Basic Metal Complexes: Crystal Structures of Cyclopentadienylcobalt(I)-bis(trimethylphosphine) and Cyclopentadienylcobalt(I)-(trimethylphosphine)(ethylene)

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The title complexes $[(C_5H_5)Co(PMe_3)_2]$ **1** and $[(C_5H_5)Co(PMe_3)(C_2H_4)]$ **2b** adopt the two-legged *piano-stool* molecular geometry, with a remarkably similar coordination geometry around the cobalt atom. The rather long carbon-carbon bond of the ethylene ligand in **2b** underlines the pronounced donor properties of the PMe_3 ligand, causing a highly basic site.

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The Lewis and Bronstedt basicity of transition metal in organometallic complexes is a concept widely used to rationalize stoichiometric and catalytic reactivity. $[(C_5H_5)Co(PMe_3)_2]$ **1** is one of the prototypal representatives of basic metal complexes, and its chemistry has been extensively studied. The metal and/or carbon-centered nucleophilic reactivity in the series $[(C_5H_5)M(PMe_3)_{2-n}(C_2H_4)_n]$ ($M = Co, Rh, Ir; n = 1, 2$) is of particular importance. For example, as a consequence of the variation of the metal basicity, the protonation of $[(C_5H_5)Rh(PMe_3)(C_2H_4)]$ **2a** occurs at the metal to give the hydrido complex cation $[(C_5H_5)Rh(H)(PMe_3)(C_2H_4)]^+$, whereas in $[(C_5H_5)Co(PMe_3)(C_2H_4)]$ **2b** a metal carbon bond is protonated to form an agostic ethyl complex, viz. $[(C_5H_5)Co(PMe_3)(\eta^2-C_2H_5)]^+$ **3**.¹ Here we report on the crystal and molecular structures of **1** and **2b**, the latter being the precursor to **3**, one of the best mechanistically characterized late-metal polymerization catalysts. Apart from catalytic applications, the series $[(C_5H_5)Co(PMe_3)_{2-n}(C_2H_4)_n]$ ($n = 0 - 2$) constitutes important reference molecules for MO-theoretical calculations, due to their relative simplicity and symmetrical structures.

The title complexes were prepared in quantitative yield by the slow addition of two or one, respectively, molar equivalents of PMe_3 to a hexane solution of $[(C_5H_5)Co(C_2H_4)_2]$ at $-20^\circ C$, followed by warming up to ambient temperature and removal of the solvent *in vacuo*. Single crystals suitable for intensity data

collection were obtained by cooling pentane solutions to $-20^\circ C$.

The structures were solved by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors² and refined by full-matrix least-squares methods based on F^2 .³ All non-hydrogen atoms were given anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier syntheses. During refinement, the hydrogens of the methyl groups were treated as variable metric rigid groups, with ideal bond angles. All other hydrogen atoms were freely refined.

Both **1** and **2b** adopt the two-legged *piano-stool* geometry (Fig. 2). The coordination geometry around the cobalt atom is remarkably similar in both complexes. The plane of the C_5H_5

Table 1 Crystal and experimental data

	1	2b
Formula	$C_{11}H_{23}CoP_2$	$C_{10}H_{18}CoP$
Formula weight	276.16	228.14
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n, Z = 4$	$P2_1/n, Z = 4$
$a/\text{\AA}$	9.4926(9)	7.3687(5)
$b/\text{\AA}$	13.8577(13)	14.9016(10)
$c/\text{\AA}$	10.8787(10)	10.4652(7)
$\beta/^\circ$	108.6630(10)	107.4040(10)
$V/\text{\AA}^3$	1355.8(2)	1096.53(13)
$D_x/\text{Mg m}^{-3}$	1.353	1.382
No. of reflections used	4501	3733
$2\theta_{\text{max}}$ with Mo $K\alpha$	63.0	64.0
$R(F)$ [$F_o > 4\sigma(F_o)$]	0.0293	0.0258
$wR(F^2)$ (all data)	0.0762	0.0704
$(\Delta/\sigma)_{\text{max}}$	0.000	0.001
$(\Delta\rho)_{\text{max}}$	0.883	0.720
$(\Delta\rho)_{\text{min}}$	-0.278	-0.269
Measurement	Bruker AXS Smart 1000 CCD diffractometer, $T = 100\text{ K}$	
Program system	Smart, Saint	
Structure determination	DIRDIF-08	
Refinement	SHELXL-97	
CCDC deposit number	CCDC-685058	CCDC-685059

Fig. 1 Structure diagrams of **1** and **2b**.

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Fig. 2 Molecular structures of **1** and **2b**. Displacement ellipsoids are drawn at the 50% probability level.

Table 2a Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for **1**

Atom	x	y	z	U_{eq}
C(1)	-1567(2)	533(1)	1253(2)	24(1)
C(2)	-83(2)	224(1)	1710(2)	18(1)
C(3)	462(2)	363(1)	3089(2)	20(1)
C(4)	-683(2)	768(1)	3474(2)	26(1)
C(5)	-1930(2)	897(1)	2332(2)	30(1)
C(11)	-3103(2)	3137(1)	1803(2)	23(1)
C(12)	-445(2)	3724(1)	3703(2)	21(1)
C(13)	-916(2)	4031(1)	1044(2)	24(1)
C(21)	3294(2)	1231(1)	2084(2)	22(1)
C(22)	1744(2)	2538(1)	204(2)	26(1)
C(23)	2924(2)	3121(1)	2819(2)	21(1)
Co	-160(1)	1680(1)	2141(1)	12(1)
P(1)	-1082(1)	3073(1)	2154(1)	13(1)
P(2)	1824(1)	2142(1)	1835(1)	15(1)

Table 2b Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for **2b**

Atom	x	y	z	U_{eq}
C(1)	1838(2)	3226(1)	4332(2)	26(1)
C(2)	2488(2)	2939(1)	3261(2)	24(1)
C(3)	1001(2)	3088(1)	2026(2)	23(1)
C(4)	-563(2)	3454(1)	2343(2)	25(1)
C(5)	-71(2)	3529(1)	3764(2)	25(1)
C(11)	1988(2)	960(1)	1246(1)	26(1)
C(12)	3071(2)	450(1)	3942(1)	23(1)
C(13)	-601(2)	16(1)	2267(2)	29(1)
C(21)	-1002(3)	1619(1)	4556(2)	34(1)
C(22)	-2424(2)	1784(1)	3322(2)	37(1)
Co	103(1)	2200(1)	3250(1)	14(1)
P	1067(1)	952(1)	2683(1)	15(1)

Table 3 Selected bond lengths ($\text{\AA}$) and angles ($^\circ$)

	1	2b
Co-C1...C5	2.066(2)---2.101(2)	2.067(1)---2.095(1)
Co-P	2.1218(4), 2.1138(4)	2.1368(4)
Co-C21/C22		1.9868(14)/1.9853(15)
C1-C2		1.410(2)
P1-Co-P2	96.62(2)	

ligand is at a distance of 1.7029(7) (**1**) and 1.6931(6) $\text{\AA}$ (**2b**) from the metal. The P-Co-L plane is essentially perpendicular to the cyclopentadienyl ring (L = PMe_3 , $88.10(5)^\circ$; L = midpoint of C_2H_4 , $87.29(5)^\circ$), illustrating the high symmetry of the complexes. The carbon-carbon bond of the ethylene ligand in **2b** (1.420(3) $\text{\AA}$) is longer than in comparable cyclopentadienyl cobalt ethylene complexes with strong donor ligands L, e.g. L = $(\text{C}_5\text{R}_5)\text{Co}(\text{cyclopentadienylidene})$ (1.407(7) $\text{\AA}$ (R = Me), 1.393(13) $\text{\AA}$ (R = H)),⁴ and L = (1,3-*i*Pr₂-4,5-Me₂-1*H*-imidazol-2-ylidene) (1.355(13) $\text{\AA}$).⁵ This underlines the pronounced donor properties of the PMe_3 ligand.

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