Journal of Organometallic Chemistry, 326 (1987) 139–149
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

TRIMETHYLPHOSPHINE-COBALT(I) COMPLEXES. CRYSTAL AND MOLECULAR STRUCTURE OF THE (NORBORNADIENE)TRIS(TRIMETHYLPHOSPHINE)COBALT(I) TETRAPHENYLBORATE COMPLEX, $[Co(\eta^4\text{-}C_7H_8)(PMe_3)_3]BPh_4$

MICHÈLE DARTIGUENAVE*, LUIZ CARLOS ANANIAS DE CARVALHO,
YVES DARTIGUENAVE,

*Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier,
205 route de Narbonne 31077 Toulouse-cedex (France)*

FRANCINE BÉLANGER-GARIÉPY, MICHEL SIMARD and ANDRÉ L. BEAUCHAMP*

Département de Chimie, Université de Montréal, C.P. 6128, Succ. A, Montréal. Québec, H3C 3J7 (Canada)

(Received August 5th, 1986)

Summary

Reaction of $CoBr(PMe_3)_3$ with norbornadiene, a non-conjugated diene, in presence of $NaBPh_4$ gives rise to a high yield of the $[Co(\eta^4\text{-}C_7H_8)(PMe_3)_3]BPh_4$ complex. Its crystal structure has been determined by X-ray diffraction techniques. The compound belongs to the orthorhombic space group $Pmn2_1$, with a 15.114(11), b 10.006(7), c 12.316(11) Å and $Z = 2$ formula units per cell. The structure was solved from a set of 1482 nonzero Mo-$K_{\bar{\alpha}}$ reflections collected at 170 K and refined to $R = 0.047$. The crystal consists of discrete BPh_4^- anions and $[Co(PMe_3)_3$-(norbornadiene)$]^+$ cations. The BPh_4^- ion sits on the crystallographic mirror plane and it is not disordered. The complex cation is involved in a two-fold disorder in which two individuals are related by the crystallographic mirror plane. In addition, one of the phosphines shows two-fold orientation disorder of the methyl groups about the Co–P bond. The complex cation has no crystallographic symmetry of its own. Its environment is best described as a distorted square pyramid (mean L_{apical}–Co–L_{basal} 103.6°), with one of the PMe_3 ligands (Co–P(1) 2.290(3) Å) occupying the apical position. Norbornadiene spans two adjacent basal sites (Co–mid || 2.010(10) and 1.935(11) Å), whereas the two remaining basal sites are occupied by PMe_3 molecules (Co–P(2) 2.243(2), Co–P(3) 2.182(3) Å). Multinuclear NMR studies (183–293 K) show that the complex is stereochemically non-rigid in this temperature range.

0022-328X/87/$03.50

Introduction

In previous papers, we reported on the reactions of $CoBr(PMe_3)_3$ with 4e donor ligands such as C_2Ph_2 [1], butadiene [2], 1,1,3,4-tetramethylsilole and 1,1,3,4-tetramethylgermole [3]. In the solid state, all these complexes present structures which approximate the square-pyramidal geometry. However, $[Co(C_2Ph_2)(PMe_3)_3]BPh_4$ and $[Co(metallole)(PMe_3)_3]BPh_4$ are stereochemically non-rigid at $-100\,°C$, whereas $[Co(C_4H_6)(PMe_3)_3]BPh_4$ is already rigid at room temperature.

In order to better understand the bonding in these $Co-PMe_3$ complexes, we extended our work to non-conjugated dienes. No reaction occurred with 1,5-cyclooctadiene and, surprisingly, even with 1,3-cyclooctadiene. However, with norbornadiene (NBD), the cationic cobalt(I) complex $[Co(NBD)(PMe_3)_3]^+$ was obtained.

NBD possesses a rigid carbon skeleton, retaining the double bond mutually parallel and at a suitable distance to lead to a bidentate chelating interaction with metal ions. This is indeed the most common type of coordination, which has been observed for square planar rhodium [4] and palladium compounds [5,6], and for octahedral ruthenium [7–9] and chromium [10] species. Five-coordinate compounds of iridium [11] and cobalt [12–15] belonging to this class are also known. However, examples of monodentate coordination have been reported for manganese [16], nickel [17] and copper [18]. Bridging NBD molecules have been observed in the d^{10} $[Ag(NO_3)]_2(NBD)$ [19] and d^9 $[Co(PMe_3)_3]_2(NBD)$ [20] compounds.

Experimental

All operations were performed under vacuum or in an inert atmosphere. Solvents were dried and distilled as previously reported [2]. Variable temperature ^1H, ^{31}P, ^{13}C FT NMR spectra were recorded on a Bruker WM-250 spectrometer. Field frequency stabilization was achieved on an internal ^2D signal at 38.39 kG. $SiMe_4$ was used as external reference for ^1H and ^{13}C chemical shifts, and H_3PO_4 (62.5%) in D_2O for ^{31}P. CD_2Cl_2 or $(CD_3)_2CO$ were used as solvents. $CoBr(PMe_3)_3$ was prepared following Klein and Karsch [21].

The microanalyses were performed by the Service de Microanalyse du CNRS, Lyon.

Preparation of $[Co(NBD)(PMe_3)_3]Br$

$CoBr(PMe_3)_3$ (1.4 g, 3.8 mmol) was dissolved in acetone (15 ml), and a five-fold excess of NBD was added. The originally blue-violet solution turned yellow-brown. Rapid stirring of the solution for few minutes at room temperature produced a yellow-brown solid, which was collected, filtered, and stored under argon (yield 80%). Anal. Found: C, 41.46; H, 7.62; Co, 13.12; P, 19.94, Br, 17.19. $C_{16}H_{35}BrCoP_3$ calc.: C, 41.85; H, 7.68; Co, 12.83; P, 20.23; Br, 17.40%.

Preparation of $[Co(NBD)(PMe_3)_3]BPh_4$

To $CoBr(PMe_3)_3$ (1.4 g, 3.8 mmol) and a five-fold excess of NBD dissolved in 15 ml of acetone was added a methanol solution (15 ml) of $NaBPh_4$ (1.3 g; 3.81 mmol). A yellow precipitate immediately formed. It was filtered, dried and stored under argon (yield 85%). Single crystals suitable for X-ray work were obtained by recrystallization in acetone at −5 ° C overnight. Anal. Found: C, 68.47; H, 7.95; Co, 8.20; P, 13.68. $C_{40}H_{55}BCoP_3$ calc.: C, 68.78; H, 7.94; Co, 8.44; P, 13.30%.

BF_4^- and PF_6^- complexes were also synthesized by this same method. Once isolated, the powders of the four compounds can be handled in air for a few minutes without apparent decomposition. Large crystals of the BPh_4^- salt had not deteriorated after several days in air.

Crystal data. Formula: $C_{40}H_{55}BCoP_3$, M_w 698.55, Orthorhombic, $Pmn2_1$, a 15.114(11), b 10.006(7), c 12.316(11) Å. V 1863 Å^3, D_c 1.245 g cm^{-3}, $Z = 2$, λ(Mo-$K_{\bar{\alpha}}$) 0.71069 Å (graphite monochromator), μ(Mo-K_α) 5.9 cm^{-1}, T 170 K.

Crystallographic measurements and structure resolution

The resolution of this structure required considerable effort. As the problems encountered were first ascribed to suspected twinning, camera work was carried out on four crystals from different recrystallizations. Weissenberg or precession/cone-axis photographs invariably indicated orthorhombic Laue symmetry and no evidence of twinning was detected. The systematic absences ($h0l$, $h + l \neq 2n$) were consistent with space groups *Pmnm* (alternate orientation of *Pmmn*, No. 59), $Pmn2_1$ (No. 31) and $P2_1nm$ (alternate orientation of $Pmn2_1$, No. 31).

The data set used in the present report was obtained with a crystal of dimensions 0.40 × 0.40 × 0.50 mm^3. A set of 1793 nonequivalent Mo-$K_{\bar{\alpha}}$ reflections ($2\theta \leqslant 50$ °) was collected at 170 K with an Enraf–Nonius CAD-4 diffractometer, according to a procedure described elsewhere [22]. The fluctuations on the standards during data collection remained within ±3.6%. All reflections with $I \leqslant 3.0\ \sigma(I)$ were assigned zero weight and the remaining 1482 nonzero reflections were used to solve the structure. These data were corrected for the effect of Lorentz and polarization. An absorption correction was deemed unnecessary in view of the low absorption coefficient (μ 6.1 cm^{-1}) and nearly equal dimensions of the crystal.

In space group *Pmnm*, the two Co and the two B atoms would have to occupy sites of *mm* symmetry (equipoints $2a$ or $2b$). This symmetry would be unusual for BPh_4^- and it would not correspond to the expected structure for the $[Co(NBD)(PMe_3)_3]^+$ cation. Since the distribution of the normalized structure factors clearly pointed to a non-centric space group, no great effort was devoted to solve the structure in *Pmnm* at first. Nevertheless, after a number of unsuccessful attempts with the other two space groups, the centric *Pmnm* space group was tested, but it failed to yield any recognizable structural pattern.

In space groups $Pmn2_1$ or $P2_1nm$, ordered B and Co atoms would lie on mirror planes (equipoint $2a$). This appeared to be more consistent with the expected geometries of the ions present. Although positions for Co and one P atom could be found in either space group by using various approaches (Patterson synthesis, direct methods (MULTAN [23]) with or without introducing known fragments in E calculations), it was generally impossible to develop this initial model into a recognizable structure. After a tedious series of attempts, the structure was finally solved in space group $Pmn2_1$ by using the known atomic positions to progressively improve the phase relationships. The initial fragment consisted of 5 atoms (Co,P(1),P(2),C(4) and C(1A)) lying on the crystallographic mirror plane. In the subsequent E-map, P(3) and portions of the BPh_4^- ion began to emerge. These positions were added to those already used to set up the relationships, and this same procedure was repeated a number of times. When the whole BPh_4^- ion was found, the environment of Co consisted of four phosphine positions: P(1) and P(2) were on the mirror planes, whereas two symmetry-equivalent P(3) groups were on general positions. Although this model was chemically reasonable, the Co–P(3) distances (1.8 Å) were too short. Furthermore, when refined, P(3) showed much higher thermal motion than P(1) or P(2).

The rest of the interpretation was done by structure factor and difference Fourier (ΔF) calculations. The first ΔF map showed high residual electron density of 3.2 e/Å^3 at mirror-related positions only 0.8 Å away from Co. This and the apparent high thermal motion of P(3) suggested that the complex cation could be involved in two-fold disorder: phosphines P(1) and P(2) occupied positions common to both individuals on the mirror plane, whereas phosphine P(3) and Co (now moved away from the mirror) with occupancy factors of 0.50 were not coincident in the two individuals. In this model, the distance from the Co position to the P(3) atom on the other side of the mirror was more reasonable (2.28 Å). The next ΔF map revealed the positions of the seven half-carbons for a norbornadiene unit also involved in the two-fold disorder across the mirror plane. This model was refined isotropically, leading to agreement factors $R = \Sigma \| F_0 | - | F_c \| / \Sigma | F_0 |$ of 0.185 and $R_w = [\Sigma w(| F_0 | - | F_c |)^2 / \Sigma w | F_0 |^2]^{\frac{1}{2}}$ of 0.238. The hydrogen atoms on the phenyl rings and the half-hydrogens of the norbornadiene unit were fixed at their ideal positions (C–H 0.95 Å, B 5.0 Å^2 (phenyl) or 6.3 Å^2 (norbornadiene)). Positions for all methyl hydrogens were found in the ΔF map and ideal positions were defined by means of the Co–P–C–H torsion angle τ (C–H 0.95 Å, P–C–H = 109.5°, $\Delta\tau$ 120°) in order to give the best fit with the positions observed in the map. The hydrogen parameters were not refined, but the coordinates were recalculated after each least-squares cycle. All nonhydrogen atoms were then refined anisotropically, which reduced R to 0.075 and R_w to 0.093. The thermal ellipsoids were normal, except for P(1) and the attached methyl groups, whose ellipsoids were much more elongated than those of the other phosphines, and greater than expected for measurements at 170 K. Careful examination of the ΔF map revealed first, that P(1) did not lie exactly on the mirror plane. Second, another set of peaks was found for methyl groups around P(1). Therefore, in addition to the two-fold disorder across the mirror plane, this region of the cation shows an orientation disorder of phosphine P(1) about the Co–P(1) bond. P(1) was shifted out of the mirror plane and refined with an occupancy factor of 0.50 fixed by symmetry. Two sets of methyl carbons (A and B) were defined and initially assigned occupancy factors of 0.25, assuming equally populated orientations about the Co–P(1) bond. The ΔF map showed peaks at reasonable positions for most of the fractional hydrogens of these two sets of methyl carbons. Idealized coordinates were calculated as mentioned above. The fractional carbons were refined isotropically. At convergence, thermal motion for set B was found to be systematically lower than for set A. Therefore, a few extra cycles of refinement were run, in which the occupancy factors of these six fractional carbon atoms were also refined. They indicated that occupancy for orientation B was ~ 1.5 as high as for set A. Accordingly, fixed normalized values of 0.20 (set A) and 0.30 (set B) were used to complete the refinement.

The final residuals were $R = 0.047$ and $R_w = 0.056$. The goodness-of-fit ratio was 2.12. There was no evidence for disordering in the case of phosphine P(2) and of the BPh_4^- ion. The final ΔF map was essentially featureless, the general background being between +0.29 and −0.42 e/Å^3.

TABLE 1

REFINED COORDINATES ($\times 10^4$) AND EQUIVALENT TEMPERATURE FACTORS ($\times 10^3$) FOR THE NON-HYDROGEN ATOMS OF [Co(NBD)(PMe$_3$)$_3$]BPh$_4$

Atom	x	y	z	U_{eq}
Co	4693(1)	8355(1)	0	27
P(1)	4777(2)	8203(2)	1852(2)	38
P(2)	5000	6252(2)	−506(2)	35
P(3)	6074(2)	8908(3)	−255(2)	39
C(1A) [a]	5000	6618(16)	2521(14)	28
C(1B) [a]	4527(9)	6697(15)	2478(13)	26
C(2A) [a]	5334(13)	9474(22)	2589(19)	30
C(2B) [a]	5624(12)	9154(19)	2583(16)	48
C(3A) [a]	3888(23)	7871(37)	2546(31)	68
C(3B) [a]	3747(13)	8993(21)	2568(17)	54
C(4)	5000	5962(7)	−1968(6)	42
C(5)	5917(3)	5213(5)	−64(5)	45
C(6)	6555(8)	8684(10)	−1584(9)	49
C(7)	6358(7)	10688(9)	−106(12)	52
C(8)	6986(7)	8125(11)	556(10)	48
C(10)	3525(9)	9396(13)	−1516(10)	60
C(11)	3490(7)	8115(13)	−911(11)	57
C(12)	3310(6)	8344(9)	175(8)	29
C(13)	3216(10)	9831(14)	228(11)	71
C(14)	4111(9)	10243(11)	105(11)	57
C(15)	4390(7)	9926(12)	−1000(10)	44
C(16)	2834(8)	10161(14)	−927(13)	67
C(21)	5856(3)	3327(5)	6095(4)	32
C(22)	6230(3)	4530(5)	5706(4)	36
C(23)	6900(3)	5187(5)	6250(5)	45
C(24)	7227(3)	4694(6)	7210(5)	50
C(25)	6871(3)	3534(6)	7620(5)	45
C(26)	6201(3)	2868(5)	7069(4)	37
C(31)	5000	2798(7)	4166(6)	35
C(32)	5789(4)	2826(5)	3581(4)	40
C(33)	5780(4)	2875(6)	2440(5)	53
C(34)	5000	2894(7)	1892(6)	58
C(41)	5000	967(7)	5639(6)	36
C(42)	5775(4)	231(5)	5634(5)	46
C(43)	5779(5)	−1168(6)	5631(5)	58
C(44)	5000	−1840(8)	5623(8)	71
B	5000	2634(8)	5510(7)	33

[a] Refined isotropically, occupancy factors 0.20 (set A), 0.30 (set B).

The refined coordinates for nonhydrogen atoms are listed in Table 1. The list of temperature factors and the structure factor table are part of the supplementary material *.

The scattering curves were from standard sources [24]. The f' and f'' contributions of Co and P to anomalous dispersion were taken from Cromer [25]. This structure was solved by using the MULTAN package [23] and a set of other programs listed elsewhere [26].

---

* See NAPS document no. 04469 for 18 pages of supplementary material. Order from NAPS % Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY, 10163.

Results and discussion

Reaction of $CoBr(PMe_3)_3$ with an excess of norbornadiene (NBD) in acetone results in high yields (80%) of the cationic $[Co(NBD)(PMe_3)_3]Br$ complex as the only product. Adding larger counterions, such as BF_4^-, PF_6^- and BPh_4^-, leads to compounds with better crystallinity.

As usual, no characteristic ν(C=C) stretching vibration is observed for the coordinated double bond in the IR spectrum. Moreover, the multinuclear NMR data are deceivingly poor. No effect of temperature is detected between 293 and 183 K, which indicates that the complex remains fluxional at 183 K. Only a broad singlet at 11 ppm is apparent at 188 K on the $^{31}P\{^{1}H\}$ NMR spectrum. Coordinated NBD is characterized by three broad resonances: in $^{1}H\{^{31}P\}$ NMR at 2.4 (=CH), 3.3 (CH) and 1.2 ppm (CH_2); in $^{13}C\{^{1}H\}$ NMR at 42 (=CH; J(CH) 191 Hz), 45 (CH; J(CH) 154 Hz) and 58.7 ppm (CH_2; J(CH) 131 Hz). These values are in agreement with those previously reported for NBD–metal complexes. However, to our knowledge, only the cobalt(I) complex remains fluxional at such a low temperature. The mechanism to explain this fluxionality can be based either on diene rotation or Berry pseudo-rotation [2]. Both are indistinguishable on the NMR time scale. However, the latter has been suggested for the five-coordinate Ir–NBD complex [11], since the distortion observed in the crystal structure is in agreement with the structural changes expected along the Berry pseudorotational pathway.

In order to determine what happens in the cobalt complex, namely if its structure is a distorted trigonal bipyramidal as the iridium complex or a square pyramid as the other Co–diene species, we have determined the crystal structure of $[Co(NBD)(PMe_3)_3]BPh_4$.

TABLE 2

SELECTED INTERATOMIC DISTANCES (Å) FOR $[Co(NBD)(PMe_3)_3]BPh_4$

Around Co			
Co–P(1)	2.290(3)	Co–C(14)	2.088(11)
Co–P(2)	2.243(2)	Co–C(15)	2.049(12)
Co–P(3)	2.182(3)	Co–Cx [a]	2.010(10)
Co–C(11)	2.150(12)	Co–Cy [a]	1.935(11)
Co–C(12)	2.101(8)		
Phosphine			
P(1)–C(1A)	1.82(2)	P(2)–C(4)	1.824(8)
P(1)–C(2A)	1.78(2)	P(2)–C(5)	1.816(5)
P(1)–C(3A)	1.63(4)	P(3)–C(6)	1.805(12)
P(1)–C(1B)	1.73(2)	P(3)–C(7)	1.841(10)
P(1)–C(2B)	1.83(2)	P(3)–C(8)	1.874(12)
P(1)–C(3B)	1.96(2)		
Norbornadiene			
C(10)–C(11)	1.48(2)	C(12)–C(13)	1.50(2)
C(10)–C(15)	1.55(2)	C(13)–C(14)	1.42(2)
C(10)–C(16)	1.48(2)	C(13)–C(16)	1.57(2)
C(11)–C(12)	1.38(2)	C(14)–C(15)	1.46(2)

[a] Cx = midpoint of C(11)–C(12), Cy = midpoint of C(14)–C(15).

TABLE 3

SELECTED BOND ANGLES (deg) FOR $[Co(NBD)(PMe_3)_3]BPh_4$

Around cobalt			
P(1)–Co–P(2)	101.7(1)	P(2)–Co–Cy	146.2(4)
P(1)–Co–P(3)	96.1(1)	P(3)–Co–Cx	156.0(4)
P(1)–Co–Cx	105.9(4)	P(3)–Co–Cy	93.6(4)
P(1)–Co–Cy	111.3(4)	Cx–Co–Cy	69.8(5)
P(2)–Co–P(3)	90.0(1)	C(11)–Co–C(12)	38.0(4)
P(2)–Co–Cx	94.6(4)	C(14)–Co–C(15)	41.3(5)
Phosphine			
Co–P(1)–C(1A)	121.3(4)	C(2B)–P(1)–C(3B)	97.2(9)
Co–P(1)–C(2A)	119.2(7)	Co–P(2)–C(4)	115.1(2)
Co–P(1)–C(3A)	119.4(13)	Co–P(2)–C(5)	127.7(2)
C(1A)–P(1)–C(2A)	107.8(8)	C(5)–P(2)–C(5) [a]	99.5(2)
C(1A)–P(1)–C(3A)	74.8(14)	C(4)–P(2)–C(5)	101.8(3)
C(2A)–P(1)–C(3A)	105.6(15)	Co–P(3)–C(6)	119.0(4)
Co–P(1)–C(1B)	119.2(5)	Co–P(3)–C(7)	117.0(4)
Co–P(1)–C(2B)	119.6(6)	Co–P(3)–C(8)	121.4(4)
Co–P(1)–C(3B)	112.2(6)	C(6)–P(3)–C(7)	96.7(5)
C(1B)–P(1)–C(2B)	112.6(8)	C(6)–P(3)–C(8)	97.8(5)
C(1B)–P(1)–C(3B)	88.7(8)	C(7)–P(3)–C(8)	100.4(5)
Norbornadiene			
Co–C(11)–C(12)	69.1(6)	C(11)–C(10)–C(16)	100.1(10)
Co–C(11)–C(10)	97.8(8)	C(15)–C(10)–C(16)	102.5(10)
Co–C(12)–C(11)	72.9(6)	C(10)–C(11)–C(12)	110.4(10)
Co–C(12)–C(13)	95.4(7)	C(11)–C(12)–C(13)	103.0(9)
Co–C(14)–C(13)	98.3(9)	C(12)–C(13)–C(14)	101.2(10)
Co–C(14)–C(15)	67.9(7)	C(12)–C(13)–C(16)	101.8(10)
Co–C(15)–C(10)	100.0(8)	C(14)–C(13)–C(16)	101.1(11)
Co–C(15)–C(14)	70.8(7)	C(13)–C(14)–C(15)	108.1(11)
C(11)–C(10)–C(15)	96.9(10)	C(10)–C(15)–C(14)	102.3(10)
		C(10)–C(16)–C(13)	94.3(10)

[a] $1-x, y, z$.

The crystal contains well separated BPh_4^- anions and $[Co(NBD)(PMe_3)_3]^+$ cations. Interatomic distances and bond angles in the cation are listed in Tables 2 and 3, respectively.

The $[Co(NBD)(PMe_3)_3]^+$ cation (Fig. 1) is best described as a square pyramid in which P(1) occupies the apical position. The basal Co–PMe_3 distances (Co–P(2) 2.243(2), Co–P(3) 2.182(3) Å) lie within the range of Co–PMe_3 distances (2.12–2.26 Å) observed for other five-coordinate Co complexes [2,27]. The Co–P(1) distance (2.290(3) Å) is above this range. Although the significant crystal disorder which is present will produce errors somewhat greater than indicated by the esd's, the differences between the Co–P distances are large and probably significant. A longer Co–P (apical) bond is in good agreement with theoretical predictions for a d^8 system [28]. The Co–C(olefin) distances (Table 2) are also in the normal range observed for Co–NBD compounds (2.08–2.19 Å). The double bond is perpendicular within 2° to the Co–midpoint vector as expected.

Defining the coordination geometry of five-coordinate molecules showing large departure from both the trigonal bipyramid (TBP) and the square pyramid (SP)

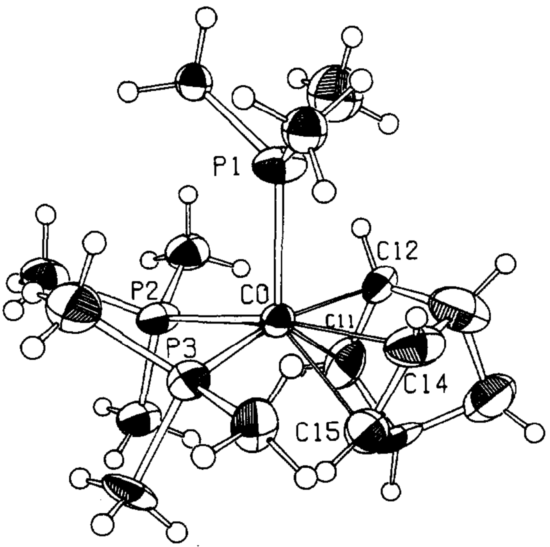

Fig. 1. ORTEP drawing of the $[Co(NBD)(PMe_3)_3]^+$ cation in the BPh_4^- salt. The methyl groups attached to P(1) are found in two sets of positions, only one of which is represented. Ellipsoids correspond to 50% probability. Hydrogens are shown as small spheres of arbitrary size.

invariably raises the problem of deciding which polyhedron better approximates the actual structure. The choice of SP here is based on a procedure described earlier [29], whereby the M–L bonds, normalized to unit length, are fitted by a least-squares technique described by Dollase [30], so as to minimize the sum of the squared distances Σd_i^2, where d_i is the distance between the ith apices in the actual and the ideal polyhedra, respectively. For SP symmetry, where the apical–M–basal angle L_a–M–L_b is not fixed by symmetry, provision is made to adjust this angle as well in the minimization procedure. Table 4 shows that the figure of merit (FOM = $(\Sigma d_i/5)^{\frac{1}{2}}$) is definitely less favorable for TBP (0.217 Å) than for SP (0.111 Å) with L_a–Co–L_b = 103.6°.

Table 4 includes data for other five-coordinate NBD-containing compounds. In all cases, the best descriptions for the TBP and the SP geometries have been determined, and FOM have been calculated. It can be seen that NBD does not induce a particular geometry in these molecules, as the compounds listed cover a continuous spectrum, with half of the compounds on the TBP side and the other half on the SP side. This table also shows that the small "bite" of NBD (~ 70°) imposes constraints on the sites to be occupied in both geometries. The 120° angle in the equatorial plane of TBP is too large to accept both double bonds on equatorial sites. In all molecules listed of Table 4, when envisaged as TBP, one of the double bonds is axial, the other equatorial. For similar reasons, the NBD double bonds span a pair of basal sites in SP, the small L_b–M–L_b angle being more favorable than the L_a–M–L_b angle (101–106°).

The geometry of coordinated norbornadiene has been discussed by other workers [4,6,9]. In spite of the disorder, the distances and angles in norbornadiene are in good general agreement with their results (Tables 2 and 3). Our average distances are: C(olefin)–C(olefin) 1.42 Å, C(olefin)–C(bridgehead) 1.49 Å and

TABLE 4

CHOICE OF THE BEST COORDINATION POLYHEDRON FOR FIVE-COORDINATE NORBORNADIENE COMPLEXES

Compound	Trigonal bipyramid		Square pyramid			Ref.
	axial sites	FOM [b]	apical site	α [a]	FOM [b]	
$[Co(NBD)(PMe_3)_3]BPh_4$	$PMe_3, \parallel$	0.217 (12.4)	PMe_3	103.6	0.111 (6.4)	this work
$(\mu_2\text{-}CO)_2[Co(CO)_2(NBD)]_2$	$\mu_2\text{-}CO, \parallel$	0.245 (14.1)	CO	101.2	0.112 (6.4)	13
$[Fe(CO)Cp](\mu_2\text{-}CO)_2[Co(CO)NBD)]$	$\mu_2\text{-}CO, \parallel$	0.257 (14.8)	CO	103.1	0.115 (6.6)	14
$[Ir(PMe_2Ph)_2(SnCl_3)(NBD)]$	$PMe_2Ph, \parallel$	0.227 (13.0)	$SnCl_3$	102.3	0.139 (8.0)	11
$(\mu_2\text{-}SnPh_2)[Co(CO)_2(NBD)]_2$	$\mu_2\text{-}SnPh_2, \parallel$	0.165 (9.5)	CO	106.1	0.165 (9.5)	12
$(\mu_2\text{-}SnPh_2)[Co(CO)_2(NBD)]_2$	$\mu_2\text{-}SnPh_2, \parallel$	0.139 (8.0)	CO	105.8	0.192 (11.0)	12
$(\mu_2\text{-}SnCl_2)[Co(CO)_2(NBD)]_2$	$\mu_2\text{-}SnCl_2, \parallel$	0.143 (8.2)	CO	104.8	0.197 (11.3)	12
$(\mu_2\text{-}SnCl_2)[Co(CO)_2(NBD)]_2$	$\mu_2\text{-}SnCl_2, \parallel$	0.141 (8.1)	CO	104.7	0.203 (11.7)	12
$[Fe(CO)_4](\mu_2\text{-}AsMe_2)[Co(CO)_2(NBD)]$	$\mu_2\text{-}AsMe_2, \parallel$	0.129 (7.4)	CO	105.4	0.181 (10.4)	15

[a] Mean L(apical)–M–L(basal) angle. [b] Average distance (Å) between corresponding apices of the ideal and the actual polyhedra, in which all M–L bonds are normalized to 1 Å (see text). The average angle (deg) between corresponding bonds in the ideal and the actual polyhedra given within brackets.

C(bridgehead)–C(methylene) 1.52 Å. The average angles are: C(olefin)–C(olefin)–C(bridgehead) 106.0°, C(bridgehead)–C(methylene)–C(bridgehead) 94.3°, C(olefin)–C(bridgehead)–C(olefin) 99.0°, and C(olefin)–C(bridgehead)–C(methylene) 101.4°.

In the coordinated PMe_3 molecules, the P–C distances (av. 1.829 Å) are normal and the C–P–C angles (av. 99.7°) are smaller than 109.5° as usual. These average values do not include the environment of P(1), where orientational disorder about the Co–P(1) bond leads to less reliable positions for the fractional methyl groups.

Details on the geometry of the BPh_4^- ion are provided in the supplementary material. The B–C bond lengths average 1.658 Å and the usual pattern is found for the phenyl ring angles: (av.) C(*ortho*)–C(B)–C(*ortho*) 116.2°, C(B)–C(*ortho*)–C(*meta*) 121.8°, others 120.0°. The rings are planar within 1.0 σ (0.005 Å), but B is usually significantly out of the planes.

A diagram of the unit cell is provided in the supplementary material. The Van der Waals contacts between the two sorts of ions are normal.

In conclusion, NBD coordinates to the cobalt fragment $[Co(PMe_3)_3]^+$ in a similar way as conjugated dienes. This may be related to the presence in NBD of relatively low-lying molecular orbitals resulting from a through-space interaction of the π levels, as observed in conjugated dienes. They are of suitable energy to match with the $[Co(PMe_3)_3]^+$ orbitals [31]. However, the NBD complex is more distorted, especially within the $[Co(PMe_3)_3]^+$ moiety. This may result, following Hoffmann et al. [32], from the ability of the 14e $[Co(PMe_3)_3]^+$ fragment, which possesses a doubly occupied degenerate *e* orbital, to undergo distortion in order to better accommodate the particular electronic requirement of the NBD ligand.

No reaction of this complex toward nucleophiles was observed. This behavior, which is a constant throughout the series of $[Co(diene)(PMe_3)_3]^+$ complexes, is related to the presence of the basic PMe_3 donor as ancillary ligand [33].

Acknowledgements

We wish to thank M.J. Olivier who collected the X-ray data. This work was made possible by travel grants in the framework of the Programme d'Échanges Interuniversitaire Franco-Québécois. Financial support from the Centre National de la Recherche Scientifique (France), the Natural Science and Engineering Research Council (Canada), the Ministère de l'Éducation (Québec), and the Conselho Nacional de Desenvolvimento Cientifico e Tecnologico CNPq (Brasil) (LCAC) is gratefully acknowledged.

References

1 B. Capelle, A.L. Beauchamp, M. Dartiguenave, and Y. Dartiguenave, J. Chem. Soc. Chem. Comm., (1982) 566; J. Am. Chem. Soc. 105 (1983) 4662.
2 L.C. Ananias de Carvalho, Y. Pérès, M. Dartiguenave, Y. Dartiguenave, and A.L. Beauchamp, Organometallics, 4 (1985) 2021.
3 L.C. Ananias de Carvalho, M. Dartiguenave, Y. Dartiguenave, J. Dubac, Y. Laporterie, G. Manuel, and F. Iloughmane, Organometallics, 5 (1986) 2205.
4 E.P. Kyba, R.E. Davis, P.N. Juri, and K.R. Shirley, Inorg. Chem., 20 (1981) 3616; M. Cocivera, G. Ferguson, B. Kaitner, F.J. Lalor, D.J. O'Sullivan, M. Parvez, and B. Ruhl, Organometallics, 1 (1982) 1132; W.R. Cullen, T.J. Kim, F.W.B. Einstein, and T. Jones, ibid., 2 (1983) 714; M.P. Anderson, B.M. Mattson, and L.H. Pignolet, Inorg. Chem., 22 (1983) 2644; J.D. Oliver and D.P. Riley, Organometallics, 2 (1983) 1032; A.H. Reis, Jr., C. Willi, S. Siegel, and B. Tani, Inorg. Chem., 18 (1979) 1859; W.R. Cullen, F.W.B. Einstein, C.H. Huang, A.C. Willis, and E.S. Yeh, J. Am. Chem. Soc., 102 (1980) 988; A.A. Koridze, I.T. Chizhevsky, P.V. Petrovskii, E.I. Fedin, N.E. Kolobova, L.E. Vinogradova, L.A. Leites, V.G. Andrianov, and Yu.T. Struchkov, J. Organomet. Chem., 206 (1981) 373; I.T. Chizhevsky, A.A. Koridze, V.I. Bakhmutov, N.E. Kolobova, V.G. Andrianov, and Yu.T. Struchkov, ibid., 215 (1981) 403.
5 N.C. Baenziger, G.F. Richards, and J.R. Doyle, Acta Crystallogr., 18 (1965) 924.
6 H. Suzuki, K. Itoh, Y. Ishii, K. Simon, and J.A. Ibers, J. Am. Chem. Soc., 98 (1976) 8494.
7 J.M. Manoli, A.P. Gaughan, Jr., and J.A. Ibers, J. Organomet. Chem., 72 (1974) 247.
8 C. Potvin, J.M. Manoli, G. Pannetier, R. Chevalier, and N. Platzer, J. Organomet. Chem., 113 (1976) 273.
9 D.E. Bergbreiter, B.E. Bursten, M.S. Bursten, and F.A. Cotton, J. Organomet. Chem., 205 (1981) 407.
10 J.P. Declercq, G. Germain, M. Van Meerssche, and S.A. Chawdhury, Acta Crystallogr., B, 31 (1975) 2896.
11 M.R. Churchill and K.K.G. Lin, J. Am. Chem. Soc., 96 (1974) 76.
12 F.P. Boer and J.J. Flynn, J. Am. Chem. Soc., 93 (1971) 6495.
13 F.S. Stephens, J. Chem. Soc. Dalton Trans., (1972) 1754.
14 I.L.C. Campbell and F.S. Stephens, J. Chem. Soc. Dalton Trans., (1975) 226.
15 H.J. Langenbach, E. Keller, and H. Vahrenkamp, J. Organomet. Chem., 171 (1979) 259.
16 P.A. Vella, M. Beno, A.J. Schultz, and J.M. Williams, J. Organomet. Chem., 105 (1981) 71.
17 R.M. Wing, G.C. Tustin, and W.H. Okamura, J. Am. Chem. Soc., 92 (1970) 1935.
18 N.C. Baenziger, H.L. Haight, and J.R. Doyle, Inorg. Chem., 3 (1964) 1535.
19 N.C. Baenziger, H.L. Haight, R. Alexander, and J.R. Doyle, Inorg. Chem., 5 (1966) 1399.
20 H.F. Klein, L. Fabry, H. Witty, U. Schubert, H. Lueken, and U. Stamm, Inorg. Chem., 24 (1985) 683.
21 H.F. Klein and H.H. Karsch, Inorg. Chem., 14 (1975) 473.
22 F. Bélanger-Gariépy, A.L. Beauchamp, J. Am. Chem. Soc., 102 (1980) 3461.
23 P. Main, M.M. Woolfson, L. Lessinger, L. Germain and J. Declercq, MULTAN, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, University of York, U.K. and Louvain, Belgium, 1980.
24 D.T. Cromer and J.T. Waber, Acta Crystallogr., 18 (1965) 104; R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
25 D.T. Cromer, Acta Crystallogr., 18 (1965) 17.
26 M. Authier-Martin and A.L. Beauchamp, Can. J. Chem., 55 (1977) 1213.

27 B. Capelle, A.L. Beauchamp, M. Dartiguenave, Y. Dartiguenave, and H.F. Klein, J. Am. Chem. Soc., 104 (1982) 3891.
28 A.R. Rossi and R. Hoffmann, Inorg. Chem., 14 (1975) 365.
29 A.L. Beauchamp, F. Bélanger-Gariépy, and S. Arabi, Inorg. Chem., 24 (1985) 1860.
30 W.A. Dollase, Acta Crystallogr., A, 30 (1974) 513.
31 R. Hoffmann, E. Heilbronner, and R. Gleiter, J. Am. Chem. Soc., 92 (1970) 706; R. Hoffmann, Acc. Chem. Res., 4 (1971) 1.
32 M. Elian and R. Hoffmann, Inorg. Chem., 14 (1975) 1058.
33 L.S. Barinelli, K. Tao, and K.M. Nicholas, Organometallics, 5 (1986) 588.