Journal of Organometallic Chemistry, 175(1979) C19—C20

Preliminary communication

INSERTION OF SULPHUR DIOXIDE INTO NICKEL—CARBON σ BONDS. X-RAY STRUCTURE OF [BIS(2-DIPHENYLPHOSPHINOETHYL)PHENYLPHOSPHINENICKEL-*O*-METHYLSULFINATO] TETRAPHENYLBORATE

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(Received June 12th, 1979)

Summary

Sulphur dioxide reacts with $[NiCH_3(ppp)]BPh_4$ (ppp = bis(2-diphenylphosphinoethyl)phenylphosphine) to give the *O*-methylsulfinate complex $[NiOS(O)CH_3(ppp)]BPh_4$. The crystal structure of the compound has been determined by X-ray diffraction analysis.

The insertion of sulphur dioxide into M—C σ bonds may give rise to several structures for the M—(SO_2)R moiety [1]. The *S*-sulphinate linkage is by far the most common; *O*-sulphinate derivatives were obtained only by insertion of sulphur dioxide into carbon—titanium [2] or carbon—zirconium [3] bonds. This structure was detected also in the intermediate products derived by insertion of SO_2 into a number of manganese [4], titanium [5] and iron [4] complexes.

The insertion of sulphur dioxide into Ni—C bond with *S*-sulfinate formation [6], has been reported only for the compound $CpNiPR_3Me$ (R = Ph or n-Bu) [7].

We have found that the cationic tetracoordinate complex $[NiCH_3(ppp)]BPh_4$ (ppp = bis(2-diphenylphosphinoethyl)phenylphosphine) reacts with liquid sulphur dioxide to give the *O*-sulfinate derivative of formula $[NiOS(O)Me(ppp)]$-BPh_4. This compound, which decomposes in the air, exhibits sulphur—oxygen stretching frequencies $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ at 1098 and at 860 cm^{-1}, respectively; these frequencies are characteristic of *O*-sulfinate complexes [8]. (Found: C, 71.25; H, 5.76; Ni, 5.79; P, 9.15; S, 3.11. $C_{59}H_{56}BNiO_2P_3S$ calcd.: C, 71.46; H, 5.69; Ni, 5.92; P, 9.37; S, 3.23%.)

The structure of the compound has been determined by X-ray analysis. The crystals are triclinic, space group $P\bar{1}$, *a* 16.726(4). *b* 15.350(4), *c* 11.632(3) Å, α 65.55(4), β 73.37(4), γ 74.75(4)°; *Z* 2. The intensities of 2841 reflections with $I \geqslant 2.5\sigma(I)$ were measured on a Philips PW 1100 diffractometer. The structure was solved by direct methods and refined by full matrix least squares using the SHELX system [9] of programs. The final conventional *R* factor is 0.076.

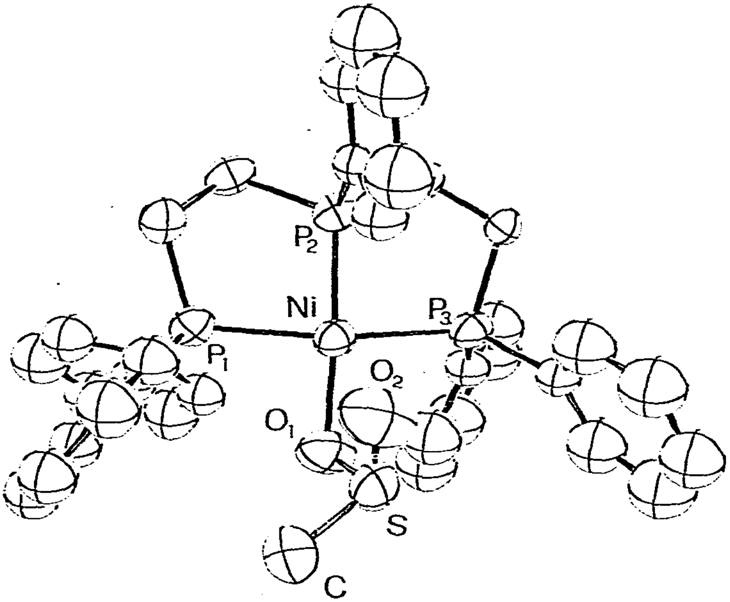

Fig. 1. Molecular structure of the cation $[NiOS(O)CH_3(ppp)]^+$.

The structure of the complex consists of $[NiOS(O)CH_3(ppp)]^+$ cations (Fig. 1) and tetraphenylborate anions. The nickel atom is four coordinated, by three phosphorus atoms of the ligand ppp and one oxygen atom of the sulfinate group. The coordination polyhedron has a distorted square planar geometry, as the bond distances significantly differ from each other and the angles do not closely approach the ideal values 90 or 180°. Thus the distance to the nickel of the central phosphorus atom of the ppp ligand is 2.111(2) Å, about 0.1 Å shorter than the other Ni—P distances (2.199(2), 2.214(2) Å). The Ni—O(1) distance is 1.937(11) Å. The P—Ni—P angles have values 85.0(2), 85.2(2) and 162.4(2)°, whereas the O(1)—Ni—P(1) and O(1)—Ni—P(3) angles are 91.2(4) and 98.7(4)°, respectively. The geometric requirements of the ppp ligand and the steric repulsion of its terminal phenyl groups toward the $OS(O)CH_3$ group, are probably at the origin of the observed distortions from an exact square planarity. Finally the S—O bonds are almost equal (1.513(13) Å (ave.)) and about 0.25 Å shorter than the S—C bond (1.765(19) Å).

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