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η^6-Arene–cobalt(I) complexes

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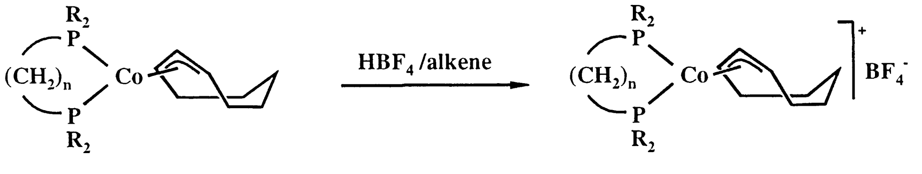
Abstract

(η^6-Arene)Co(I) complexes stabilized by bisphosphines, e.g. $[(\eta^6\text{-MeC}_6\text{H}_5)\text{Co}(\text{Pr}^i_2\text{PC}_2\text{H}_4\text{PPr}^i_2)]^+\text{BF}_4^-$, have been prepared by reacting (η^3-cyclooctenyl)Co(bisphosphine) species with HBF_4 in the presence of an arene. The (η^6-C_6H_6)Co(I) compounds can also be prepared by hydrogen abstraction from the corresponding (η^5-cyclohexadienyl)Co(I) complex or by hydrogenation of (η^3-cyclooctenyl)Co(II) species in the presence of benzene. Facile arene-exchange occurs upon treatment of these compounds with a second arene. In contrast, (η^3-cyclohexenyl)Co(I) and (η^5-cycloheptadienyl)Co(I) complexes are oxidized by HBF_4 in the presence of an alkene to give (η^3-cyclohexenyl)Co(II) and (η^5-cycloheptadienyl)Co(II) species: the former have been characterized as their diamagnetic NO adducts and the latter by a crystal structure determination.

Keywords: Cobalt; Arene; Benzene; Allyl; Dienyl

1. Introduction

In an earlier publication [1] we reported that treatment of the (η^3-cyclooctenyl)Co(bisphosphine) complexes with HBF_4 in the presence of an alkene results in the oxidation of the metal to give novel, paramagnetic organocobalt(II) species (Eq. 1).



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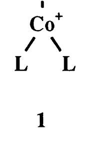
Attempts to extend the scope of this reaction (which is suggested to proceed by homolytic cleavage of a Co–C bond in an intermediate Co–alkyl species) have now shown that whereas the bisphosphine-stabilized (η^3-allyl)Co(I), (η^3-cyclohexenyl)Co(I) and (η^5-cycloheptadienyl)Co(I) compounds react with HBF_4 in a manner similar to that shown above, the (η^5-cyclohexadienyl)Co(I) complexes react with hydride-abstraction to give $[(\eta^6\text{-C}_6\text{H}_6)\text{Co(bisphosphine)}]^+\text{BF}_4^-$ species.

(η^6-Arene)Co(I) complexes are rare; as far as we are aware examples are confined to the tetraphenylborate complex **1** [2] and a series of (η^6-arene)(η^4-diene)Co(I) compounds, e.g. **2** [3,4], which moreover react with donor ligands with arene displacement, and we therefore decided to explore this class of compound further in anticipation that the bisphosphine stabilized derivatives would act as a convenient source of the electronically and coordinatively unsatuated (bisphosphine)Co (I) fragment for stoichiometric and catalytic reactions.



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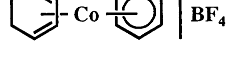

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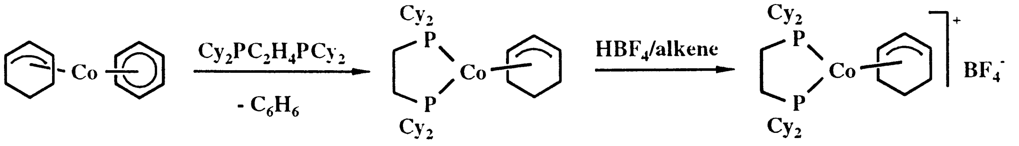
2. Results and discussion

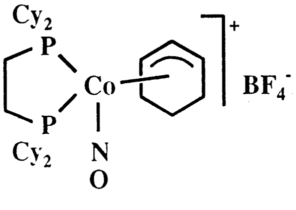
The (η^3-cyclohexenyl)Co(I) complex **4**, which has been reported previously [5] as the product of the reaction between the (η^3-cyclohexenyl)Co(I) species **3** and the bisphosphine, reacts with HBF_4 in the presence of alkenes such as butadiene with oxidation to give **5** (Eq. 2).



(2)

3 **4** **5**

The corresponding $Cy_2PC_3H_6PCy_2$-stabilized species [5] react similarly. Both compounds react with NO to give diamagnetic adducts (e.g. **6**) and their NMR spectra indicate that these have structures similar to that of $[(\eta^3\text{-cyclooctenyl})Co(Cy_2PC_2H_4PCy_2)(NO)]^+BF_4^-$ whose crystal structure has been reported [1].



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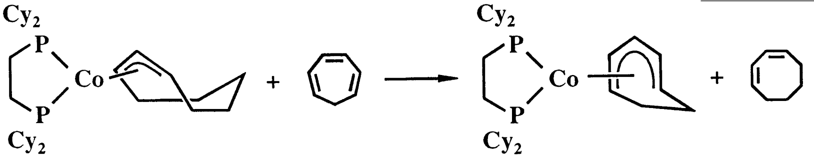
We next turned our attention to the (η^5-cycloheptadienyl)Co(I) species. The appropriate Co(I) compound **7** was prepared in high yield by reacting the bisphosphine-stabilized (η^3-cyclooctenyl)Co(I) compound with cycloheptatriene (Eq. 3).



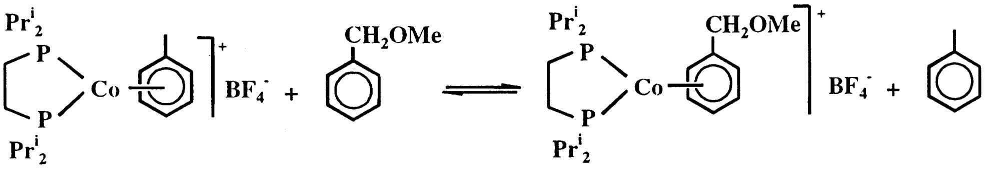
(3)

7

The observation of only four signals for the 7-ring C-atoms of the cycloheptadienyl group in the ^{13}C-NMR spectrum of **7** and a double doublet in the ^{31}P-NMR spectrum (AB spin system) indicate that the compound has a symmetrical structure, with a mirror plane through the central C-atom of the ring and the two P-atoms, similar to that confirmed by X-ray diffraction for (η^5-cyclohexadienyl)Co($Cy_2PC_2H_4PCy_2$) [5]. Treatment of **7** with HBF_4 (or Ph_3CBF_4) does not result in H-abstraction (to give a (η^6-cycloheptatriene)Co(I) species), instead oxidation occurs to give $[(\eta^5\text{-cycloheptadienyl})Co(Cy_2PC_2H_4PCy_2)]^+BF_4^-$ (**8**) and here again, high yields are obtained only if the reaction is carried out in the presence of an auxiliary alkene (butadiene). As expected for a low spin Co(II) species, **8** is paramagnetic with a magnetic moment of 1.6 BM (Evans method). The crystal structure has been determined by X-ray diffraction and the molecular structure of the cation is shown in Fig. 1 (the BF_4 anion is disordered and has been included in the refinement with a 50% occupancy factor for the F-atoms). The two P-atoms and the centre of the pentadienyl fragment adopt a distorted trigonal arrangement around the Co-atom with a plane through the central C-atom and the two P-atoms. The five pentadienyl C-atoms are coplanar and the centre lies 1.574 Å from the metal atom. The C1/C7/C6/C5- and the pentadienyl planes form a dihedral angle of 42.1° to each other.

If the reaction between the (η^3-cyclooctenyl)Co(I) species and HBF_4 shown in Eq. 1 is carried out in thepresence of an arene instead of an alkene, the oxidation is suppressed and instead a conventional protonolysis occurs to give a (η^6-arene)Co(I) species in high yield (Eq. 4). This reaction has been used to prepare the majority of the compounds shown in Table 1 and Table 3. Further examples have been prepared by arene exchange from the (η^6-C_6H_6)Co(I) or (η^6-toluene)Co(I) species and excess of a second arene (Eq. 5).

$$(\eta^3\text{-cyclo-}C_8H_{13})Co(R_2P(CH_2)_nPR_2) + HBF_4 + \text{arene} \rightarrow [(\eta^6\text{-arene})Co(R_2P(CH_2)_nPR_2)]^+BF_4^- + C_8H_{14} \quad (4)$$



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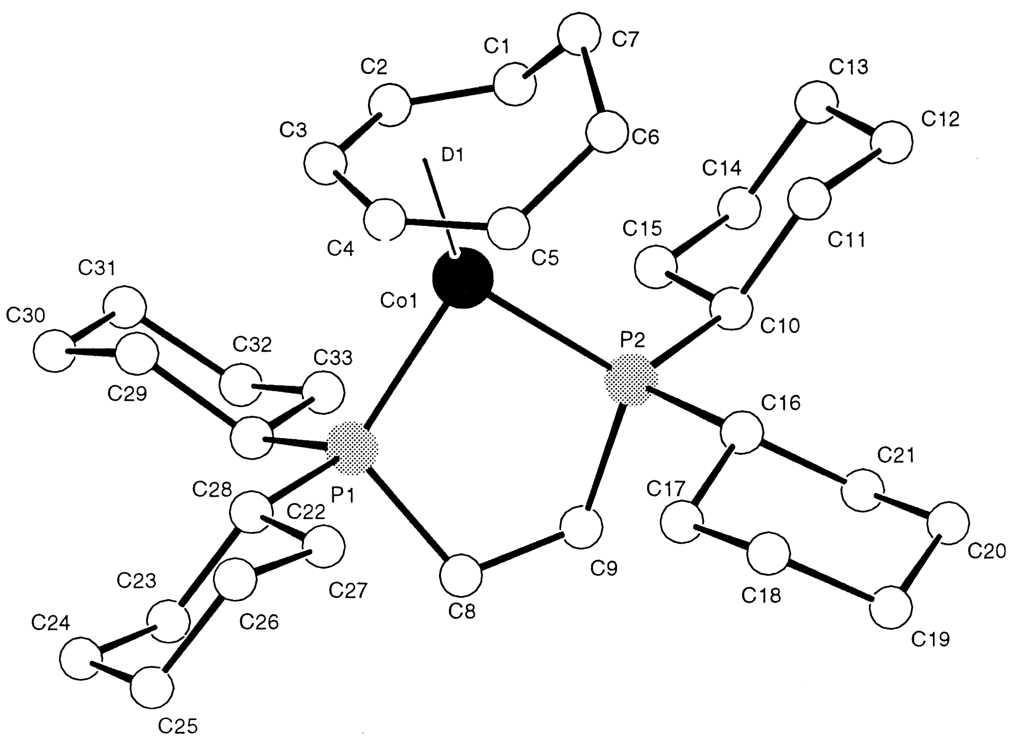
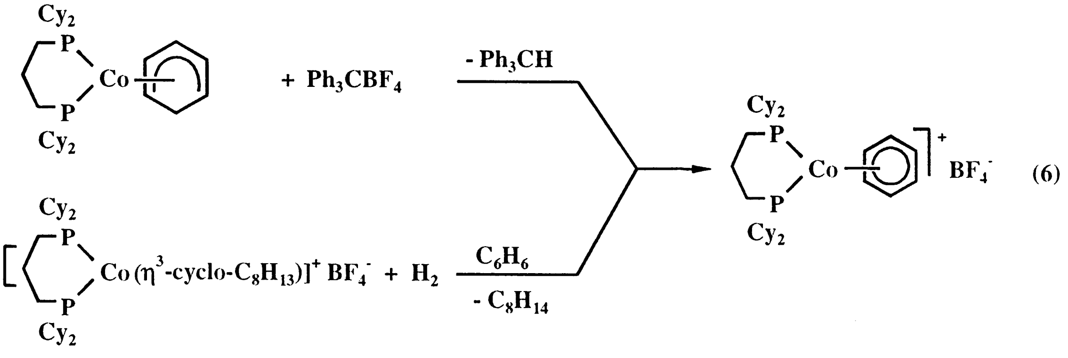


Fig. 1. The molecular structure of $[(\eta^5\text{-cyclo-}C_7H_9)Co(Cy_2PC_2H_4PCy_2)]^+BF4^-$ (**8**) showing only the complex cation. Selected bond distances and angles: Co–P1 2.237(1), Co–P2 2.217(1), Co–C1 2.199(4), Co–C2 2.064(5), Co–C3 2.069(5), Co–C4 2.120(5), Co–C5 2.230(5), Co–D1 1.574 Å; P1–Co–P2 88.6(1), C1–Co–C5 80.3(2), C2–Co–C4 73.1(2), C3–Co–P1 100.3(1), C1–C2–C3 122.5(5), C2–C3–C4 123.9(4), C3–C4–C5 128.6(5), C4–C5–C6 129.0(5), C1–C7–C6 113.4(4), C7–C6–C5 114.5(5)°.

These exchange reactions only proceed satisfactorily in acetone suggesting that they are assisted by solvent complexation.

In addition to these two general preparative reactions, individual $(\eta^6$-arene)Co(I) compounds have been prepared by hydride abstraction from the corresponding $(\eta^5$-cyclohexadienyl)Co(I) and by hydrogenation of an $(\eta^3$-allyl)Co(II) species in the presence of the arene (Eq.6).

The ease with which arene exchange occurs in these compounds suggest that they should act as a convenient source of the $[(R_2P(CH_2)_nPR_2)Co]^+$ fragment for stoichiometric and catalytic reactions and indeed they do show catalytic activity for the dimerization of butadiene at 60°C whereby $[(\eta^6\text{-}MeC_6H_5)Co(Cy_2PC_2H_4PCy_2)]^+ BF_4^-$ has the highest activity with cycloocta-1,5-diene as the principal product. This aspect will be pursued further.



(6)

The $[(\eta^6\text{-arene})Co(R_2P(CH_2)_nPR_2)]^+BF_4^-$ compounds are diamagnetic and their NMR spectroscopic data are collected together in Table 1. A crystal structure analysis of $[(\eta^6\text{-}ClC_6H_5)Co(Cy_2PC_2H_4PCy_2)]^+BF_4^-$ has confirmed the η^6-complexation of the arene molecule to the Co-atom; unfortunately the presence of disordered solvent molecules in the crystal prevented a satisfactory refinement of the data [6].

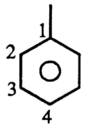
3. Experimental section

The organocobalt complexes described below are air sensitive and all reactions were carried out in an atmosphere of argon. Samples of $[(\eta^3\text{-cyclo-}C_8H_{13})Co(R_2P(CH_2)_nPR_2)]^+BF_4^-$ and $[(\eta^3\text{-2-Bu}^tC_3H_4)Co(Cy_2PC_3H_6PCy_2)]^+BF_4^-$ were prepared by oxidation of the

Table 1
NMR spectroscopic data for $[(\eta^6\text{-arene})Co(R_2P(CH_2)_nPR_2)]^+BF_4^-$ and related compounds[a]

Arene	Bisphosphine	^{1}H-NMR (arene)	^{13}C-NMR (arene)	^{31}P-NMR
C_6H_6	$Cy_2PCH_2PCy_2$	6.36	92.1	−0.28
	$Cy_2PC_2H_4PCy_2$	6.36	91.1	98.3
	$Cy_2PC_3H_6PCy_2$	6.43	90.5	31.0
	$Pr^i_2PC_2H_4PPr^i_2$	6.38	92.3	107.0
	$Pr^i_2PC_3H_6PPr^i_2$	6.44[b]	92.1	39.3
MeC_6H_6[c]	$Cy_2PCH_2PCy_2$	2.45(Me), 6.13(2/3), 6.65(4)[b]	21.2(Me), 109.3(1), 91.5(2), 89.3(3), 93.2(4)[b]	−0.3[b]
	$Cy_2PC_2H_4PCy_2$	2.55(Me), 5.95(2), 6.03(3), 6.96(4)	20.9(Me), 90.7(2), 88.5(3), 96.7(4)	97.2
	$Cy_2PC_2H_4PCy_2$[d]	2.55(Me), 5.95(2), 6.03(3), 6.96(4)	20.9(Me), 113.3(1), 90.7(2), 88.5(3), 96.7(4)	97.2
	$Cy_2PC_3H_6PCy_2$	6.9(br)	—	29.1[e]
	$Pr^i_2PC_2H_4PPr^i_2$	2.51(Me), 5.95(2), 6.03(3), 6.97(4)[b]	19.8(Me), 112.0(1), 89.5(2), 87.4(3), 95.6(4)[b]	106.4[b]
	$Pr^i_2PC_2H_4PPr^i_2$[f]	2.56(Me), 6.0(2/3), 6.97(4)	20.7(Me), 90.7(2), 88.4(3), 96.5(4)	106.5
	$Pr^i_2PC_3H_6PPr^i_2$	2.56(Me), 5.8(2), 5.9(3), 7.0(4)[b]	21.8(Me), 114.6(1), 89.9(2), 87.4(3), 96.6(4)[b]	38.3/33.5[b]
1,2-$Me_2C_6H_4$[g]	$Cy_2PC_2H_4PCy_2$	2.39(Me), 5.31(2), 6.77(3)	19.0(Me), 115.1(1), 94.7(2), 83.6(3)	95.7
	$Pr^i_2PC_2H_4PPr^i_2$	2.40(Me), 5.40(2), 6.69(3)	19.4(Me), 112.2(1), 94.4(2), 84.5(3)	104.9
	$Pr^i_2PC_3H_6PPr^i_2$	2.39(Me), 4.92(2), 7.16(3)[b]	114.4(1), 94.3(2), 81.0(3)[b]	44.7/33.5[b]
1,3,5-$Bu^t_3C_6H_3$	$Cy_2PC_2H_4PCy_2$	1.31(Me), 5.6(2)[b]	31.2(Me), 35.0/150.0(Bu^t), 119.5(2)[b]	76.0[b]
Me_6C_6	$Cy_2PC_2H_4PCy_2$	2.18(Me)[b]	16.6(Me), 131.7[b]	75.5[b]
$MeCOCH_2C_6H_5$	$Pr^i_2PC_2H_4PPr^i_2$	2.24(Me), 4.10(CH_2), 5.97(2), 6.06(3), 7.04(4)	204.6/48.0($COCH_2$), 109.1(1), 90.8(2), 88.1(3), 96.4(4)[b]	106.2
$MeOC_6H_5$	$Cy_2PCH_2PCy_2$	3.96(Me), 6.11/6.19(br)	56.5(Me), 89.6(2), 88.3(3), 91.9(4)	0.48
$H_2NC_6H_5$	$Pr^i_2PC_2H_4PPr^i_2$	6.10/5.97/5.84/5.73, 5.47/2.55(NH)	76.4(2), 88.4(3), 85.8(4)[b]	105.4[b]
$O_2NC_6H_5$	$Pr^i_2PC_2H_4PPr^i_2$	Broad	Broad	65.63
ClC_6H_5	$Cy_2PCH_2PCy_2$	6.4(2/3), 6.5(4)	92.7(2), 90.3(3)	0.12/−1.37

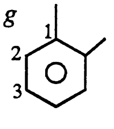
[a] AC 200; 300 K; d_6-acetone. [b] AMX 300; 243 K; d_6-acetone. [c]



[d] $SO_3CF_3^-$-complex.

[e] P-exchange; 29.3/25.4 (-30°C); 30.4 (-80°C); 29.1 (RT). [f] $[B(C_6H_3(CF_3)_2\text{-}3,5)_4]^-$-complex.

[g]



corresponding neutral species [1]. A sample of (η^4-cyclo-C_6H_8)Co($Cy_2PC_3H_6PCy_2$)H was prepared by reacting the corresponding (η^5-cyclo-C_6H_7)Co(I) species with cyclohexa-1,3-diene as described earlier [5]. The NMR spectrometers used have been listed earlier as have the details of the crystal structure determination [1].

3.1. *(η^3-Cyclo-C_6H_9)Co($Cy_2PC_2H_4PCy_2$) (**4**, [5])*

A sample of (η^3-cyclo-C_6H_9)(C_6H_6)Co (0.73 g, 3.3 mmol) [5] and $Cy_2PC_2H_4PCy_2$ (1.27 g, 3.0 mmol) were stirred in THF (20 ml) at 50°C for 4 h. The resulting red–brown suspension was evaporated to dryness and the residue dissolved in pentane. The filtered solution was cooled to −78°C to give the compound as a red–brown solid. Yield 1.14 g (67% theory). MS: *m*/*e* M^+. The crystal structure has been established by X-ray diffraction [5].

3.2. *$[(\eta^3$-Cyclo-$C_6H_9)Co(Cy_2PC_2H_4PCy_2)]^+BF_4^-$ (**5**)*

A sample of (η^3-cyclo-C_6H_9)Co($Cy_2PC_2H_4PCy_2$) (**4**) (1.03 g, 1.83 mmol) was dissolved in diethyl ether (50 ml) and treated at −45°C with butadiene (5 ml) and ethereal HBF_4 (0.25 ml, 1.83 mmol). The resulting ochre coloured precipitate was stirred for 3 h at room temperature (r.t.), isolated and recrystallized from acetone/diethyl ether to give the compound as a pink solid. Yield 0.97 g (81% theory). Found: C, 59.3; H, 8.9; Co, 9.2; P, 9.4; B, 1.7; F, 11.5. $C_{32}H_{57}CoP_2.BF_4$ calc.: C, 59.2; H, 8.9; Co, 9.1; P, 9.5; B, 1.7; F, 11.7%. IR (KBr): ν 2925s, 2850s, 1450s; 1055 (BF_4). MS (ESI): *m*/*e* 562 (M^+, 100%), 481 (< 5%). Magn. suscept. (μ_{eff}): 2.6 μ_B.

The compound can also be prepared by reacting **4** with Ph_3CBF_4 (yield 84%) whereby the formation of the tritylium dimer and Ph_3CH was confirmed spectroscopically (NMR, IR).

3.3. $[(\eta^3\text{-Cyclo-}C_6H_9)Co(Cy_2PC_3H_6PCy_2)]^+ BF_4^-$

A sample of $[(\eta^4\text{-cyclo-}C_6H_8)Co(Cy_2PC_3H_6PCy_2)]H$ [5] (0.18 g, 0.31 mmol) was suspended in benzene (7 ml) and treated with $C_7H_7BF_4$ (0.09 g, 0.51 mmol) and the reaction mixture was stirred at r.t. for 8 h. The resulting pale-beige precipitate was filtered off, washed with toluene and dried under high vacuum. The simultaneous formation of bitropyl in the filtrate was confirmed by IR spectroscopy. Yield 0.17 g (84% theory). Found: C, 59.7; H, 8.7; Co, 9.1; P, 9.3: B, 1.7; F, 11.4. $C_{33}H_{59}CoP_2 \cdot BF_4$ calc.: C, 59.7; H, 9.0; Co, 8.9; P, 9.3; B, 1.6; F, 11.5%. IR (KBr): ν 2935s, 2846s, 1447s; 1055vs (BF_4). MS (ESI): *m*/*e* 576 (M^+, 100%), 495 (5%). Magn. suscept. (μ_{eff}): 2.3 μ_B.

The same compound can be prepared (yield 83%) by reacting Ph_3CBF_4 in benzene.

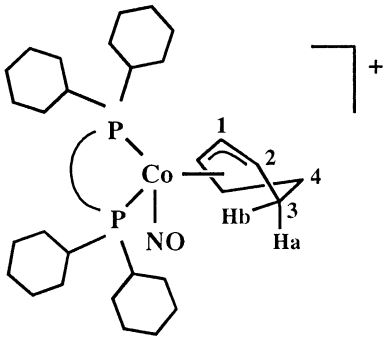
Table 2
Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for **8** with standard deviations in parentheses

Atom	*x*	*y*	*z*	U_{eq}^a
Co(1)	0.2050(1)	0.1247(1)	0.4410(1)	0.035(1)
P(1)	0.1869(1)	0.0958(1)	0.2739(1)	0.031(1)
P(2)	0.2060(1)	0.2172(1)	0.3871(1)	0.032(1)
B(1)	0.253(1)	0.3723(4)	0.0522(9)	0.117(9)
C(1)	0.1506(4)	0.1319(2)	0.5910(3)	0.053(3)
C(2)	0.1297(4)	0.0780(2)	0.5436(3)	0.053(3)
C(3)	0.2179(5)	0.0439(2)	0.5157(3)	0.055(3)
C(4)	0.3310(5)	0.0645(2)	0.5213(3)	0.056(3)
C(5)	0.3769(4)	0.1183(3)	0.5533(4)	0.058(3)
C(6)	0.3643(5)	0.1542(3)	0.6461(4)	0.065(4)
C(7)	0.2533(5)	0.1436(3)	0.6813(4)	0.062(3)
C(8)	0.1974(4)	0.1619(2)	0.1937(3)	0.036(2)
C(9)	0.1600(3)	0.2172(2)	0.2407(3)	0.034(2)
C(10)	0.1015(3)	0.2685(2)	0.4257(3)	0.039(2)
C(11)	0.1398(4)	0.2865(2)	0.5426(4)	0.050(3)
C(12)	0.0542(5)	0.3292(3)	0.5731(5)	0.065(4)
C(13)	−0.0670(5)	0.3043(3)	0.5482(5)	0.073(4)
C(14)	−0.1051(4)	0.2863(3)	0.4337(4)	0.063(4)
C(15)	−0.0213(4)	0.2430(2)	0.4017(4)	0.049(3)
C(16)	0.3448(3)	0.2583(2)	0.4143(3)	0.037(2)
C(17)	0.4337(4)	0.2295(2)	0.3632(4)	0.045(3)
C(18)	0.5505(4)	0.2597(2)	0.3953(5)	0.059(3)
C(19)	0.5404(5)	0.3252(2)	0.3682(5)	0.061(3)
C(20)	0.4504(4)	0.3540(2)	0.4143(5)	0.055(3)
C(21)	0.3330(4)	0.3235(2)	0.3837(4)	0.047(3)
C(22)	0.2916(39)	0.0427(2)	0.2422(3)	0.036(2)
C(23)	0.2654(4)	0.0209(2)	0.1276(4)	0.050(3)
C(24)	0.3516(4)	−0.0266(3)	0.1125(5)	0.062(4)
C(25)	0.4754(4)	−0.0057(3)	0.1478(5)	0.062(3)
C(26)	0.5012(4)	0.0168(3)	0.2604(4)	0.059(3)
C(27)	0.4157(4)	0.0652(2)	0.2717(4)	0.045(3)
C(28)	0.0430(3)	0.0651(2)	0.2125(3)	0.037(2)
C(29)	0.0251(4)	0.0037(2)	0.2546(4)	0.044(3)
C(30)	−0.0925(4)	−0.0208(2)	0.1990(4)	0.053(3)
C(31)	−0.1892(4)	0.0192(2)	0.2116(5)	0.061(3)
C(32)	−0.1731(4)	0.0812(2)	0.1757(5)	0.060(3)
C(33)	−0.0542(4)	0.1056(2)	0.2269(4)	0.047(3)

[a] $U_{eq} = 1/3\ \Sigma_i\ \Sigma_j\ U_{ij}a_i^*a_j^*\ \sim_i\ \sim_j$.

3.4. $[(\eta^3\text{-Cyclo-}C_6H_9)Co(Cy_2PC_2H_4PCy_2)(NO)]^+ BF_4^-$ (**6**)

A sample of $[(\eta^3\text{-cyclo-}C_6H_9)Co(Cy_2PC_2H_4PCy_2)]^+ BF_4^-$ [5] (0.24 g, 0.37 mmol) was dissolved in acetone (20 ml) and treated with NO (11.6 ml, 0.52 mmol) from a gas burette. The resulting green solution was filtered and evaporated to dryness. The residue was crystallized from acetone/diethyl ether. Yield 0.21 g (84% theory). Found: C, 55.6; H, 8.8; Co, 8.9; N, 1.9; P, 8.8. $C_{32}H_{57}CoNOP_2 \cdot BF_4$ calc.: C, 56.6; H, 8.5; Co, 8.7; N, 2.1; P, 9.1%. IR (KBr): ν 2921s, 2850s, 1450s; 1752s(NO); 1053s (BF_4). MS (ESI): *m*/*e* 592 (M^+, 100%), 481 (< 5%). ^{1}H-NMR (d_6-acetone): δ 6.18 (mbr, H-2), 4.37 (mbr, H-1), 2.45 (mbr, H-3a), 2.6–1.0 (H-3b, Cy_2PCH_2). ^{13}C-NMR (d_6-acetone): δ 95.4 (C-1), 81.5/81.3 (C-2), 18.8 (C-4); 36.9, 35.3, 28.8, 28.7, 28.1–27.6, 27.1–26.6, 26.1, 25.8, 21.7 (Cy_2PCH_2). ^{31}P-NMR (d_6-acetone, 188 K): δ 84.6 brs. numbering scheme shown below.



3.5. $[(\eta^3\text{-Cyclo-}C_6H_9)Co(Cy_2PC_3H_6PCy_2)(NO)]^+ BF_4^-)$

Prepared as a green solid (yield 87%) as described above by reacting $[(\eta^3\text{-cyclo-}C_6H_9)Co(Cy_2PC_3H_6PCy_2)]^+ BF_4^-$ with NO in acetone. Found: C, 56.3; H, 8.5; Co, 8.4; N, 1.9; P, 8.9. $C_{33}H_{59}CoNOP_2 \cdot BF_4$ calc.: C, 57.2; H, 8.6; Co, 8.5; N, 2.0; P, 8.9%. IR (KBr): ν 2932s, 2854s, 1450s; 1745s (NO), 1055s (BF_4). MS (ESI): *m*/*e* 606 (M^+, 100%). ^{1}H-NMR (d_6-acetone): δ 6.28 (mbr, H-2), 4.53 (mbr, H-1), 2.32 (mbr, H-3a); 2.5–1.1 (H-3b, $Cy_2PC_3H_6$). ^{13}C-NMR (d_6-acetone): δ 97.8 (C-1), 83.7 (C-2), 20.1/19.5 (C-4/CH_2); 39.9, 36.5, 29.1, 28.6-28.5, 28.2, 27.7–27.5, 27.3–27.1, 26.3, 26.0, 17.8 ($Cy_2PC_3H_6$). ^{31}P-NMR (d_6-acetone, 188 K): δ 25.4 brs. numbering scheme see above.

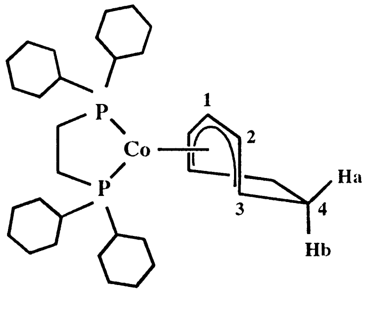
Table 3
$[(\eta^6\text{-Arene})Co(R_2P(CH_2)_nPR_2)]^+X^-$ compounds

Arene	Bisphosphine	X^-	Preparation (yield%)[a]	Elemental analysis (calc.%)				MS (*m*/*e*, Int.%)
				C	H	Co	P	
C_6H_6	$Cy_2PCH_2PCy_2$	BF_4	A(91)	58.9(58.9)	8.4(8.2)	9.2(9.3)	9.8(9.8)	544 (M^+–H, 50)
	$Cy_2PC_2H_4PCy_2$	BF_4	A(93), C(88), D(64)	58.8(59.5)	8.5(8.4)	9.0(9.1)	9.6(9.6)	559 (M^+, 100)
	$Cy_2PC_3H_6PCy_2$	BF_4	A(87), C(80), D(83)	59.9(60.0)	8.6(8.6)	9.1(8.9)	9.4(9.4)	570 (M^+–3H, <5)
	$Pr^i_2PC_2H_4PPr^i_2$	BF_4	A(50)	49.5(49.4)	7.9(7.8)	12.2(12.1)	12.7(12.8)	—
	$Pr^i_2PC_3H_6PPr^i_2$	BF_4	A(72)	50.5(50.4)	7.8(8.0)	11.6(11.8)	12.6(12.4)	410 (M^+–3H, 100)
MeC_6H_5	$Cy_2PCH_2PCy_2$	BF_4	A(90)	57.7(59.4)	8.4(8.4)	9.1(9.1)	9.6(9.6)	558 (M^+–H, 40)
	$Cy_2PC_2H_4PCy_2$	BF_4	A(89)	59.9(60.0)	8.6(8.5)	9.0(8.9)	9.4(9.4)	573 (M^+–H, 15)
	$Cy_2PC_2H_4PCy_2$	SO_3CF_3	D(99)	57.6(56.5)	7.9(7.8)	7.9(8.2)	8.4(8.6)	Dec.
	$Cy_2PC_3H_6PCy_2$	BF_4	A(63)	57.3(60.5)	8.7(8.6)	8.9(8.8)	9.1(9.2)	586 (M^+–H, 33)
	$Pr^i_2PC_2H_4PPr^i_2$	BF_4	A(92)	50.3(50.4)	8.1(8.0)	11.9(11.8)	12.3(12.4)	500 (M^+)
1,2-$Me_2C_6H_4$	$Pr^i_2PC_2H_4PPr^i_2$	BF_4	A(62), B(94)	51.3(51.2)	8.4(8.5)	11.3(11.4)	12.1(12.0)	—
$MeOC_6H_5$	$Cy_2PCH_2PCy_2$	BF_4	B(80)	—	—	9.7(8.9)	9.1(9.4)	—

[a] A: protonolysis of (η^3-cyclo-C_8H_{13})Co(I) species, B: arene-exchange, C: deprotonation of (η^5-cyclo-C_6H_7)Co(I) species, D: hydrogenation of (η^3-allyl)Co(II) species.

3.6. $[(\eta^5\text{-Cyclo-}C_7H_9)Co(Cy_2PC_2H_4PCy_2)$ (7)

A sample of (η^3-cyclo-C_8H_{13})Co($Cy_2PC_2H_4PCy_2$) (0.81 g, 1.47 mmol) and 1,3,5-cycloheptatriene (2.0 ml) were dissolved in THF (5 ml) and stirred at r.t. for 18 h to give a red–brown suspension (a parallel experiment was successful only after the introduction of hydrogen). The reaction mixture was evaporated to dryness and the residue crystallized from THF. Yield 0.73 g (86% theory). The presence of 1,3-cyclooctadiene and cyclooctene in the solvent was confirmed by GC. Found: C, 68.9; H, 9.9; Co, 10.5; P, 10.9. $C_{33}H_{57}CoP_2$ calc.: C, 69.0; H, 10.0; Co, 10.3; P, 10.8%. IR (KBr): *v* 2920s, 2850s, 1440s; 1000s. MS (EI, 140°C): *m*/*e* 574 (M^+, 100%), 481 (< 5%), 398 (5%), ^{1}H-NMR (d_8-toluene, 300 K): δ 5.17 (mbr, H-2), 5.09 (mbr, H-1), 4.26 (mbr, H-3), 2.21 (mbr, H-4a), 1.67 (mbr, H-4b); 2.0–0.9 (Cy_2PCH_2). ^{13}C-NMR (d_8-toluene, 300 K): δ 91.6 (C-2), 86.6 (C-1), 71.2 (C-3), 36.8, (C-4); 38.0, 37.8, 29.1–27.7, 27.2. ^{31}P-NMR (d_8-toluene, 185 K): δ 106.5, 79.4, *J* (A,B) 22.2 numbering scheme shown below.



3.7. $[(\eta^5\text{-Cyclo-}C_7H_9)Co(Cy_2PC_2H_4PCy_2)]^+ BF_4^-$ (8)

A sample of (η^5-cyclo-C_7H_9)Co($Cy_2PC_2H_4PCy_2$) (**7**) (1.43 g, 2.42 mmol) was dissolved in THF (20 ml) and treated at −40°C with butadiene (ca. 5 ml) and ethereal HBF_4 (0.33 ml, 2.41 mmol). The reaction mixture was warmed to r.t. and stirred for 12 h. The resulting orange–brown solid was isolated and crystallized from acetone/diethyl ether. Yield 1.47 g (92% theory). Found: C, 59.8; H, 8.7; Co, 8.9; P, 9.6; B, 1.7; F, 11.4. $C_{33}H_{57}CoP_2 \cdot BF_4$ calc.: C, 59.9; H, 8.7; Co, 8.9; P, 9.4; B, 1.6; F, 11.5%. IR (KBr): *v* 2930s, 2850s, 1450s; 1054vs (BF_4). MS (FAB): *m*/*e* 574 (M^+, 50%). Magn. suscept. (μ_{eff}): 1.6 μ_B.

Suitable crystals were grown from chlorobenzene/diethyl ether solution. Crystal structure analysis: molecular formula $C_{33}H_{57}CoP_2BF_4$, molecular weight 661.51 g mol^{-1}, crystal colour red, crystal size 0.42 × 0.32 × 0.18 mm, $a = 11.870(4)$, $b = 22.726(4)$, $c = 13.023(1)$ Å, $\beta = 103.14(1)°$, $V = 3421.4$ Å^3, $T = 293$ K, $D_{calc.}$ 1.28 g cm^{-3}, $\mu = 6.33$ cm^{-1}, $Z = 4$, monoclinic $P2_1/n$ (no. 14), Enraf-Nonius CAD 4 diffractometer, $\lambda = 0.71069$ Å, scan mode ω-2θ, measured reflections ($\pm h$, $\pm k$, $+l$) 8360, 7812 independent reflections, 4410 observed reflections ($I > 2\sigma$ (I)) for 366 refined parameters, $R = 0.058$, $R_w = 0.153$, residual electron density 0.069 Å^{-3}. Atomic positional parameters and equivalent isotropic thermal parameters are listed in Table 2 and the molecular structure with selected bond distances and angles is shown in Fig. 1.

3.8. $[(\eta^6\text{-Arene})Co(R_2P(CH_2)_nPR_2)]^+ X^-$ compounds

These compounds have been prepared by four different methods (A–D). Examples are described in detail below while the spectroscopic data and elemental analyses for all compounds are collected together in Table 1 and Table 3.

3.8.1. Method A. Protonolysis of an (η^3-cyclo-C_8H_{13})Co(I) species

3.8.1.1. $[(C_6H_6)Co(Cy_2PC_2H_4PCy_2)]^+BF_4^-$. A sample of ($\eta^3$-cyclo-$C_8H_{13}$)Co($Cy_2PC_2H_4PCy_2$) (1.11 g, 1.88 mmol) was suspended in benzene (6 ml) and treated with ethereal HBF_4 (0.30 ml, 2.22 mmol) at 0°C. The resulting red–brown solution was stirred for 2 h at r.t., evaporated to dryness and the residue crystallized from acetone/diethyl ether. Yield 1.13 g (93% theory). Anal.: see Table 3. NMR spectral data: see Table 1.

In addition to the compounds shown in Table 3, the following compounds were prepared as described above for spectroscopic purposes (Table 1): $[(MeC_6H_5)Co(Pr^i_2PC_2H_4PPr^i_2)^+[B(C_6H_3(CF_3)_2\text{-}3,5)_4]^-$, $[(MeC_6H_5)Co(Pr^i_2PC_3H_6PPr^i_2)^+BF_4^-$, $[(1,2\text{-}Me_2C_6H_4)Co(Pr^i_2PC_3H_6PPr^i_2)]^+BF_4^-$, $[(1,3,5\text{-}Bu^t_3C_6H_3)Co(Cy_2PC_2H_4PCy_2)]^+BF_4^-$, $[(Me_6C_6)Co(Cy_2PC_2H_4PCy_2)]^+BF_4^-$.

3.8.2. Method B. Arene-exchange

3.8.2.1. $[(MeOC_6H_5)Co(Cy_2PCH_2PCy_2)]^+BF_4^-$. A sample of $[(MeC_6H_5)Co(Cy_2PCH_2PCy_2)]^+BF_4^-$ (0.11 g, 0.17 mmol) was dissolved in acetone (3 ml) and anisole (3 ml) and stirred at r.t. for 16 h. The resulting orange solution was evaporated to dryness to give the compound as an orange solid. Yield 0.09 g (80% theory).

Anal.: see Table 3. NMR spectral data: see Table 1.

In addition to the compounds shown in Table 3, the following examples were prepared in solution for spectroscopic purposes (Table 1): $[(MeOCH_2C_6H_5)Co(Pr^i_2PC_2H_4PPr^i_2)^+BF_4^-$, $[(H_2NC_6H_5)Co(Pr^i_2PC_2H_4PPr^i_2)^+BF_4^-$, $[(O_2NC_6H_5)Co(Pr^i_2PC_2H_4PPr^i_2)]^+BF_4^-$, $[(ClC_6H_5)Co(Cy_2PCH_2PCy_2)]^+BF_4^-$ by reacting the appropriate $[(MeC_6H_5)Co(R_2P(CH_2)_nPR_2)]^+BF_4^-$ compound and $[(ClC_6H_5)Co(Cy_2PC_2H_4PCy_2)]^+BF_4^-$, $[(1,2\text{-}Me_2C_6H_4)Co(Pr^i_2PC_2H_4PPr^i_2)]^+BF_4^-$ by reacting the appropriate $[(C_6H_6)Co(R_2P(CH_2)_nPR_2)]^+BF_4^-$ compound.

In addition to these two principal reactions (A, B), individual examples were also prepared by the procedures described below.

3.8.3. Method C. Deprotonation of an (η^5-cyclo-C_6H_7)Co(I) species

3.8.3.1. $[(C_6H_6)Co(Cy_2PC_3H_6PCy_2)]^+BF_4^-$. A sample of ($\eta^5$-cyclo-$C_6H_7$)Co($Cy_2PC_3H_6PCy_2$) (0.17 g, 0.30 mmol) was treated with $C_7H_7BF_4$ (0.07 g, 0.39 mmol) in benzene (5 ml) and stirred for 16 h at r.t. The resulting red–brown precipitate was filtered off and crystallized from acetone/diethyl ether. Yield 0.16 g (80% theory). Anal.: see Table 3. NMR spectral data: see Table 1.

Similar results were obtained by reacting Ph_3CBF_4.

3.8.4. Method D. Hydrogenation of an (η^3-allyl)Co(II) species in the presence of arene

3.8.4.1. $[(C_6H_6)Co(Cy_2PC_2H_4PCy_2)]^+BF_4^-$. A sample of $[(\eta^3\text{-cyclo-}C_8H_{13})Co(Cy_2PC_2H_4PCy_2)]^+BF_4^-$ (0.54 g, 0.80 mmol) was suspended in benzene (3.0 ml) and the reaction vessel attached to a gas burette filled with hydrogen. Hydrogen absorption (17.2 ml, 0.77 mmol) led to the formation of a red–brown suspension of the compound which was isolated and crystallized from acetone/diethyl ether. Yield 0.33 g (64% theory). Anal.: see Table 3. NMR spectral data: see Table 1.

3.8.5. $[(C_6H_6)Co(Cy_2PC_3H_6PCy_2)]^+BF_4^-$

A sample of $[(\eta^3\text{-}2\text{-}Bu^tC_3H_4)Co(Cy_2PC_3H_6PCy_2)]^+BF_4^-$ (0.15 g, 0.18 mmol) was dissolved in benzene (2 ml) and treated with hydrogen as described above. Yield 0.10 g (83% theory). Anal.: see Table 3. NMR spectral data: see Table 1.

The complex $[(\eta^3\text{-cyclo-}C_8H_{13})Co(Cy_2PC_3H_6PCy_2)]^+BF_4^-$ reacts similarly.

3.8.6. $[(\eta^6\text{-}MeC_6H_5)Co(Cy_2PC_2H_4PCy_2)]^+SO_3CF_3^-$

A sample of $[(\eta^3\text{-cyclo-}C_8H_{13})Co(Cy_2PC_2H_4PCy_2)]^+SO_3CF_3^-$ (0.10 g, 0.14 mmol) was dissolved in toluene (8 ml) and the apparatus evacuated and filled with hydrogen (20 ml). The resulting orange solution was stirred for 3 h, evaporated to dryness and the residue washed with ether to give the compound as an orange powder. Yield 0.10 g (97% theory). Anal.: see Table 3. NMR spectral data: see Table 1.

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[6] Crystal structure analysis: molecular formula $C_{32}H_{53}ClCoP_2BF_4$, molecular weight 680.98 g mol^{-1}, crystal colour red, crystal size 0.73 × 0.66 × 0.63 mm, $a = 14.358(2)$, $b = 17.412(2)$, $c = 18.621(1)$ Å, $V = 4655.3(8)$ Å^3, $T = 293$ K, $Z = 6$, orthorhombic $P222$ (no. 19), Enraf-Nonius CAD 4 diffractometer, $\lambda = 0.71069$ Å, scan mode ω-2θ, measured reflections ($-h$, $-k$, $\pm$l) 5589, 5362 independent reflections, 3026 observed reflections ($I > 2\sigma(I)$) for 370 refined parameters, $R = 0.182$, $R_w = 0.412$, residual electron density 4.184 Å^{-3}.