Inorganica Chimica Acta, 52 (1981) 83–85

Ni(II) Complexes of Trimethylphosphine: Crystal and Molecular Structure of $NiBr_2(PMe_3)_2$. Comparison with the Pentacoordinate $NiBr_2(PMe_3)_3$ and $NiBr(PMe_3)_4BF_4$ Complexes

A. MARI, A. GLEIZES, M. DARTIGUENAVE and Y. DARTIGUENAVE

Laboratoire de Chimie de Coordination associé à l'Université P. Sabatier, 205, Route de Narbonne, 31400 Toulouse, France

Received March 14, 1981

The crystal and molecular structure of $NiBr_2(PMe_3)_2$*, obtained by sublimation at 380 K (10 mm Hg), has been determined. It crystallizes in the* $P2_{1/n}$ *space group, with two molecules in a unit cell of dimension,* a = 8.547(1) Å; b = 13.552(1) Å; c = 6.031(1) Å; β = 90.20(1)°. *The structure (*R = 0.042 *for 52 variables and 446 observations) consists of discrete* $NiBr_2(PMe_3)_2$ *molecules with a square planar geometry around the nickel atom. The main distances and angles are well within the range observed for* $Ni(II)-PR_3$ *square planar complexes. Comparison with the related pentacoordinate species* $NiBr_2(PMe_3)_3$ *and* $[NiBr(PMe_3)_4]^+$ *indicates that pentacoordination occurs with increasing of the Ni–Br bond distances (2.29 Å in tr-square planar to 2.50 Å in trigonal bipyramidal compounds), but has no effect on the Ni–P bond lengths. Interligands contact distances are minimum and have about the same value in the tr-square planar complex and in the trigonal bipyramid between the axial and equatorial ligands.*

Introduction

It is well known that dihalogenobis(tertiaryphosphine)nickel(II) $NiX_2(PR_3)_2$ may exist as square planar diamagnetic and/or tetrahedral paramagnetic isomers. The balance between the two stereochemistries is delicate and depends on ligand steric and electronic factors, solvent and temperature. In the solid state, square planar complexes have been reported with PEt_3 [1] while PPh_3 gives rise to tetrahedral species [2]. On the other hand, square planar and tetrahedral isomers have been obtained with PMe_2Ph [3] and with $PPh_2(PhCH_2)$ a species containing the two isomers in the unit cell (in the ratio SP/Td = 1/3) have been reported [4].

The finding of a magnetic moment in the range 0.9–1.3 B.M. at 295 K for $NiBr_2(PMe_3)_2$, that is higher than the values usually obtained for low spin square planar Ni(II) compounds (about 0.5 B.M.) prompted us to grow single crystals of $NiBr_2(PMe_3)_2$ in order to determine its crystal structure and to see if this value may be related to the presence of a tetrahedral species in the solid state. Moreover, since we have already determined the crystal structure of five-coordinate $NiBr_2(PMe_3)_3$ [5] and $\{NiBr(PMe_3)_4\}^+$ [6], a comparison of the steric interaction between the ligands (minimum allowed contact distance) in the four and five coordinate d^8 complexes will be possible.

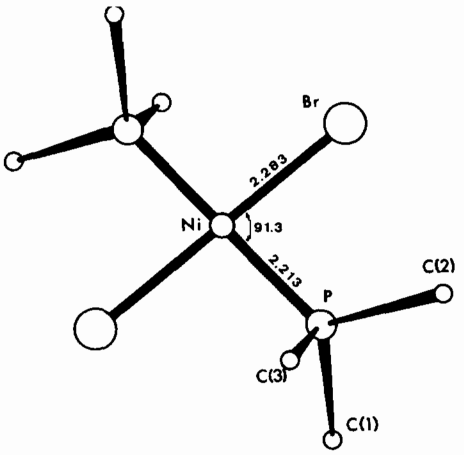

Fig. 1. A drawing of the inner coordination sphere of $NiBr_2(PMe_3)_2$.

We report here the synthesis of pure crystals of $NiBr_2(PMe_3)_2$ and their X-ray structure determination. Only the square planar isomer is present in the solid state, and the anormal value of the magnetic moment has to be attributed to impurities.

Results and Discussion

$NiBr_2(PMe_3)_2$ is obtained by adding 4 ml (40 mmol) of PMe_3 dropwise to a suspension of $NiBr_2$·

TABLE I. Selected Intramolecular Main Bond Distances (Å) and Angles (Deg) for $NiBr_2(PMe_3)_2$.

Distances (Å)		Angles (°)	
Ni–Br:	2.283(3)	Br–Ni–P:	91.3(6)
Ni–P:	2.213(7)	Ni–P–C(1):	114(2)
P–C(1):	1.73(4)	Ni–P–C(2):	121(2)
P–C(2):	1.72(4)	Ni–P–C(3):	117(1)
P–C(3):	1.77(3)	C(1)–P–C(2):	103(4)
P–Br:	3.216(8)	C(1)–P–C(3):	101(3)
		C(2)–P–C(3):	93(3)

$3H_2O$ (4.4 g, 20 mmol) in dichloromethane (30 ml). The solution immediately turns dark–blue, due to the formation of $NiBr_2(PMe_3)_3$. The solution is stirred for two hours at 308 K, until turning dark–red, which is the color of $NiBr_2(PMe_3)_2$. By adding n-decane (20 ml) and evaporating methylene chloride, dark–red microcrystals separate (yield: 70%). Further recrystallization in dichloromethane/n-decane is not sufficient to set a pure nickel(II) complex. Good results have only been obtained after sublimation under argon (10 mm of Hg; T = 380 K). The single crystals obtained are air sensitive and have to be handled in a glove box under argon.

Anal. $NiBr_2P_2C_6H_{18}$. Calc.: C%, 19.43; H%, 4.80; Ni%, 15.8. Found: C%, 19.51; H%, 4.95; Ni% 15.6.

Crystal Data: $NiBr_2(PMe_3)_2$ Space group $P2_1/n$, a = 8.547(1) Å; b = 13.552(1) Å, c = 6.031(1) Å; β = 90.20(1)°; V = 698.6 Å^3; Z = 2.

Intensity data ($0 < \sin\theta/\lambda < 0.75$) were recorded on a NONIUS CAD 4 diffractometer with graphite monochromated Mo Kα radiation. The intensities were corrected for adsorption. The structure was solved from Patterson and Fourier synthesis. Positional and anisotropic thermal parameters for all non hydrogen atoms were refined by full matrix least squares techniques. The hydrogen atoms were located on a difference Fourier map and were included as fixed contributions in last cycles of refinement. Final reliability factors were R = 0.042 and Rw = 0.040 for 52 variables and 446 observations with $I \geq 2.5\sigma(I)$.

A view of the molecule is shown on Fig. 1 and the bond lengths and bond angle values are presented in Table I.

The structure consists of discrete, well separated *trans*-square-planar $NiBr_2(PMe_3)_2$ molecules. These molecules are crystallographically required to possess a center of symmetry. The Ni–P and Ni–Br distances of 2.213(7) Å and 2.283(3) Å respectively, appear to be normal for planar Ni(II) complexes. Table II indicates the corresponding bond lengths in other tr-SP Ni(II) complexes. Using the bulkier PEt_3 and PMe_2-Ph instead of PMe_3 shows a significative increase of the Ni–P bond lengths, following the steric hindrance of the phosphorus ligands [7] but has no significative effect on the Ni–Br distance.

TABLE II. Main Bond Distances in tr-Square planar $NiBr_2(PR_3)_2$ and Trigonal Bipyramidal $NiBr_2(PMe_3)_3$ and $\{NiBr(PMe_3)_4\}$ Complexes.

Compounds	Ni–Br (Å)	Ni–P (Å)	Ref.
$NiBr(PMe_3)_4^+$	2.515 *e*	2.244 *a* 2.247 *a* 2.257 *e* 2.290 *e*	6
$NiBr_2(PMe_3)_3$ (*i*)	2.451 *e* 2.553 *e*	2.20 *a* 2.21 *a* 2.19 *e*	5
	2.426 *e* 2.58 *e*	2.20 *a* 2.21 *a* 2.20 *e*	
$NiBr_2(PEt_3)_2$	2.300	2.260	1
$NiBr_2L_2$ (*ii*)	2.293	2.272	8
$NiBr_2(PMe_2Ph)_2$	2.297	2.251	9
$NiBr_2(PMe_3)_2$	2.283	2.213	(*iii*)
$NiBr_2(PPh_2PhCH_2)_2$	2.305	2.263	4

(*a*): Axial. (*e*): Equatorial. (*i*): Two molecules per unit cell for this compound. (*ii*): L = 5-Me, 5-dibenzophosphole. (*iii*): This work.

Comparison with the related pentacoordinate trigonal bipyramidal complexes $NiBr_2(PMe_3)_3$ and $\{NiBr(PMe_3)_4\}^+$ (Br is located in equatorial position of the TBP) indicates an important increase of the Ni–Br bond length upon pentacoordination. The averaged Ni–Br distance is 2.50 Å for the TBP pentacoordinate complexes and 2.29 Å for the tr-SP tetracoordinate complexes. On the other hand no modification of the Ni–P distance is apparent upon pentacoordination: the averaged Ni–P length is 2.20 Å for the TBP complex $NiBr_2(PMe_3)_3$, 2.259 Å for the TBP complex $\{NiBr(PMe_3)_4\}^+$ and 2.213 Å for $NiBr_2(PMe_3)_2$.

If one considers the contact distance between the phosphorus and the bromine atoms as being the minimum internal contact distance allowed for a crowded system, it is apparent that the P–Br distances in the square planar species (3.216(8) Å) and the P$_{ax}$–Br distances in the TBP species (3.181(4) Å) for $\{NiBr(PMe_3)_4\}^+$ and 3.241 Å for $NiBr_2(PMe_3)_3$ (in both cases the P–Ni–Br angle being about 90°) are of the same order and less than the sum of the van der Waals radii of P and Br (3.85 Å) [10]. On the other hand, the P$_{eq}$–Br distance in TBP complexes (P$_{eq}$–Ni–Br being about 120°) are equivalent to the sum of the van der Waals radii

[6, 10]. Thus, the comparison with the tr-SP complex indicates that in the d^8 TBP complexes, the distance between axial and equatorial ligands is the minimum contact distance observed between the two ligands. This value is not exceptionally short and is compatible with the results observed in well packed molecular solids [8, 11]. This is too in good agreement with theoretical calculations since Ni–L$_{ax}$ bonds are expected to be stronger than equatorial ones (empty d$_{z^2}$ antibonding orbital) for d^8 trigonal bipyramidal complexes.

The magnetic susceptibility determination of a sublimated sample of NiBr$_2$(PMe$_3$)$_2$, handled under argon gives a value of χ_a (T = 293 K) = 293.7 10^{-6} uem cgs corresponding to an effective magnetic moment of 0.43 B.M. This value is in the range of the reported values for diamagnetic Ni(II)–phosphine complexes. When the complex is handled in air for a short time, an increase of the magnetic moment is observed but without any observable modification of the sample (no $\nu_{P=O}$ band in the infrared spectrum).

NiBr$_2$(PMe$_3$)$_2$ is monomeric in dichloroethane, as has been determined by cryoscopy at 238 K (measured molecular weight: 390 g; calculated: 370.5 g). Its electronic spectrum at 295 K and 190 K in degazed dichloromethane shows only one d–d transition at 540 nm ($\epsilon_{293\,K}$ = 430; $\epsilon_{190\,K}$ = 640) as expected for a square planar d^8 complex of C_{2v} symmetry. However, no ^{31}P{^{1}H}signal is observed at room temperature in the NMR spectrum (in CH$_2$Cl$_2$/CD$_2$Cl$_2$). By lowering the temperature at 183 K, a single line at δ = −19.2 ppm (from H$_3$PO$_4$) is present, as expected for the tr–SP isomer.

References

1 G. Giacometti, V. Scatturin and A. Turco, *Gazz. Chim. Ital., 88,* 434 (1958).
V. Scatturin and A. Turco, *J. Inorg. Nucl., 8,* 447 (1958).
2 G. Garton, D. E. Henn, H. M. Powell and L. M. Venanzi, *J. Chem. Soc. A,* 3626 (1963).
J. A. J. Jarvis, R. H. B. Mais and P. G. Owslon, *J. Chem. Soc. A,* 1473 (1968).
3 M. C. Browning, J. R. Mellor, D. J. Morgan, S. A. Pratt, L. S. Sutton and L. M. Venanzi, *J. Chem. Soc. A,* 693 (1962).
4 B. T. Kilbourn and H. M. Powell, *J. Chem. Soc. A,* 1688 (1970).
5 J. W. Dawson, T. J. McLennan, W. Robinson, A. Merle, M. Dartiguenave, Y. Dartiguenave and H. B. Gray, *J. Am. Chem. Soc., 96,* 4428 (1974).
6 M. Dartiguenave, Y. Dartiguenave, A. Gleizes, C. Saint-Joly, P. Meier and A. E. Merbach, *Inorg. Chem., 17,* 3503 (1978).
7 C. A. Tolman, *Chem. Rev., 77;* 313 (1977).
8 D. J. Watkins, *J. Chem. Soc. Dalton,* 1803 (1976).
9 J. K. Stalick and J. A. Ibers, *Inorg. Chem., 9,* 453 (1970).
10 C. Saint-Joly, A. Mari, A. Gleizes, M. Dartiguenave, Y. Dartiguenave and J. Galy, *Inorg. Chem., 19,* 2403 (1980).
11 K. J. Haller and J. H. Enemark, *Inorg. Chem., 17,* 3552 (1978).