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A Nickel–Trimethylphosphine Complex: Crystal and Molecular Structure and Decomposition Reaction of $[Ni(CH_3)(PMe_3)_4]BPh_4$

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The crystal and molecular structure of methyltetrakis(trimethylphosphine)nickel(II) tetraphenylborate has been determined by X-ray diffraction. The compound crystallizes in the monoclinic $P2_1/n$ space group with four units of $[Ni(CH_3)(PMe_3)_4]BPh_4$ in a unit cell having dimensions $a = 14.595$ (10) Å, $b = 16.779$ (5) Å, $c = 16.302$ (4) Å, and $\beta = 99.41$ (4)°. Full-matrix least-squares refinement of 208 variables gave a final value of the conventional R index (on F) of 0.047 for the 2384 reflections having $F_o^2 > 3\sigma(F_o^2)$. The structure consists of well-separated $[Ni(CH_3)(PMe_3)_4]^+$ cations and $[B(C_6H_5)_4]^-$ anions. The nickel atom is in a slightly distorted trigonal bipyramid of C_{3v} symmetry with the methyl group carbon atom in an axial position, the Ni atom being shifted by 0.24 Å above the equatorial plane toward the axial P atom. $Ni-P_{eq}$ bond lengths are quite equal (average 2.256 (3) Å) and significantly larger than the $Ni-P_{ax}$ bond (2.210 (3) Å); the Ni–C bond length is equal to 2.034 (7) Å. The $C-Ni-P_{ax}$ angle is 179.4 (5)° while the $C-Ni-P_{eq}$ angles have a mean value of 83.8 (±0.5)°. The molecule is distorted toward a monocapped tetrahedron (CH_3 lying at the capping position), i.e., on the geometrical reaction path corresponding to the homolysis of the $Ni-CH_3$ bond, giving rise to the tetrahedral Ni(I) $[Ni(PMe_3)_4]^+$ species.

Introduction

We have reported previously that recrystallization of the cationic pentacoordinate Ni(II) complex $[Ni(CH_3)(PMe_3)_4]B(C_6H_5)_4$ (I) from tetrahydrofuran solution resulted in the homolytic cleavage of the $Ni-CH_3$ bond, giving rise to the 17-e Ni(I) d^9 complex $[Ni(PMe_3)_4]B(C_6H_5)_4$ (II). This compound has been characterized by X-ray and spectroscopic methods as a tetrahedral monomeric species.[2]

Due to the major role played by σ metal–carbon bonds in organometallic chemistry, it is of importance to get a good knowledge of this reaction. This paper reports therefore the X-ray structure and the spectroscopic determination of the parent complex $[Ni(CH_3)(PMe_3)_4]B(C_6H_5)_4$ (I). A new method of preparation of II is also indicated.

Experimental Section

All operations were carried out under an argon atmosphere in Schlenk-type apparatus. An inert-atmosphere glovebox was used for handling the reagents (especially when in solution). All the solvents were purified by conventional methods, distilled before use, and degassed.

Magnetic and spectroscopic (visible and near-infrared) measurements were carried out by using methods already described.[4]

Synthesis of $[Ni(CH_3)(PMe_3)_4]B(C_6H_5)_4$. The synthesis has been made as reported by Klein et al.[5] by reacting 0.29 mL $LiCH_3$ (3.3 mmol) in ether with $[NiBr(PMe_3)_4]B(C_6H_5)_4$ (0.73 g, 3.5 mmol) dissolved in tetrahydrofuran at −70 °C. Filtration and addition of ethanol precipitate the compound as yellow crystals. They are recrystallized from THF/ethanol. Anal. Calcd for $NiBrP_4BC_{36}H_{56}$: C, 63.73; H, 8.53. Found: C, 63.76; H, 8.11. The crystals can be handled in air for a short time (5 min). The selected crystal is sealed in a thin-walled capillary for X-ray analysis.

Synthesis of $[Ni(PMe_3)_4]B(C_6H_5)_4$. This complex is isolated either by recrystallization of $[Ni(CH_3)(PMe_3)_4]B(C_6H_5)_4$ in tetrahydrofuran or by adding tetrakis(trimethylphosphine)nickel(0) (2 mmol, 0.36 g) to a solution of dichlorobis(trimethylphosphine)nickel(II) (2 mmol, 0.56 g) in THF containing 2 mL of trimethylphosphine (2.1 mmol). $NaPF_6$ (2 mmol, 0.34 g) is added to the mixture. The yellow solution is stirred at 20 °C and concentrated. Yellow crystals are separated by filtration and dried under argon (yield 80%). Anal. Calcd for $C_{12}H_{36}F_6NiP_5$: C, 28.37; H, 7.14. Found: C, 28.01; H, 7.09.

Table I. Experimental Crystallographic Data for $[Ni(CH_3)(PMe_3)_4]B(C_6H_5)_4$

(1) Physical and Crystallographic Data

monoclinic	ρ_m[a]
$a = 14.595$ (10) Å	$\rho_x = 1.17$ g/cm^3
$b = 16.779$ (5) Å	$Z = 4$
$c = 16.302$ (4) Å	parallelepiped (0.03 × 0.03 × 0.06 cm)
$\beta = 99.41$ (4)°	$\mu_{Mo\,K\alpha} = 6.73$ cm^{-1}
$V = 3960$ Å^3	

(2) Data Collection

temp: 293 K
radiation: λ(Mo Kα) = 0.710 69 Å
monochromatization: oriented graphite cryst
cryst detector dist: 207 mm
detector window: height = 4 mm; width = (3.6 + 0.7 tan θ) mm
takeoff angle: 3.5°
scan mode: θ–1.333θ
max Bragg angle: 21°
scan angle: $\Delta\theta = \Delta\theta_0 + B \tan\theta$, $\Delta\theta_0{}^b = 1.20°$, $B^b = 0.35$
values determining the scan speed: SIGPRE^b = 0.50, SIGMA^b = 0.018, VPRE^b = 2°/min, TMAX^b = 40 s
std intens reflctns: 600, 040, 022, 029 every 3600 s
independent recorded reflctns: 4225
utilized reflctns: 2823 ($F_o^2 \geq 3\sigma(F_o^2)$)

[a] Was not measured. [b] These parameters have been described in: Mosset, A.; Bonnet, J. J.; Galy, J. *Acta Crystallogr., Sect. B* 1977, *33*, 2633.

Single-Crystal X-ray Data Collection. Precession photographs taken with a single crystal placed on a Stoe camera using Mo Kα radiation showed that the complex crystallizes in the monoclinic system of space group $P2_1/n$. The same crystal was mounted on an Enraf Nonius CAD-4 computer-controlled four-circle diffractometer. Accurate unit cell constants were derived from a least-squares refinement of the setting angles of 25 reflections (Table I). Intensity measurements were made for the forms hkl and $hk\bar{l}$. Reflections with $2\theta < 42°$ were scanned as described in Table I. The data were processed with use of an ignorance factor p of 0.03 in the estimation of standard deviations.[6] No absorption corrections were applied (cylindrical $\mu R \simeq 0.12$).

Structure Determination and Refinement. The structure determination was effected by using Patterson and Fourier map techniques and the refinement by applying full-matrix least-squares techniques. Throughout the refinement, the function minimized was $\sum(F_o - |F_c|)^2$, where F_o and $|F_c|$ are the observed and calculated structure amplitudes. The reliability coefficients are defined as $R = \sum|F_o - |F_c||/\sum F_o$ and $R_w = [\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2}$. The atomic scattering factors and anomalous terms (Ni and P atoms) are those of Cromer and Waber.[7]

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0020-1669/81/1320-2372$01.25/0

Table II. Positional and Thermal Parameters for the Nongroup Atoms of $[Ni(CH_3)(PMe_3)_4]B(C_6H_5)_4$

atom	x^a	y	z	$B_{11}{}^b$	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.24698 (6)	−0.18164 (5)	−0.07809 (5)	2.52 (4)	3.51 (4)	2.91 (4)	−0.24 (4)	0.58 (3)	−0.093 (4)
P(1)	0.20851 (13)	−0.14769 (12)	−0.21328 (12)	4.05 (10)	4.36 (10)	2.98 (9)	−0.46 (8)	0.06 (8)	0.01 (8)
P(2)	0.22357 (13)	−0.09395 (13)	0.02102 (12)	3.46 (9)	4.73 (11)	3.43 (9)	0.35 (8)	0.96 (8)	−0.58 (8)
P(3)	0.25972 (14)	−0.31157 (13)	−0.04175 (13)	4.18 (10)	3.57 (10)	5.15 (11)	−0.11 (8)	1.64 (8)	0.37 (9)
P(4)	0.39775 (13)	−0.16025 (12)	−0.06884 (12)	2.64 (8)	4.82 (11)	3.79 (9)	−4.5 (8)	0.61 (7)	−0.59 (8)
C	0.1081 (5)	−0.2016 (5)	−0.0879 (5)	2.9 (3)	7.5 (6)	5.5 (5)	−0.6 (3)	0.8 (3)	0.3 (4)
C(11)	0.2918 (6)	−0.1320 (6)	−0.2843 (5)	7.5 (5)	9.7 (7)	3.7 (4)	−1.4 (5)	1.5 (4)	0.3 (4)
C(21)	0.1304 (7)	−0.2137 (6)	−0.2784 (5)	11.0 (7)	9.8 (7)	3.9 (4)	−4.8 (6)	−0.7 (4)	−0.4 (5)
C(31)	0.1475 (8)	−0.0533 (6)	−0.2280 (6)	13.8 (8)	7.7 (6)	5.6 (6)	4.3 (6)	1.1 (5)	2.5 (5)
C(12)	0.3013 (6)	−0.0105 (5)	0.0537 (6)	6.0 (5)	5.8 (5)	6.9 (5)	−0.5 (4)	1.1 (4)	−2.6 (4)
C(22)	0.1144 (6)	−0.0394 (6)	0.0076 (6)	5.0 (4)	9.1 (7)	8.2 (6)	2.4 (4)	1.9 (4)	−2.8 (5)
C(32)	0.2227 (7)	−0.1425 (6)	0.1200 (5)	8.6 (6)	9.5 (6)	3.4 (4)	−0.8 (5)	2.0 (4)	−1.0 (4)
C(13)	0.2644 (7)	−0.3795 (5)	−0.1288 (6)	10.3 (7)	4.6 (5)	8.9 (6)	−0.8 (5)	4.1 (5)	−1.3 (4)
C(23)	0.3569 (6)	−0.3480 (6)	0.0341 (6)	6.6 (5)	5.8 (5)	8.6 (6)	1.3 (4)	1.1 (4)	2.5 (5)
C(33)	0.1660 (6)	−0.3565 (5)	0.0034 (6)	6.6 (5)	5.6 (5)	8.7 (6)	−1.4 (4)	3.1 (5)	1.3 (4)
C(14)	0.4599 (5)	−0.2257 (5)	−0.1299 (6)	3.5 (4)	8.0 (6)	7.1 (6)	0.8 (4)	2.1 (4)	−0.5 (4)
C(24)	0.4328 (6)	−0.0616 (5)	−0.1019 (5)	5.3 (4)	6.1 (5)	5.8 (5)	−2.9 (4)	1.2 (4)	−0.7 (4)
C(34)	0.4711 (5)	−0.1671 (6)	0.0337 (5)	4.0 (4)	7.9 (6)	5.3 (4)	0.1 (4)	−1.1 (3)	−0.4 (4)
B	0.3008 (5)	−0.2127 (5)	0.4073 (5)	2.5 (4)	3.0 (4)	3.1 (4)	0.2 (3)	0.4 (3)	0.2 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(1)	0.093	−0.211	−0.034	5.0	H(332)	0.281	−0.166	0.140	7.0
H(2)	0.092	−0.247	−0.123	5.0	H(113)	0.263	−0.434	−0.111	8.0
H(3)	0.075	−0.157	−0.113	5.0	H(213)	0.211	−0.370	−0.171	8.0
H(111)	0.329	−0.181	−0.286	7.0	H(313)	0.319	−0.371	−0.152	8.0
H(211)	0.262	−0.122	−0.338	7.0	H(123)	0.358	−0.322	0.087	7.0
H(311)	0.334	−0.091	−0.265	7.0	H(223)	0.355	−0.403	0.042	7.0
H(121)	0.112	−0.191	−0.333	8.0	H(323)	0.415	−0.336	0.016	7.0
H(221)	0.160	−0.265	−0.286	8.0	H(133)	0.157	−0.331	0.051	7.0
H(321)	0.075	−0.224	−0.256	8.0	H(233)	0.109	−0.356	−0.037	7.0
H(131)	0.188	−0.010	−0.210	9.0	H(333)	0.180	−0.413	0.015	7.0
H(231)	0.096	−0.052	−0.200	9.0	H(114)	0.469	−0.275	−0.104	6.0
H(331)	0.124	−0.045	−0.288	9.0	H(214)	0.428	−0.230	−0.184	6.0
H(112)	0.363	−0.028	−0.070	6.0	H(314)	0.521	−0.203	−0.131	6.0
H(212)	0.303	0.025	0.005	6.0	H(124)	0.497	−0.065	−0.110	6.0
H(312)	0.281	0.021	0.094	6.0	H(224)	0.396	−0.049	−0.155	6.0
H(122)	0.110	−0.007	0.054	7.0	H(324)	0.427	−0.023	−0.062	6.0
H(222)	0.063	−0.077	0.002	7.0	H(134)	0.454	−0.129	0.070	6.0
H(322)	0.107	−0.009	−0.043	7.0	H(234)	0.466	−0.220	0.057	6.0
H(132)	0.209	−0.102	0.160	7.0	H(334)	0.536	−0.159	0.028	6.0
H(232)	0.175	−0.181	0.115	7.0					

[a] Estimated standard deviations in the last significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[0.25(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$.

The position of the nickel atom was derived from the Patterson map; the remaining nonhydrogen atooms were located on two Fourier maps. An isotropic refinement treating the phenyl groups as rigid bodies resulted in $R = 0.10$. Introducing anisotropic temperature factors for nongroup atoms yielded $R = 0.063$ and $R_w = 0.077$. Methyl group hydrogen atoms were located from Fourier difference maps of plane sections perpendicular to P–C bonds. Their positions were introduced as fixed contributions. Convergence was achieved with $R = 0.047$ and $R_w = 0.053$ for the 2384 observations above background and 208 variables. The error in an observation of unit weight was 1.29 e. The final difference Fourier map did not exhibit peaks higher than $^1/_5$ of the peaks corresponding to carbon atoms on the Fourier map. The most significant of those peaks were located around the phenyl groups, thus revealing the need for the phenyl group atoms to be refined individually. This was not done. A listing of observed and calculated structure amplitudes is available as supplementary material. Refined atomic parameters are listed in Table II and in Table III.

Results and Discussion

The structure consists of discrete, well-separated $[Ni(CH_3)(PMe_3)_4]^+$ cations and $B(C_6H_5)_4^-$ anions. A perspective view of the $[Ni(CH_3)(PMe_3)_4]^+$ cation is shown in Figure 1.

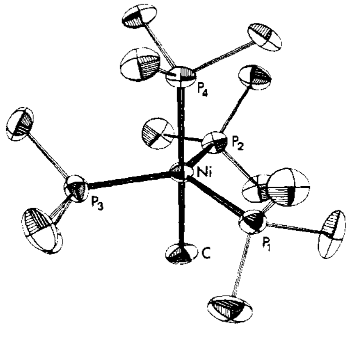

Figure 1. Perspective view of the $[Ni(CH_3)(PMe_3)_4]^+$ cation.

Bond lengths and angles are given in Table IV.

The nickel atom is pentacoordinated, linked to the four PMe_3 ligands and to the carbon atom of the methyl group. The geometry of the coordination polyhedron can be considered as a distorted trigonal bipyramid, with CH_3 and one PMe_3 ligand in axial positions. The Ni–P distances are well in the range of the observed values in Ni–PR_3 complexes.[4] The axial Ni–P(4) distance of 2.210 (7) Å is significantly shorter than the three equatorial and nearly equivalent Ni–P distances (mean value 2.256 Å). The Ni–CH_3 distance (2.034 (7) Å) is quite reasonable, being in the same order as the Ni–CH_3 distance found in $[Ni(CH_3)(np_3)]^+$ (2.02 (2) Å) (CH_3 occupying an axial position in the TBP) but slightly longer than

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(7) All calculations have been performed with use of the CII Iris 80 computer of the Centre Interuniversitaire de Calcul de Toulouse. In addition to various local programs, modified versions of the following programs were employed: Zalkin's FORDAP Fourier summation program; Johnson's ORTEP thermal ellipsoid plotting program; Busing and Levy's ORFFE error function program; Ibers' NUCLS full-matrix least-squares program which in its nongroup version resembles Busing and Levy's ORFLS program.

Table III. Derived Parameters for the Rigid Group Atoms of $[Ni(CH_3)(PMe_3)_4]B(C_6H_5)_4$

Positional and Thermal Parameters

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
C(1)G1	0.2788 (3)	−0.2901 (2)	0.3432 (3)	2.90 (13)	H(2)G1	0.1426 (3)	−0.2682 (3)	0.2984 (4)	3.5
C(2)G1	0.1923 (2)	−0.3039 (2)	0.2955 (3)	3.53 (14)	H(3)G1	0.1195 (3)	−0.3793 (4)	0.2110 (4)	4.9
C(3)G1	0.1786 (3)	−0.3699 (3)	0.2435 (3)	4.88 (18)	H(4)G1	0.2421 (5)	−0.4673 (3)	0.2038 (4)	5.3
C(4)G1	0.2514 (3)	−0.4222 (2)	0.2393 (3)	5.27 (18)	H(5)G1	0.3877 (4)	−0.4442 (3)	0.2840 (4)	5.0
C(5)G1	0.3380 (3)	−0.4085 (3)	0.2869 (3)	4.97 (18)	H(6)G1	0.4107 (3)	−0.3330 (4)	0.3714 (4)	4.1
C(6)G1	0.3517 (2)	−0.3424 (3)	0.3389 (3)	4.11 (16)	H(2)G2	0.4021 (5)	−0.2106 (3)	0.2740 (4)	3.8
C(1)G2	0.3764 (3)	−0.1480 (2)	0.3748 (3)	2.89 (13)	H(3)G2	0.5023 (5)	−0.1171 (4)	0.2299 (3)	4.8
C(2)G2	0.4158 (3)	−0.1627 (2)	0.3043 (3)	3.82 (15)	H(4)G2	0.5362 (4)	0.0012 (3)	0.3045 (4)	4.8
C(3)G2	0.4754 (3)	−0.1071 (3)	0.2781 (2)	4.77 (18)	H(5)G2	0.4699 (5)	0.0259 (3)	0.4232 (4)	4.6
C(4)G2	0.4956 (3)	−0.0368 (3)	0.3224 (3)	4.77 (18)	H(6)G2	0.3697 (4)	−0.0676 (4)	0.4673 (3)	3.8
C(5)G2	0.4562 (3)	−0.0221 (2)	0.3929 (3)	4.55 (17)	H(2)G3	0.4658 (4)	−0.1921 (4)	0.5265 (4)	4.5
C(6)G2	0.3966 (3)	−0.0776 (3)	0.4191 (2)	3.84 (15)	H(3)G3	0.5190 (3)	−0.2554 (5)	0.6531 (4)	5.6
C(1)G3	0.3423 (3)	−0.2508 (3)	0.5020 (2)	3.37 (14)	H(4)G3	0.4270 (5)	−0.3517 (5)	0.7039 (3)	6.5
C(2)G3	0.4285 (3)	−0.2312 (3)	0.5471 (3)	4.51 (17)	H(5)G3	0.2818 (5)	−0.3847 (4)	0.6281 (5)	6.5
C(3)G3	0.4601 (3)	−0.2688 (3)	0.6224 (3)	5.6 (2)	H(6)G3	0.2287 (3)	−0.3214 (4)	0.5014 (4)	5.0
C(4)G3	0.4054 (4)	−0.3261 (3)	0.6525 (3)	6.5 (2)	H(2)G4	0.2025 (4)	−0.1722 (4)	0.5367 (2)	3.7
C(5)G3	0.3192 (4)	−0.3457 (3)	0.6075 (3)	6.5 (2)	H(3)G4	0.0719 (4)	−0.0927 (4)	0.5410 (3)	4.8
C(6)G3	0.2876 (3)	−0.3081 (3)	0.5322 (3)	4.95 (18)	H(4)G4	−0.0034 (3)	−0.0310 (4)	0.4199 (4)	4.2
C(1)G4	0.2048 (2)	−0.1579 (2)	0.4130 (3)	2.72 (13)	H(5)G4	0.0519 (4)	−0.0489 (3)	0.2944 (3)	4.1
C(2)G4	0.1719 (3)	−0.1472 (3)	0.4875 (2)	3.68 (15)	H(6)G4	0.1825 (4)	−0.1285 (4)	0.2901 (2)	3.8
C(3)G4	0.0943 (3)	−0.0999 (3)	0.4901 (2)	4.77 (18)					
C(4)G4	0.0496 (3)	−0.0633 (3)	0.4181 (3)	4.22 (16)					
C(5)G4	0.0824 (3)	−0.0739 (3)	0.3435 (2)	4.15 (16)					
C(6)G4	0.1601 (3)	−0.1212 (3)	0.3410 (2)	3.75 (15)					

Rigid Group Parameters

group	x_c[a]	y_c	z_c	ϕ[b]	θ	ρ
G1	0.2651 (2)	−0.35618 (18)	0.29121 (18)	0.405 (3)	−2.686 (3)	0.474 (3)
G2	0.4360 (2)	−0.09237 (19)	0.34860 (19)	2.644 (3)	3.098 (2)	1.111 (3)
G3	0.3738 (2)	−0.2884 (2)	0.5773 (2)	−0.206 (4)	2.313 (3)	−2.544 (4)
G4	0.1272 (2)	−0.11057 (17)	0.41554 (18)	−2.245 (3)	−2.786 (2)	−1.683 (3)

[a] x_c, y_c, and z_c are the fractional coordinates of the origin of the rigid group. [b] The rigid group orientation angles (radians) have been defined in: La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* **1965**, *18*, 511.

Table IV. Selected Distances (Å) and Angles (Deg) in $[Ni(CH_3)(PMe_3)_4]B(C_6H_5)_4$

		Around Ni Atom			
Ni–P(1)	2.257 (2)	P(1)–Ni–P(2)	119.5 (9)	P(3)–Ni–P(4)	97.8 (9)
Ni–P(2)	2.252 (2)	P(1)–Ni–P(3)	119.8 (9)	P(1)–Ni–C	83.0 (2)
Ni–P(3)	2.259 (3)	P(1)–Ni–P(4)	94.4 (9)	P(2)–Ni–C	84.1 (3)
Ni–P(4)	2.210 (3)	P(2)–Ni–P(3)	117.3 (9)	P(3)–Ni–C	84.3 (3)
Ni–C	2.034 (7)	P(2)–Ni–P(4)	96.4 (9)	P(4)–Ni–C	179.4 (5)
		Around P Atoms			
P(1)–C(11)	1.830 (10)	Ni–P(1)–C(11)	124.7 (3)	Ni–P(3)–C(13)	114.2 (3)
P(1)–C(21)	1.805 (10)	Ni–P(1)–C(21)	116.8 (3)	Ni–P(3)–C(23)	121.4 (3)
P(1)–C(31)	1.813 (11)	Ni–P(1)–C(31)	112.8 (3)	Ni–P(3)–C(33)	118.1 (3)
P(2)–C(12)	1.826 (9)	C(11)–P(1)–C(21)	97.9 (4)	C(13)–P(3)–C(23)	101.2 (4)
P(2)–C(22)	1.820 (9)	C(11)–P(1)–C(31)	98.8 (5)	C(13)–P(3)–C(33)	100.4 (5)
P(2)–C(32)	1.809 (9)	C(21)–P(1)–C(31)	102.1 (5)	C(23)–P(3)–C(33)	98.0 (4)
P(3)–C(13)	1.830 (10)	Ni–P(2)–C(12)	123.4 (3)	Ni–P(4)–C(14)	116.4 (3)
P(3)–C(23)	1.828 (9)	Ni–P(2)–C(22)	118.3 (3)	Ni–P(4)–C(24)	116.6 (3)
P(3)–C(33)	1.819 (10)	Ni–P(2)–C(32)	111.7 (3)	Ni–P(4)–C(34)	118.6 (3)
P(4)–C(14)	1.821 (9)	C(12)–P(2)–C(22)	98.1 (4)	C(14)–P(4)–C(24)	101.3 (4)
P(4)–C(24)	1.839 (9)	C(12)–P(2)–C(32)	100.3 (4)	C(14)–P(4)–C(34)	101.0 (4)
P(4)–C(34)	1.835 (8)	C(22)–P(2)–C(32)	101.5 (5)	C(24)–P(4)–C(34)	100.0 (4)
		Ligand-Ligand Distances			
P(1)–P(2)	3.896 (3)	P(4)–P(1)	3.330 (3)	C–P(1)	2.849 (9)
P(1)–P(3)	3.906 (3)	P(4)–P(2)	3.326 (3)	C–P(2)	2.876 (8)
P(2)–P(3)	3.852 (3)	P(4)–P(3)	3.315 (3)	C–P(3)	2.885 (8)
		Around B Atom			
B–C(1)G1	1.666 (8)	C(1)G1–B–C(1)G2	111.8 (5)	C(1)G2–B–C(1)G3	112.0 (4)
B–C(1)G2	1.694 (9)	C(1)G1–B–C(1)G3	106.3 (5)	C(1)G2–B–C(1)G4	104.9 (5)
B–C(1)G3	1.689 (8)	C(1)G1–B–C(1)G4	112.5 (4)	C(1)G3–B–C(1)G4	109.4 (5)
B–C(1)G4	1.690 (9)				

the distance reported for other tetracoordinate nickel complexes (1.97 and 1.94 Å).[8] The P(4)–Ni–C angle of 179.4 (5)° is very near to the 180° value for the regular TBP.

One particular feature of the structure is the position of the nickel atom, which is located 0.24 Å above the equatorial plane made by the three phosphorus atoms P(1), P(2), and P(3) toward P(4) and indicates a distortion of the TBP toward the

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[8] Sacconi, L.; Dapporto, P.; Stoppioni, P.; Innocenti, P.; Benelli, C. *Inorg. Chem.* **1977**, *16*, 1669.

Table V. Dihedral Angles (Deg) for $[Ni(CH_3)(PMe_3)_4]^+$ Compared with the Equivalent Ones Calculated for Ideal Trigonal Bipyramidal and Monocapped Tetrahedral Geometries

dihedral angle	ideal monocapped tetrahedron	obsd angles	ideal trigonal bipyramid
P(4)-P(1)	109.5	105.2	101.5
P(4)-P(2)	109.5	103.8	101.5
P(4)-P(3)	109.5	104.2	101.5
C-P(1)	90.0	99.7	101.5
C-P(2)	90.0	97.6	101.5
C-P(3)	90.0	97.7	101.5
P(1)-P(2)	54.7	52.7	53.1
P(1)-P(3)	54.7	52.2	53.1
P(2)-P(3)	54.7	54.9	53.1

monocapped tetrahedron (CH_3 being located in the capping position). Such a distortion of the TBP toward a monocapped tetrahedron is known for pentacoordinate Co(I) and Co(II) complexes[9] but is reported for the first time in pentacoordinate nickel(II) complexes with monodentate ligands. In $[Ni(CH_3)(PMe_3)_4]^+$ such a geometry accommodates well the electronic properties of the d^8 Ni(II) center and of the CH_3^- ligand (a σ-donor ligand). A $Ni-P_{ax}$ distance shorter than the equatorial one is expected for a low-spin d^8 TBP complex due to the presence of the empty d_{z^2} orbital and an axial site preference for CH_3^-. It accommodates too the steric effects of the ligands, which are important in determining the deformation of the trigonal bipyramid. The lower steric requirement of the CH_3 ligand and the nonbonding repulsions between the axial and equatorial phosphine ligands may explain the presence of $C-Ni-P_{eq}$ angles lower than 90 °C. In Table IV, we have reported the distances between the axial–equatorial or equatorial–equatorial ligands, compared to the sum of the van der Waals radii of the bonding atoms. It is obvious that, if in the equatorial plane the P–P distance is slightly larger than the sum of the phosphorus van der Waals radii (3.8 Å), the distances between each of the two axial ligands CH_3 and P(4) and the equatorial phosphorus atoms P(1), P(2), and P(3) are lower by 15%. These shorter values are directly comparable to the one observed in $NiBr_2(PMe_3)_3$, $[NiBr(PMe_3)_4]BF_4$ and in $NiI_2(CO)(PMe_3)_2$.

The importance of the distortion of the trigonal bipyramid toward the monocapped tetrahedron is determined by using the dihedral angle criteria.[10] Table V allows the comparison with the dihedral angles ideal values calculated for the trigonal bipyramid (C_{3v} symmetry) and the monocapped tetrahedron (C_{3v} symmetry). It indicates that $[Ni(CH_3)(PMe_3)_4]^+$ is located halfway inbetween the two ideal structures. A better representation of this distortion is schematized by Figure 2. We have indicated the geometric reaction path going from the regular TBP (C_{3v} symmetry) to the regular tetrahedron, calculated by measuring the normalized shift parameters $s = (\bar{d} - 3\Delta)/\bar{d}$, and correlating it with the sum of the angles at the central atom respectively along (Σ_1) and around (Σ_2) the threefold axis.[11] $\bar{d}$ is the averaged metal–ligand distance around the threefold axis, and Δ is the elevation of the central atom from the base of the pyramid. In $[Ni(CH_3)(PMe_3)_4]^+$, the values are $s = 0.68$, $\Sigma_1 = 356.6°$, and $\Sigma_2 = 288.6°$, which

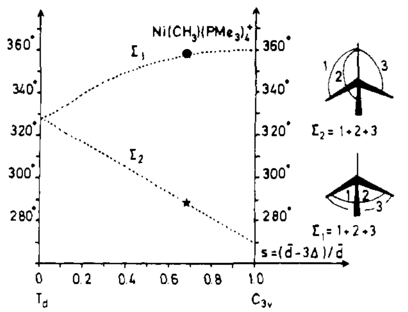

Figure 2. $T_d \rightarrow C_{3v}$ transition, variations of the sums of angles Σ_1 and Σ_2 defined as on the left side of the figure, against the normalized shift parameter. The dotted lines represent the calculated pathways.

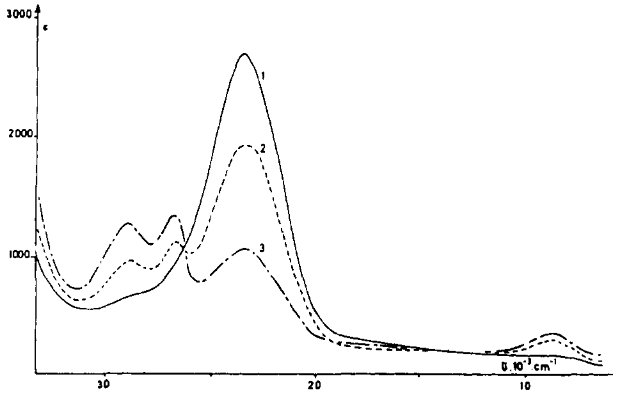

Figure 3. Time dependence of the electronic spectrum of $[Ni(CH_3)(PMe_3)_4]^+$ at 190 K in dichloromethane: (1) $t = 0$ min; (2) $t = 5$ min; (3) $t = 3$ h.

indicate that the complex lies on the geometrical reaction path (Figure 2).

The detailed geometry of the $[B(C_6H_5)_4]^-$ anion is given in Table IV and shows no unexpected features.

$[Ni(CH_3)(PMe_3)_4](BPh_4)$ is low spin in the solid state. The experimental value $\mu_{eff} = 0.57$ μ_B is consistent with the previously reported value for low-spin Ni(II) pentacoordinate complexes.[4] No increase of the magnetic moment, due to the tetrahedral distortion of the molecule, is observed, as has been reported for pentacoordinate Co(II) complexes.[13] The existence of the C_{3v} microsymmetry is preserved in dichloromethane solutions as has been shown by ^{31}P NMR where a doublet (δ −37.8) and a quartet (δ −62.2) (approximatively in the ratio 3:1) has been observed at 193 K.[5] The 190 K electronic spectrum, measured in degassed CH_2Cl_2 solution with excess PMe_3, presents the expected feature for a trigonal bipyramid of C_{3v} symmetry, i.e., an intense ligand field transition $^1A_1 \rightarrow {}^1E$ at 23 530 cm^{-1} (ϵ 2500). A shoulder is present at about 28 500 cm^{-1} (ϵ 500), which certainly results from partial decomposition of the complex in solution. Figure 3 indicates that the complex is not stable in CH_2Cl_2 solution, even with excess PMe_3. With time, at 190 K, the lower energy ligand field transition decreases in intensity while simultaneously a new band increases at about 8500 cm^{-1}. This new transition is characteristic of the tetrahedral nickel(I) species $[Ni(PMe_3)_4]^+$, thus indicating that a $Ni-CH_3$ bondbreaking is occurring in dichloromethane.

In order for information to be obtained on the decomposition process, analyses of the reaction products, resulting from the thermal and photochemical dissociation of $[Ni(CH_3)(PMe_3)_4]^+$ in tetrahydrofuran, have been performed by gas chromatography. The presence of CH_4 and C_2H_6 has been detected in both reactions, but CH_4 is the major product when the thermal

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(12) Ni(II)-PMe_3 complexes are slowly decomposed by air in the solid state but quickly in solution. This decomposition is followed by an increase of the magnetic moment, and we think that the presence of a slight amount of this impurity (O–PMe_3 complex) is responsible for the magnetic moment value.

(13) Sacconi, L. *Coord. Chem. Rev.* **1972**, *8*, 351.

dissociation is considered (333 K, CH_4/C_2H_6 in the ratio 4:1) while C_2H_6 is more abundant in the photochemical process (diffuse daylight, 293 K, CH_4/C_2H_6 in the ratio 1:3). Thus the cleavage of the methyl-nickel bond may occur through two different pathways. However, more investigations are still necessary to understand these results.

In conclusion, it is tempting to write that the surprising production of a Ni(I) complex $[Ni(PMe_3)_4]BPh_4$ by homolysis of the Ni-C bond in $[Ni(CH_3)(PMe_3)_4]BPh_4$ can be predicted by the X-ray structure of $[Ni(CH_3)(PMe_3)_4]BPh_4$ since the molecule lies on the geometrical reaction path going from the trigonal bipyramid (C_{3v}) to the tetrahedron. However no simple mechanistic interpretation of the production of a mixture of CH_4 and C_2H_6 can now be proposed.

Registry No. I, 52166-20-8; $[Ni(PMe_3)_4]PF_6$, 77342-02-0; $Ni(PMe_3)_4$, 28069-69-4; $NiCl_2(PMe_3)_2$, 19232-05-4.

Supplementary Material Available: A listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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Thermal Decomposition of (Triphenylphosphoranediyl)aminocyclotrithiazene and (Triphenylarsoranediyl)aminocyclotrithiazene, $Ph_3E{=}NS_3N_3$ (E = P, As). Preparation and Structure of (Triphenylphosphoranediyl)amine (Thiosulfinyl)amine Sulfide, $Ph_3P{=}NSN{=}S{=}S$, and a Novel Synthesis of Disulfur Dinitride

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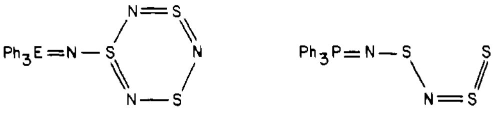
The thermolysis of (triphenylphosphoranediyl)aminocyclotrithiazene, $Ph_3P{=}NS_3N_3$, produces the open-chain (thiosulfinyl)amine derivative $Ph_3P{=}NSN{=}S{=}S$, the structure of which has been determined by X-ray crystallography. The crystals are monoclinic, of space group $P2_1/c$, with $a = 12.573$ (1) Å, $b = 11.170$ (1) Å, $c = 14.816$ (2) Å, $\beta = 115.96$ (1)°, $V = 1872.2$ Å^3, and D_{calcd} (for $Z = 4$) = 1.37 g cm^{-3}. The structure was solved by direct methods and was refined by full-matrix least-squares procedures to a final $R = 0.040$ and $R_w = 0.062$ for 1747 reflections with $I > 3\sigma(I)$. The structure consists of an open-chain $Ph_3P{=}NSN{=}S{=}S$ sequence with the sulfur and nitrogen atoms lying in a nearly planar cis-trans arrangement. The short terminal sulfur-sulfur bond (1.908 (2) Å) indicates a bond order significantly greater than one. The two S-N bonds of the terminal S_3N group are almost equal (1.592 (4) and 1.587 (4) Å). In contrast to the behavior of $Ph_3P{=}NS_3N_3$ the thermal decomposition of $Ph_3As{=}NS_3N_3$ leads to the elimination of S_2N_2. When the thermolysis is carried out in acetonitrile solution, S_2N_2 rapidly dimerizes to S_4N_4, but when the reaction is performed in the solid state at ca. 130 °C/10^{-3} torr, S_2N_2 can be isolated and converted to the $(SN)_x$ polymer.

Introduction

The rapid and often violent thermal decomposition of many binary sulfur nitride molecules and ions $S_xN_y^{n\pm}$ is a well-known but little understood feature of their chemistry. One thermolytic process, namely, the cracking of S_4N_4 vapor over silver (or glass) wool, has been extensively studied since it is the conventional source of S_2N_2, the molecular precursor of the $(SN)_x$ polymer.[2] However, despite much research, the mechanism of the reaction remains in doubt. Many neutral species other than S_2N_2 (e.g., S_4N_2, S_3N_3, SN, S_2) can also be produced,[3] and the balance between them is a delicate function of temperature and pressure.

Recently we demonstrated the facile thermal interconversion of the three binary SN anions $S_4N_5^-$, $S_3N_3^-$, and S_4N^-,[4] and this discovery has prompted us to investigate more generally the thermal decomposition of other sulfur nitride derivatives. We have begun by examining the thermal degradation of the group 5 imine derivatives of cyclotrithiazene (**1**). The reactions depend on the group 5 element (P or As) involved, but both processes indicate the importance of the loss of N_2S or S_2N_2 as primary decomposition pathways. In this paper we discuss possible mechanisms for these reactions and report the preparation and structure of the open-chain (thiosulfinyl)amine sulfide species **2**, as well as a novel method for preparing S_2N_2 and $(SN)_x$.[5]



1 (E = P, As)   2

Experimental Section

Reagents and General Procedures. *N*-(Trimethylsilyl)(triphenylphosphoranediyl)amine,[6] (triphenylarsoranediyl)amine,[7] and tetrasulfur tetranitride[8] were all prepared according to literature methods. The phosphoranediylaminocyclotrithiazene $Ph_3P{=}NS_3N_3$ was prepared by the reaction of $Ph_3P{=}NSiMe_3$ with S_4N_4.[9] Triphenylphosphine (Baker) and triphenylarsine (Eastman) were commercial products and were used as received. All the solvents employed were of reagent grade and were dried before use: dichloromethane by distillation from P_2O_5 and acetonitrile by distillation from P_2O_5 followed by distillation from calcium hydride. All reactions were carried out under an atmosphere of nitrogen (99.99% purity) passed through Ridox and silica gel. Infrared spectra were recorded on Nujol mulls (CsI win-

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