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Trimethylphosphine cobalt(I) complexes: reaction with cycloheptatriene and cyclooctatetraene. Crystal structure of $[Co(\eta^4\text{-}C_7H_8)(PMe_3)_3]BPh_4$

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Abstract

Reaction of $CoBr(PMe_3)_3$ with cycloheptatriene and cyclooctatetraene yielded cationic $[Co(\eta^4\text{-polyene})(PMe_3)_3]^+$ complexes (polyene = 1,3,5-C_7H_8, **1**; 1,3,5,7-C_8H_8, **2**). The crystal structure of **1** has been determined by X-ray diffraction techniques. The complex belongs to the monoclinic space group $P2_1/n$, with a, 14.367(2); b, 18.512(3); c 14.591(2) Å; β, 98.102(13)° and $Z = 4$. The structure was solved from a set of 3080 non zero Mo-K_α reflections and refined to $R = 0.0436$ ($R_w = 0.0442$). The crystal consists of discrete BPh_4^- anions and $[Co(\eta^4\text{-}C_7H_8)(PMe_3)_3]^+$ cations. The geometry of the complex cation is best described as a three leggered piano stool, with nearly equivalent Co–P distances (mean value: 2.238(2) Å). Cycloheptatriene acts as a tetrahapto ligand coordinated by a butadiene moiety. Multinuclear NMR studies indicate that the complex **1** is stereochemically rigid at 183 K. A similar structure is assigned to $[Co(\eta^4\text{-}C_8H_8)(PMe_3)_3]Br$ (**2**) on the basis of NMR data.

Introduction

We previously found that $CoBr(PMe_3)_3$ reacted with 1,3-dienes (diene = butadiene, isoprene, dimethylbutadiene [1], 1,1,3,4-tetramethylsilole and 1,1,3,4-tetramethylgermole [2]), i.e. 4e donor ligands, to give high yields of the cations $[Co[\eta^4\text{-diene})(PMe_3)_3]^+$. Surprisingly, 1,3- or 1,5-cyclooctadiene gave no reaction, but the norbornadiene analogue has been made [3].

In general only a few reactions of cobalt-phosphine complexes with dienes have been reported [4], but making use of the triphos ligand (1,1,1-tris(diphenylphosphinomethyl)ethane), Sacconi et al. made the cationic complexes $[Co(diene)(triphos)]ClO_4$ with butadiene, isoprene, and 1,3-cyclohexadiene [5]. They also prepared the 1,3,5-cycloheptatriene and 1,3,5,7-cyclooctatetraene complexes.

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Since we observed no reaction when $CoBr(PMe_3)_3$ was added to cyclooctadiene, it was of interest to study its reaction with cycloheptatriene and cyclooctatetraene and we report here on these reactions. An X-ray structural analysis has been carried out on $[Co(\eta^4\text{-}C_7H_8)(PMe_3)_3]BPh_4$ in order to determine the mode of binding of the triene molecule (a potential 6e donor) to the cobalt fragment (14e).

Experimental

Materials and methods

Solvent distillations and all other manipulations were performed under argon by Schlenk techniques. Methanol and acetone were distilled over molecular sieves. All solvents were degassed by three freeze-thaw cycles before use. Trimethylphosphine [6] and $CoBr(PMe_3)_3$ [7] were made by published methods. The polyenes were checked by NMR and purified by chromatography on alumina when necessary.

Elemental analyses were performed by the Service Central de Microanalyse du CNRS, Lyon, France.

Infrared spectra were recorded on a Perkin–Elmer 983 spectrometer with Nujol mulls prepared in a glove box. The ^1H and $^1H\{^{31}P\}$ spectra were recorded at low temperature on a WH 90 instrument or on a Bruker WM 250 instrument equipped with a phosphorus decoupling probe, with CD_2Cl_2 as solvent. The ^{13}C, $^{13}C\{^1H\}$ (62.89 MHz) and ^{31}P, $^{31}P\{^1H\}$ (101.27 MHz) spectra were also recorded on the Bruker WM 250 spectrometer. Chemical shifts were referenced to the residual solvent signals for ^1H and ^{13}C (CD_2Cl_2; $\delta(H)$, 5.33 and $\delta(C)$, 53.6 ppm; $(CD_3)_2CO$: $\delta(H)$, 2.17 and $\delta(C)$, 29.2 ppm), and to external H_3PO_4 (62.5% in D_2O: δ, 0 ppm) for ^{31}P NMR spectra. The ^{13}C and ^1H spectra of complex **1** contain the following BPh_4^- signals, which will not be further discussed: ^{13}C, 121, 125, 135 and 164 ppm; ^1H, 6.9, 7.1 and 7.3 ppm.

$[Co(\eta^4\text{-}1,3,C_7H_8)(PMe_3)_3]BPh_4$ (1)

To an acetone solution (15 ml) of $CoBr(PMe_3)_3$ (1.3 g; 3.5 mmol) was added an excess of C_7H_8 (0.6 ml; 5.8 mmol). The originally blue-violet solution darkened immediately. A solution of an equimolar amount of $NaBPh_4$ in methanol was added, and after half an hour of stirring a yellow solution was formed from which an orange-red solid separated. It was filtered off, dried and stored under argon. Recrystallization from acetone at 0 °C overnight gave single crystals suitable for the structural determination.

Analysis. Found: C, 67.67; H, 7.92; B, 1.51; Co, 8.38; P, 13.32. $C_{40}H_{55}BCoP_3$ calc.: C, 68.78; H, 7.93; B, 1.55; Co, 8.44; P, 13.30%, ^{31}P NMR (CD_2Cl_2; 163 K): 10.6; 11.3 PMe_3. ^{13}C NMR [$(CD_3)_2CO$, 183 K]: 16.7 (dd, $P(CH_3)_3$, $J(CP) = 24$ Hz); 18.3 (br, $P(CH_3)_3$); 51 (d, $C10$, $J(CH)$ 146 Hz); 54 (d, $C13$, $J(CH)$ 146 Hz); 88 (d, $C11$, $J(CH)$ 161 Hz); 96 (d, $C12$, $J(CH)$ 164 Hz); 126, 129 (d, $C14$, $C15$, $J(CH)$ 149 Hz); 31, (t, $C16$). ^1H NMR [CD_2Cl_2, 193K]: 1.2 (dd, $P(CH_3)_3$, $J(HP2)$ 6 Hz, $J(HP3)$ 5 Hz); 1.5 ($P(CH_3)_3$, $J(HP1)$ 8 Hz); 2 (br, $H16_{exo}$); 2.2 (s, $H16_{endo}$); 2.7 (br, H10, H13); 4.5, 4.7 (br, H11, H12); 5.5, 5.7 (br, H14, H15).

$[Co(\eta^4\text{-}1,3\ C_8H_8)(PMe_3)_3]Br$

To a solution of $CoBr(PMe_3)_3$ (1.6 g; 4.4 mmol) in 20 ml of acetone was added an excess of C_8H_8. The blue violet solution turned dark brown immediately, and a microscopic black powder separated. This was filtrated off, dried, and stored under argon. Dark brown air sensitive microcrystals were obtained by stirring the solution at 0 °C overnight.

Analysis. Found: C, 43.40; H, 7.40; Br, 16.91; Co, 12.87; P, 19.81. $C_{17}H_{35}BrCoP_3$ calc.: C, 43.33; H, 7.43; Br, 16.96; Co, 12.51; P, 19.72%. ^{31}P NMR. [CD_2Cl_2, 233 K]: 15 (br, PMe_3); ^{13}C NMR [$(CD_3)_2CO$, 176 K]: 18 (br, $P(CH_3)_3$, J(CH) 129 Hz); 100 (br, coord C_8H_8, J(CH) 157 Hz); 131 (s, free C_8H_8, J(CH) 155 Hz). ^1H NMR [$(CD_3)_2CO$, 187 K]: 1.6 (br, $P(CH_3)_3$); 5.4 (br., coord C_8H_8); 5.9 (s, free C_8H_8).

Crystallographic measurements and structure determination

The crystallographic studies were carried out with an Enraf–Nonius CAD-4 diffractometer. The crystals were mounted and sealed under argon in a thin-walled glass capillary.

A set of 25 random reflections was collected by using the SEARCH procedure of the Enraf–Nonius CAD-4 software. After several recentering operations, the reduced cell was determined by the INDEX routine and its parameters were calculated by least-squares refinement on the setting angles of the 25 reflections. The Niggli parameters clearly indicated a primitive monoclinic cell. The systematic absences determined by inspection of the complete data set unambiguously identified the space group as $P2_1/n$. The crystal data are summarized in Table 1.

Three standard reflections checked every hour fluctuated within ±0.2% during data collection. Crystal orientation was checked every 100 measurements and no significant misorientation was detected. The data were corrected for polarization

Table 1

Crystal data for $\{Co(\eta^4\text{-}C_7H_8)(P(CH_3)_3)_3\}^+\{B(C_6H_5)_4\}^-$

Formula	$C_{40}H_{55}BCoP_3$
fw,	698.54
Cryst. system	Monoclinic
Space group	$P2_1/n$
a, Å	14.367(2)
b, Å	18.512(3)
c, Å	14.591(2)
β°	98.102(13)
V, Å^3	3842(2)
Z	4
d_{calc}, g/cm^3	1.207
μ (Mo-K_α), cm^{-1}	5.48
Temp, °C	20±2
Scan method	ω
Data collection range (θ), deg	$1 < \theta < 23$
no. of reflections measured	5116
no. of unique data with $(I) > 3\ \sigma(I)$	3080
no. of parameters refined	406
R [a]	0.0436
R_w [b]	0.0443

[a] $\Sigma || F_o | - F_c || / \Sigma | F_o |$. [b] $R_w = [\Sigma_w(|| F_o | - | F_c ||)^2 / \Sigma_w | F_o |^2]^{1/2}$, $w = 1/\sigma^2(| F_o |)$.

Table 2

Fractional atomic coordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Co	0.23171(6)	0.50101(5)	0.29891(6)
P(1)	0.0761(1)	0.5104(1)	0.2787(1)
P(2)	0.2659(2)	0.5561(1)	0.1703(1)
P(3)	0.2640(2)	0.5965(1)	0.3916(1)
C(1)	0.0160(5)	0.4738(5)	0.1711(5)
C(2)	0.0116(5)	0.4668(4)	0.3627(5)
C(3)	0.0230(5)	0.5991(4)	0.2784(6)
C(4)	0.2611(6)	0.5017(6)	0.0655(5)
C(5)	0.3843(6)	0.5907(5)	0.1810(6)
C(6)	0.1966(7)	0.6321(5)	0.1211(6)
C(7)	0.2014(6)	0.5997(4)	0.4924(5)
C(8)	0.2445(7)	0.6894(4)	0.3505(6)
C(9)	0.3859(5)	0.6028(5)	0.4456(5)
C(10)	0.2725(6)	0.4405(5)	0.4211(6)
C(11)	0.3422(5)	0.4415(4)	0.3612(6)
C(12)	0.3187(6)	0.4197(4)	0.2706(6)
C(13)	0.2249(6)	0.3960(5)	0.2376(6)
C(14)	0.1733(6)	0.3405(5)	0.2823(9)
C(15)	0.1736(7)	0.3309(5)	0.373(1)
C(16)	0.2161(7)	0.3786(5)	0.4451(7)

and Lorentz effects. An empirical absorption correction based on psi scans for three reflections was also applied.

The structure was solved by the heavy-atom method with SHELXS 86 [8]. Refinement was carried out on F_o with the SHELX76 package. The non-hydrogen atoms were refined isotropically, then anisotropically. The cation and anion were refined as independent blocs. Initially the phenyl groups were fixed as rigid groups, then they were refined isotropically and anisotropically. Only in the last cycles of refinement were all atoms refined simultaneously to converge to $R = 0.0436$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.442$, and a goodness-of-fit ratio of 1.97. The final ΔF map showed a general background below ± 0.5 e/Å^3.

The final atomic coordinates are given in Table 2. The scattering curves for the non-hydrogen atoms were taken from ref. 9, and those for hydrogen from ref. 10. The anomalous dispersion coefficients f' and f'' were included in the structure factor calculations for Co and P [11].

Results and discussion

Reaction of $CoBr(PMe_3)_3$ with an excess of 1,3,5-cycloheptatriene gave an 80% yield of the cation $[Co(\eta^4\text{-}C_7H_8)(PMe_3)_3]^+$ which was isolated as its BPh_4 salt. The solid can be handled in air for a few minutes, but the solution must be kept under an inert atmosphere to prevent oxidation of the PMe_3 ligand.

$$CoBr(PMe_3)_3 + C_7H_8 + NaBPh_4 \rightarrow \left[Co(\eta^4\text{-}C_7H_8)(PMe_3)_3\right]BPh_4 + NaBr \qquad (1)$$

The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 at 163 K showed a pattern of two broad signals, in approximately 2/1 ratio at 11.3 and 10.6 ppm, characteristic of a

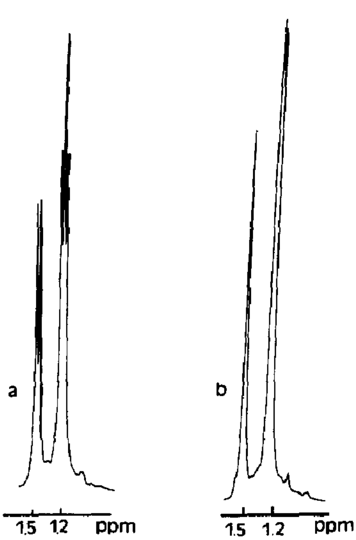

Fig. 1. ^{1}H NMR spectra of the PMe_3 ligands in **1**: (a) ^{1}H (CD_2Cl_2, 193 K), (b) $^{1}H\{^{31}P\}$ (CD_2Cl_2, 193 K).

stereorigid molecule. The J(PP) coupling constant values are < 20 Hz [12*], which excludes a trigonal bipyramidal geometry [1]. The better resolution of the ^{1}H and ^{13}C spectra showed the presence of the three magnetically independent PMe_3 ligands expected as a consequence of the low symmetry of the coordinated cycloheptatriene (Fig. 1). Such an ABC spin system has been reported previously for the cation $[Co(isoprene)(PMe_3)_3]^+$, while $[Co(butadiene)(PMe_3)_3]^+$ and $[Co(dimethylbutadiene)(PMe_3)_3]^+$ gave an AB_2 spectra. The signals appeared at 1.2 (P2, P3) and 1.5 (P1) ppm with coupling constants of J(HP2) 6 Hz; J (HP3) 5 Hz; J(HP1) 8 Hz in the ^{1}H NMR spectrum. The corresponding ^{13}C signals appeared at 16.7 (P2; P3; J(CP) 24 Hz) and 18.3 (P1). Increasing the temperature resulted in the coalescence of the PMe_3 signals at about room temperature [13*], with no change in the signals from the cycloheptatriene ligand.

The loss of symmetry of the complexed cycloheptatriene and the presence of an uncomplexed C=C bond was observed by ^{13}C NMR spectroscopy. For free cycloheptatriene, the signals from carbon atoms C12 and C13, C11 and C14, C15 and C10 appeared at 130.9, 126.6, and 120.4 ppm, respectively, while that from the methylene carbon was at 28.1 ppm [14]. Shifting of the C10 (51 ppm), C11 (88 ppm), C12 (96 ppm) and C13 (84 ppm) signals to higher field indicated that coordination involved the butadiene fragment C10,C11,C12,C13. Table 3 shows a comparison of the chemical shifts with that for the butadiene, isopropene and dimethylbutadiene analogues. There is no significant shift of the signals from the C14, C15, C16 carbons, indicating that the C14–C15 double bond does not participate in the bonding. The ^{1}H NMR data for the coordinated cycloheptatriene are in good agreement with those reported for isoelectronic $Fe(\eta^4\text{-}C_7H_8)(CO)_3$ [15]: 2 ($H16_{exo}$); 2.2 ($H16_{endo}$); 2.7 (H10,H13); 4.5, 4.7 (H11,H12); 5.5, 5.7 (H14,H15).

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* Reference number with asterisk indicates a note in the list of references.

Table 3

^{13}C NMR chemical shifts of d^8 η^4-butadiene-, isoprene-, and dimethylbutadiene-metal complexes

Complexes	Chemical shifts (ppm)				Ref.
	δ(C10)	δC(11)	δ(C12)	δ(C13)	
$[Co(\eta^4\text{-}C_4H_6)(PMe_3)_3]^+$	40.4	89	89	40.5	1
$[Co(\eta^4\text{-}C_5H_8)(PMe_3)_3]^+$	39.3	102.5	87.3	39.3	1
$[Co(\eta^4\text{-}C_6H_{10})(PMe_3)_3]^+$	42.8	100.6	100.6	42.8	1
$[Fe(\eta^4\text{-}C_4H_6)(CO)_3]^+$	40.5	85.5	85.5	40.5	24
$[Ru(\eta^4\text{-}C_4H_6)(CO)_3]^+$	32.7	86.3	86.3	32.7	25
$[Co(\eta^4\text{-}C_7H_8)(PMe_3)_3]^+$	51	88	96	54	this work

The NMR data gave clear information about the mode of coordination of the cycloheptatriene to the cobalt center, but the metal coordination sphere could be established only by a crystal structure determination.

X-ray structure of $[Co(\eta^4\text{-}C_7H_8)(PMe_3)_3]BPh_4$ (1)

The unit cell contains the BPh_4^- anion and the $[Co(C_7H_8)(PMe_3)_3]^+$ cation. The perspective view of the complex cation is shown in Fig. 2, with the atom numbering scheme. Selected interatomic distances and angles are listed in Table 4.

As expected, the 1,3,5-cycloheptatriene is η^4-coordinated to the cobalt by the butadiene system C10,C11,C12,C13. The Co–C distances (2.082 Å av.) are in the normal range observed for butadienecobalt compounds (2.07 Å av), the inner bonds (2.039(8) and 2.036(8) Å) being shorter than the outer ones (2.117(8) and 2.136(9) Å) as usual. Loss of planarity of the cycloheptatriene molecule is observed, as expected; it results from the distortion of the *p* orbitals of the diene carbon atoms in order to increase their overlap with the metal *d* orbitals. The dihedral angles between the two parts of the ring, defined by the C10,C11,C12,C13 plane and the

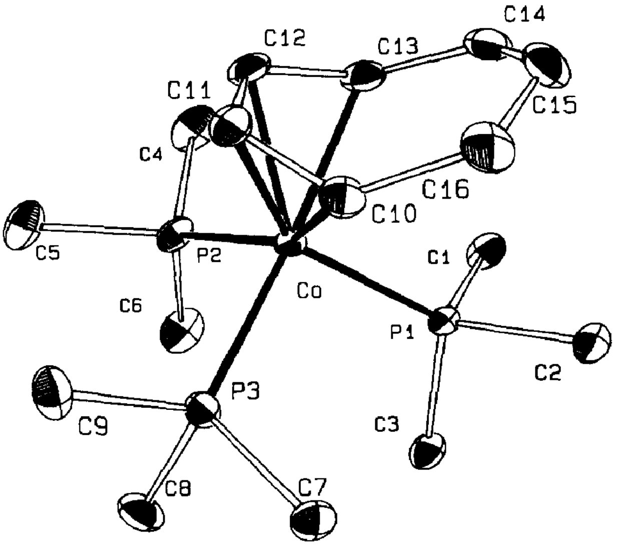


Fig. 2. ORTEP drawing of the cation complex $[Co(\eta^4\text{-}C_7H_8)(PMe_3)_3]^+$.

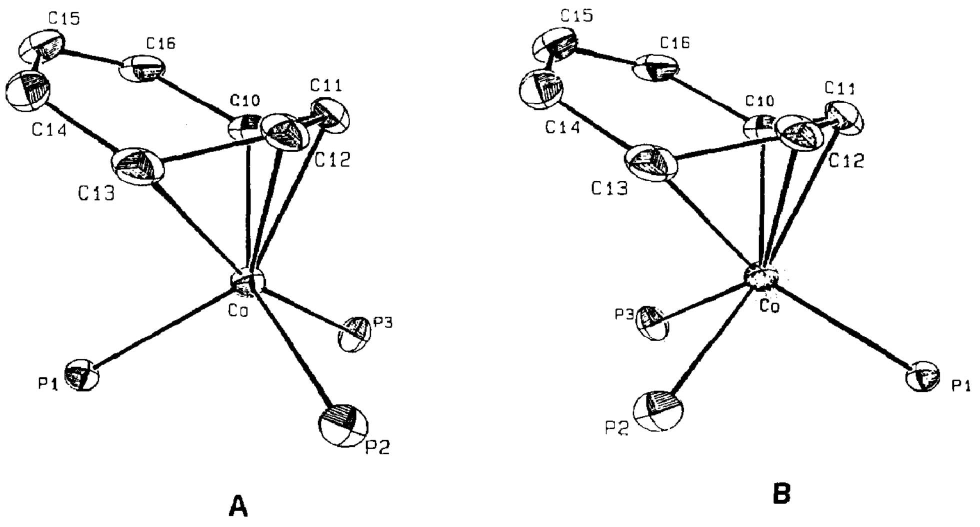
Table 4

Selected distances (Å) and angles (°) in $\{Co(\eta^4\text{-}C_7H_8)(P(CH_3)_3)_3\}^+\{B(C_6H_5)_4\}^-$

Bond distances					
Co-P1	2.221(2)	Co-C10	2.117(8)		
Co-P2	2.249(2)	Co-C11	2.039(8)		
Co-P3	2.234(2)	Co-C12	2.036(8)		
P1-C1	1.813(7)	Co-C13	2.136(9)		
P1-C2	1.825(8)	C10-C11	1.42(1)		
P1-C3	1.810(8)	C11-C12	1.38(1)		
P2-C4	1.825(9)	C12-C13	1.43(1)		
P2-C5	1.804(9)	C13-C14	1.47(1)		
P2-C6	1.814(9)	C14-C15	1.34(2)		
P3-C7	1.829(9)	C15-C16	1.45(2)		
P3-C8	1.830(8)	C10-C16	1.47(1)		
P3-C9	1.822(8)	C10-C16	1.47(1)		
P3-C9	1.822(8)				
Bond angles					
P1-Co-P2	100.87(8)	Co-P1-C1	115.7(3)	Co-P2-C4	117.5(3)
P1-Co-P3	97.91(9)	Co-P1-C2	118.3(2)	Co-P2-C5	113.8(3)
P1-Co-C10	107.9(2)	Co-P1-C3	119.1(3)	Co-P2-C6	120.7(3)
P1-Co-C11	143.9(2)	C1-P1-C2	101.1(3)	C4-P2-C5	101.2(4)
P1-Co-C12	131.8(2)	C1-P1-C3	100.9(4)	C4-P2-C6	98.1(5)
P1-Co-C13	91.7(2)	C2-P1-C3	98.6(4)	Co-P3-C7	115.4(3)
C10-Co-C11	39.9(3)	C5-P2-C6	102.5(4)	Co-P3-C8	122.5(3)
C10-Co-C12	71.0(4)	C7-P3-C8	99.4(4)	Co-P3-C9	114.7(3)
C10-Co-C13	82.1(3)	C7-P3-C9	101.7(4)	C8-P3-C9	100.0(4)
C11-Co-C12	39.5(3)	Co-C10-C11	67.1(5)	C10-C11-C12	119.2(8)
C11-Co-C13	71.5(3)	Co-C10-C16	121.0(6)	C11-C12-C13	120.3(8)
C12-Co-C13	40.1(3)	Co-C11-C10	73.1(5)	C12-C13-C14	124.9(8)
P2-Co-P3	95.49(9)	Co-C11-C12	70.1(5)	C13-C14-C15	127 (1)
P2-Co-C10	151.0(2)	Co-C12-C11	70.3(5)	C14-C15-C16	126 (1)
P2-Co-C11	111.6(3)	Co-C12-C13	73.8(5)	C15-C16-C10	120 (1)
P2-Co-C12	87.3(3)	Co-C13-C12	66.2(5)	C11-C10-C16	128.0(9)
P2-Co-C13	93.7(3)	Co-C13-C14	116.5(7)		
P3-Co-C10	84.2(2)	P3-Co-C12	128.8(2)		
P3-Co-C11	84.3(2)	P3-Co-C13	165.2(2)		

C13,C14,C15,C16,C10 plane, respectively, is 42.36°. This value is similar to those observed in the $[Co(silole)(PMe_3)_3]^+$ and $[Co(germole)(PMe_3)_3]^+$ cations (41.2° and 44.5°, respectively), as experted since they result from the same electronic interactions. The pattern of the C–C bond lengths of the coordinated butadiene (1.42, 1.38, 1.43 Å) is also as expected for a η^4-metal bonded ligand.

The three Co–P distances are close to each other (2.221(2); 2.249(2), and 2.234(2) Å) and are in the usual range. The plane defined by these three phosphorus atoms is nearly parallel to the butadiene plane (dihedral angle of 10.44°). Thus, the best description of the geometry around the metal is the three legged pianostool arrangement, which resembles that observed in the butadiene and diphenylacetylene complex but is less distorted in the present case. There are only small differences in the Co–P and Co–C bond lengths and bond angles in the complex. This structure is similar to that adopted by the cation $[Co(\eta^4\text{-}C_7H_8)(tripod)]^+$, but more accurate bond distance and angle values have been obtained for the butadiene system.



Scheme 1

The conformation **A** adopted by the complex (with the butadiene *trans* to the phosphine P1) is adopted by all the Co(PMe_3)$_3$-acyclic and -cyclic diene compounds, even when it may be sterically crowded (Scheme 1). Moreover, this conformation is usually found in d^8 ML_3-diene complexes. Hoffmann et al. have calculated the height of the rotational barrier between the two possible conformers **A** and **B** [16]; it depends on the orbital interaction between the HOMO of the ML_3 fragment and the HOMO and LUMO of the diene and increases with the number of atoms in the diene. The presence of a stereorigid heptatriene complex was thus not surprising, because the butadiene analog is also stereorigid [1].

The average P–C bond length in PMe_3 shows a normal value of 1.819 Å. There is the usual departure from tetrahedral symmetry around P: Co–P–C 117.5° (av) and C–P–C 100.4° (av). The BPh_4^- ion has also its usual structure; details of this are available from the authors along with tables of thermal parameters and structure factors.

[Co(η^4-C_8H_8)(PMe_3)$_3$]Br (2)

This complex, isolated as dark brown crystals, was reasonably stable in air as a solid, but labile in solution since free C_8H_8 was always observable in the NMR spectra. Interest in this ligand arose because C_8H_8 possesses two butadiene entities able to coordinate a 14e [Co(PMe_3)$_3$]$^+$ fragment. However, as previously observed with Fe [17], Ru [18], Rh [19], Ir [19], Co [20] complexes, a single resonance is usually present in the ^1H and ^{13}C NMR spectra, corresponding to the coordinated cyclooctatetraene: at 100 ppm in the ^{13}C and at 5.4 ppm in the ^1H NMR spectrum (at 173 K). This indicates equivalence of all the carbon atoms of coordinated cyclooctatetraene [16]. The molecule remains still fluxional at 163 K, as indicated by the presence of only a single broad resonance in the ^{31} P NMR spectrum.

Elemental analysis and NMR measurements showed that the complex cation probably has a structure similar to that of **1**, with the cobalt linked to one of the two butadiene fragments of the ring.

Conclusion

The $[Co(PMe_3)_3]^+$ fragment requires 4e to complete its shell, and this can be provided by a η^4-dienyl ligand. 1,3-Diene and molecules possessing the 1,3-diene fragment are good examples of appropriate donors, and give reasonably stable $[Co(diene)(PMe_3)_3]^+$ complexes. Surprisingly, no reaction occurs with 1,3-cyclooctadiene.

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