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Preliminary communication

UNPRECEDENTED INTRAMOLECULAR ATTACK BY A PHOSPHINE ON A η^2-DITHIOMETHYL ESTER GROUP. X-RAY CRYSTAL STRUCTURE OF THE COMPLEX $[Ph_2\overline{PCH_2CH_2N(CH_2CH_2PPh_2)_2Ni(C}S_2Me)]BPh_4$

CLAUDIO BIANCHINI*, CARLO A. GHILARDI, ANDREA MELI and
ANNABELLA ORLANDINI

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione del C.N.R., Via Guerrazzi 27, 50132 Florence (Italy)

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Summary

The complex $[Ph_2\overline{PCH_2CH_2N(CH_2CH_2PPh_2)_2Ni(C}S_2Me)]BPh_4$ is obtained by treating the nickel(0) complex $[(np_3)Ni]$ [np_3 = tris(2-diphenylphosphinoethyl)-amine] in neat CS_2 with $MeOSO_2F$, followed by a metathetical reaction with $NaBPh_4$. An X-ray crystal structure determination has showed that the nickel atom is coordinated by two phosphorus atoms of np_3 and by an unprecedented phosphoniodithiomethyl ester group through carbon and the un-methylated sulfur atom. The N—Ni distance indicates that there is a significant interaction.

The nickel(0) complex $[(np_3)Ni]$ (1) [np_3 = tris(2-diphenylphosphinoethyl)-amine] [1] reacts in neat carbon disulfide with $MeOSO_2F$ producing a dark brown oil. Crystallization from acetone/ethanol in the presence of $NaBPh_4$ affords brown crystals of formula $[Ph_2\overline{PCH_2CH_2N(CH_2CH_2PPh_2)_2Ni(C}S_2Me)]BPh_4$ (2) (yield ca. 80%). This diamagnetic complex is quite air stable in the solid state, but decomposes in solution unless air is excluded. It is soluble in most organic solvents in which it behaves as a 1/1 electrolyte (molar conductance value in 10^{-3} *M* nitroethane solution: 42 cm^2 ohm^{-1} mol^{-1}; IR Nujol $\nu(C{=}S)$ 1110 cm^{-1}).

The molecular structure of 2 has been determined by X-ray diffraction methods. The crystals are monoclinic, space group *C2/c*, with the following cell parameters: *a* 28.148(16), *b* 14.448(8), *c* 33.922(17) Å, β 112.11(4)°, $Z = 8$. Intensity data were collected within $2\theta \leqslant 40°$ on a Philips PW 1100 automatic diffractometer using the ω-2θ scan technique and the graphite monochromatized Mo-K_α radiation. The structure was solved by the heavy atom method and refined by full-matrix least-squares. Refinements converged at the R and R_w factors values of 0.095 and 0.095 for the 1989 reflections having $I \geqslant 3\sigma(I)$.

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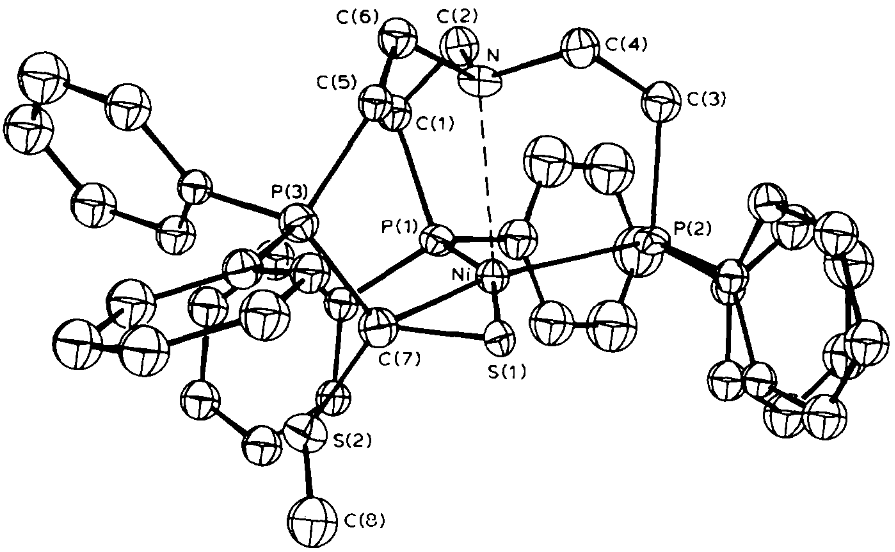


Fig. 1. Perspective view of the complex cation. Ortep drawing with 30% probability ellipsoids.

TABLE 1

SELECTED BOND DISTANCES (Å) AND ANGLES (DEG)

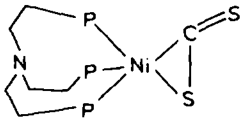
Ni—P(1)	2.179(10)	P(3)—C(7)	1.82(2)
Ni—P(2)	2.188(9)	S(1)—C(7)	1.72(3)
Ni—S(1)	2.117(9)	S(2)—C(7)	1.77(3)
Ni—C(7)	2.027(24)	S(2)—C(8)	1.85(3)
Ni—N	2.592(18)		
P(1)—Ni—P(2)	106.5(3)	N—Ni—C(7)	103.1(8)
P(1)—Ni—S(1)	159.7(3)	Ni—S(1)—C(7)	62.7(8)
P(1)—Ni—N	79.2(6)	C(7)—S(2)—C(8)	102.1(14)
P(1)—Ni—C(7)	111.4(9)	Ni—C(7)—P(3)	114.7(12)
P(2)—Ni—S(1)	93.4(3)	Ni—C(7)—S(1)	68.2(9)
P(2)—Ni—N	81.6(5)	Ni—C(7)—S(2)	122.2(14)
P(2)—Ni—C(7)	142.0(9)	P(3)—C(7)—S(1)	111.2(15)
S(1)—Ni—N	108.3(5)	P(3)—C(7)—S(2)	112.2(14)
S(1)—Ni—C(7)	49.0(8)	S(1)—C(7)—S(2)	121.5(14)

The molecular structure consists of $[Ph_2PCH_2CH_2N(CH_2CH_2PPh_2)_2Ni(CS_2Me)]^+$ cations and BPh_4^- anions. Figure 1 shows a perspective view of the cation, whose selected bond distances and angles are given in Table 1.

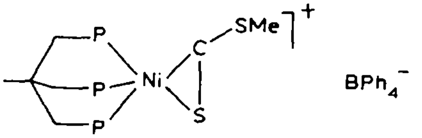
The nickel atom is coordinated by two phosphorus atoms of the np_3 ligand and by carbon and the un-methylated sulfur atom of a phosphoniodithiomethyl ester group in a distorted square pyramidal geometry. At the apex of the pyramid lies the nitrogen atom of the np_3 ligand at the significantly long distance from the metal of 2.592(18) Å. The third phosphorus atom of the np_3, which is attached to the CS_2Me carbon atom, is at 3.24(1) Å from the nickel. There are no contacts shorter than 3.40 Å between the metal and the phenyl groups carbon atoms. The geometric environment of the carbon of the CS_2 group merits comment. Apart from the Ni—C(7)—S(1) angle, which is constrained to the value of 68.2(9)°, the other angles range from 111.2(15) to 122.2(14)°, indicating the sp^3 character of this carbon; indeed a systematic lengthening of all the distances involving the C(7 atom is observed compared to the corresponding values reported for the η^2-CS_2 cobalt and nickel complexes [(triphos)Co(η^2-CS_2)] [2] and [(triphos)Ni(η^2-CS_2)] [3].

The $^{31}P\{^1H\}$ NMR spectrum [4] in CD_2Cl_2 is compatible with the structure found in the solid state. The presence of three types of phosphorus centres is revealed, giving resonances in a 1/1/1 ratio. A doublet of doublets with a chemical shift of 7.48 ppm is assigned to the P_A phosphorus atom *trans* to the carbon atom of the PCS_2Me group, while two doublets at 17.79 ($^3J(P_A{-}P_B)$ 14 Hz), and 20.21 ppm ($^2J(P_A{-}P_C)$ 8 Hz) are assigned to the P_B phosphorus atom *cis* to P_A and to the P_C phosphonium atom, respectively.

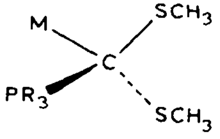
The mechanism of the formation of 2 may be envisaged as involving initial formation of an η^2-CS_2 complex. Methylation of the exocyclic sulfur atom of the CS_2 molecule to give an η^2-dithiomethyl ester group could then be followed by nucleophilic attack by a phosphorus atom of np_3 on the η^2-CS_2Me carbon atom. Support for this mechanism is provided both by the reaction of 1 with CS_2 to give the η^2-CS_2 complex [(np_3)Ni(η^2-CS_2)] (I) [5], and by the reaction of the complex [(triphos)Ni(η^2-CS_2)] [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane] [6] with $MeOSO_2F$ to give the η^2-dithiomethyl ester complex [(triphos)Ni(η^2-CS_2Me)]BPh_4 (II) [5].



(I)



(II)



(III)

Moreover, the carbon atom of η^2-CS_2Me groups has been recently observed to be a reactive site, undergoing attack by sulfur and selenium to give methyltrithiocarbonate and *S*-methyl monoselenodithiocarbonate metal complexes, respectively [7].

The reaction reported in this paper may be regarded as further evidence for the proposed carbenoid nature of the metal-CS_2Me moiety [7,8]. A close analogy, in fact, can be found in the reactions of dithiocarbene complexes with tertiary phosphines, which have been suggested to proceed via the intermediate (III) [9].

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