to the disordered array of the solvent molecules.

The structure of the complex consists of  $[\text{NiCOCH}_3(\text{np}_3)]^+$  cations (Fig. 1), tetraphenylborate anions, and interposed tetrahydrofuran molecules. The nickel atom is five coordinate, being bound to the four donor atoms of the  $\text{np}_3$  ligand and to the carbon atom of the acetyl group. The coordination polyhedron is a distorted trigonal bipyramid. Distances and angles around the nickel atom are Ni—N 2.33(3), Ni—P(av) 2.29(2) Å, N—Ni—C 178.2(21), N—Ni—P(av) 84.0(9) and P—Ni—C(av) 96.0(19)°. The nickel—acetyl-carbon distance, 2.02(6) Å, is equal to the nickel—carbon distance (2.02 Å) found for the complex  $[\text{NiCH}_3(\text{np}_3)]\text{BPh}_4$  [5]. The C—O and C—C distances of the acetyl group are 1.35(8) and 1.41(8) Å, respectively. Bond angles around the ketonic carbon atom (Ni—C—O 113(5), Ni—C—C 116(4) and O—C—C 125(6)° are not far from the expected  $sp^2$  bond angle.

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