Supporting Information

Highly Reactive Cyclopentadienylcobalt(I) Olefin-Complexes

Marko Hapke, Nico Weding, Anke Spannenberg*

Leibniz-Institut für Katalyse e.V. an der Universität Rostock (LIKAT)

Albert-Einstein-Str. 29a, 18059 Rostock, Germany

E-mail: marko.hapke@catalysis.de

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1. General Methods

NMR

The NMR spectra were recorded on a Bruker AV 400 spectrometer. Chemical shifts are reported in ppm relative to the ^1H and ^{13}C residue of the deuterated solvent.

MS

Mass spectra were obtained with a Finnigan MAT 95-XP (Thermo Electron) instrument at an ionizing voltage of 70 eV. Relative intensities in percentages are given in parentheses.

X-ray crystallographic analysis

Data were collected on a STOE IPDS II diffractometer using graphite-monochromated Mo- K_α radiation. The structures were solved by direct methods (SHELXS-97)¹ and refined by full-matrix least-squares techniques on F^2 (SHELXL-97).² XP (Bruker AXS) was used for graphical representations.

2. Structural Elucidations

Crystallographic details of the complexes 6 - 9.

Table S1. Crystallographic Details of 6 - 9.

	6	7	8	9
Chem. Formula	C ₁₅ H ₂₉ CoSi ₂	C ₉ H ₁₁ Cl ₆ CoSi ₂	C ₁₁ H ₁₅ CoO	C ₁₁ H ₁₅ Co
Form. Wght. [g mol ⁻¹]	324.49	446.99	222.16	206.16
Colour	red	red	orange	red
Cryst. form	plate	prism	prism	prism
Cryst. size [mm]	0.50x0.22x0.09	0.30x0.15x0.08	0.20x0.15x0.10	0.25x0.20x0.15
Cryst. system	triclinic	monoclinic	monocline	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> <i>n</i>
<i>a</i> [Å]	6.8151 (5)	15.9701 (11)	11.3734 (4)	5.6233 (6)
<i>b</i> [Å]	11.5177 (9)	6.8829 (3)	7.4820 (3)	12.5738 (13)
<i>c</i> [Å]	11.9438 (9)	15.3137 (9)	11.7728 (5)	6.7557 (7)
α [°]	77.994 (6)	90.00	90.00	90.00
β [°]	75.525 (6)	96.381 (5)	106.919 (3)	100.803 (8)
γ [°]	87.846 (6)	90.00	90.00	90.00
<i>V</i> [Å ³]	887.80 (12)	1672.9 (2)	958.45 (7)	469.20 (8)
<i>Z</i>	2	4	4	2
$\rho_{\text{calc.}}$ [g cm ⁻³]	1.214	1.775	1.540	1.459
μ [mm ⁻¹]	1.086	2.106	1.744	1.767
MoK α [Å]	0.71073	0.71073	0.71073	0.71073
<i>T</i> [K]	200 (2)	200 (2)	200 (2)	200 (2)
Measured reflections	10000	8882	11675	5314
Independent reflections	3758	1573	2032	1911
Reflections with $I > 2\sigma(I)$	3187	1210	1623	1734
Θ_{max} [°]	26.75	25.49	26.72	26.73
<i>R</i> _{int} .	0.0334	0.0450	0.0314	0.0454
<i>R</i> ₁ ($I > 2\sigma(I)$)	0.0265	0.0313	0.0210	0.0412
<i>wR</i> ₂ (all data)	0.0696	0.0765	0.0478	0.0930
largest peak diff. and hole [e Å ⁻³]	0.366 and -0.255	0.361 and -0.278	0.302 and -0.184	0.931 and -0.471
GOF	1.034	0.938	0.913	1.054
Parameters	193	102	142	108
CCDC #	764739	764740	764741	764742

Figure S1. Numbering scheme of **6**.

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	1042(3)	8404(2)	10876(2)	50(1)
C(2)	592(2)	7182(2)	11289(1)	43(1)
C(3)	2109(3)	6452(2)	9075(2)	45(1)
C(4)	1764(3)	7662(2)	8667(1)	41(1)
C(5)	1795(3)	7094(2)	13640(2)	67(1)
C(6)	-2345(3)	6274(2)	13607(2)	65(1)
C(7)	1228(3)	4781(2)	12857(2)	62(1)
C(8)	662(3)	8893(2)	6445(2)	66(1)
C(9)	4656(4)	7639(2)	6239(2)	68(1)
C(10)	4020(4)	9972(2)	7134(2)	71(1)
C(11)	5996(2)	6517(2)	9756(2)	45(1)
C(12)	6228(2)	7630(2)	8974(2)	49(1)
C(13)	5843(3)	8514(2)	9643(2)	56(1)
C(14)	5317(3)	7934(2)	10835(2)	55(1)
C(15)	5445(2)	6703(2)	10903(2)	48(1)
Co(1)	3249(1)	7449(1)	9999(1)	34(1)
Si(1)	402(1)	6349(1)	12822(1)	43(1)
Si(2)	2831(1)	8532(1)	7152(1)	44(1)

Table S3. Bond lengths [$\text{\AA}$] and angles [deg] for **6**.

C(1)-C(2)	1.388(8)	C(9)-C(10)-Co(1)	69.7(3)
C(1)-Co(1)	2.001(5)	C(11)-C(10)-Co(1)	68.1(4)
C(2)-C(3A)	1.513(5)	C(10)-C(11)-C(7)	109.9(6)
C(2)-C(3B)	1.513(5)	C(10)-C(11)-Co(1)	72.6(4)
C(2)-Co(1)	2.013(4)	C(7)-C(11)-Co(1)	70.8(3)
C(5)-C(6)	1.409(8)	C(1)-Co(1)-C(2)	40.4(2)
C(5)-C(4A)	1.512(5)	C(1)-Co(1)-C(5)	97.4(2)
C(5)-C(4B)	1.513(5)	C(2)-Co(1)-C(5)	83.8(2)

C(5)-Co(1)	2.019(4)	C(1)-Co(1)-C(6)	93.2(2)
C(6)-Co(1)	2.039(5)	C(2)-Co(1)-C(6)	106.6(2)
C(7)-C(8)	1.398(9)	C(5)-Co(1)-C(6)	40.6(2)
C(7)-C(11)	1.403(10)	C(1)-Co(1)-C(11)	97.8(3)
C(7)-Co(1)	2.069(5)	C(2)-Co(1)-C(11)	95.9(2)
C(8)-C(9)	1.409(7)	C(5)-Co(1)-C(11)	155.9(3)
C(8)-Co(1)	2.084(5)	C(6)-Co(1)-C(11)	155.5(2)
C(9)-C(10)	1.393(8)	C(1)-Co(1)-C(7)	126.3(3)
C(9)-Co(1)	2.088(4)	C(2)-Co(1)-C(7)	100.7(2)
C(10)-C(11)	1.402(8)	C(5)-Co(1)-C(7)	116.5(3)
C(10)-Co(1)	2.111(7)	C(6)-Co(1)-C(7)	139.6(3)
C(11)-Co(1)	2.051(5)	C(11)-Co(1)-C(7)	39.8(3)
C(3A)-C(4A)	1.513(5)	C(1)-Co(1)-C(8)	163.7(2)
C(3B)-C(4B)	1.513(5)	C(2)-Co(1)-C(8)	135.6(2)
C(2)-C(1)-Co(1)	70.2(3)	C(5)-Co(1)-C(8)	97.6(2)
C(1)-C(2)-C(3A)	128.2(6)	C(6)-Co(1)-C(8)	102.4(2)
C(1)-C(2)-C(3B)	102.0(2)	C(11)-Co(1)-C(8)	66.0(3)
C(3A)-C(2)-C(3B)	26.9(15)	C(7)-Co(1)-C(8)	39.3(3)
C(1)-C(2)-Co(1)	69.3(3)	C(1)-Co(1)-C(9)	136.5(2)
C(3A)-C(2)-Co(1)	111.4(4)	C(2)-Co(1)-C(9)	161.1(2)
C(3B)-C(2)-Co(1)	111.8(13)	C(5)-Co(1)-C(9)	113.8(2)
C(6)-C(5)-C(4A)	117.2(6)	C(6)-Co(1)-C(9)	91.8(2)
C(6)-C(5)-C(4B)	141.0(2)	C(11)-Co(1)-C(9)	65.3(2)
C(4A)-C(5)-C(4B)	24.0(2)	C(7)-Co(1)-C(9)	66.0(2)
C(6)-C(5)-Co(1)	70.4(3)	C(8)-Co(1)-C(9)	39.5(2)
C(4A)-C(5)-Co(1)	110.2(4)	C(1)-Co(1)-C(10)	102.7(3)
C(4B)-C(5)-Co(1)	109.1(15)	C(2)-Co(1)-C(10)	124.8(2)
C(5)-C(6)-Co(1)	68.9(3)	C(5)-Co(1)-C(10)	151.1(2)
C(8)-C(7)-C(11)	107.0(5)	C(6)-Co(1)-C(10)	116.8(2)
C(8)-C(7)-Co(1)	70.9(3)	C(11)-Co(1)-C(10)	39.3(2)
C(11)-C(7)-Co(1)	69.4(3)	C(7)-Co(1)-C(10)	66.6(2)
C(7)-C(8)-C(9)	107.6(5)	C(8)-Co(1)-C(10)	66.1(2)
C(7)-C(8)-Co(1)	69.8(3)	C(9)-Co(1)-C(10)	38.8(2)
C(9)-C(8)-Co(1)	70.4(3)	C(2)-C(3A)-C(4A)	106.2(5)
C(10)-C(9)-C(8)	109.4(5)	C(5)-C(4A)-C(3A)	109.0(5)
C(10)-C(9)-Co(1)	71.5(3)	C(4B)-C(3B)-C(2)	105(2)
C(8)-C(9)-Co(1)	70.1(3)	C(3B)-C(4B)-C(5)	109(2)
C(9)-C(10)-C(11)	106.1(6)		

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6**. The anisotropic displacement factor exponent takes the form:
 $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	46(1)	50(1)	49(1)	-8(1)	-5(1)	16(1)
C(2)	34(1)	55(1)	37(1)	-4(1)	-8(1)	3(1)
C(3)	50(1)	42(1)	45(1)	-3(1)	-19(1)	-9(1)
C(4)	35(1)	49(1)	39(1)	-4(1)	-11(1)	1(1)
C(5)	69(1)	85(2)	51(1)	-21(1)	-16(1)	-4(1)
C(6)	50(1)	90(2)	44(1)	-4(1)	-4(1)	5(1)
C(7)	73(1)	53(1)	51(1)	-2(1)	-8(1)	8(1)
C(8)	67(1)	75(1)	51(1)	5(1)	-21(1)	8(1)
C(9)	75(1)	74(1)	51(1)	-14(1)	-8(1)	18(1)
C(10)	92(2)	47(1)	68(1)	5(1)	-21(1)	-12(1)
C(11)	33(1)	44(1)	62(1)	-15(1)	-13(1)	7(1)
C(12)	31(1)	61(1)	49(1)	-7(1)	-4(1)	-1(1)
C(13)	40(1)	41(1)	87(1)	-11(1)	-15(1)	-7(1)
C(14)	41(1)	70(1)	66(1)	-33(1)	-19(1)	-2(1)
C(15)	35(1)	59(1)	51(1)	-4(1)	-17(1)	2(1)
Co(1)	32(1)	32(1)	38(1)	-6(1)	-9(1)	2(1)
Si(1)	41(1)	50(1)	36(1)	-7(1)	-9(1)	5(1)
Si(2)	48(1)	42(1)	39(1)	-2(1)	-10(1)	3(1)

Figure S2. Numbering scheme of **7**.

Table S5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **7**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Co(1)	0	2619(1)	2500	32(1)
Si(1)	1372(1)	1050(2)	1159(1)	45(1)
Cl(2)	1866(1)	-1483(2)	757(1)	77(1)
Cl(3)	2355(1)	2866(2)	1496(1)	82(1)
Cl(1)	702(1)	2180(2)	78(1)	80(1)
C(1)	1015(3)	989(7)	2946(3)	53(1)
C(2)	764(2)	542(3)	2079(2)	41(1)
C(3)	-530(2)	5158(3)	1866(2)	49(2)
C(4)	354(2)	5135(3)	1829(2)	42(2)
C(5)	755(2)	5107(3)	2704(2)	62(2)
C(6)	119(2)	5114(3)	3282(2)	69(2)
C(7)	-675(2)	5145(3)	2764(2)	63(2)

Table S6. Bond lengths [$\text{\AA}$] and angles [deg] for **7**.

Co(1)-C(1)	2.027(4)	C(5)#1-Co(1)-C(7)#1	66.18(6)
Co(1)-C(1)#1	2.027(4)	C(1)-Co(1)-C(7)	143.02(16)
Co(1)-C(2)	2.030(2)	C(1)#1-Co(1)-C(7)	96.53(15)
Co(1)-C(2)#1	2.030(2)	C(2)-Co(1)-C(7)	168.40(13)
Co(1)-C(6)#1	2.090(2)	C(2)#1-Co(1)-C(7)	100.468(13)
Co(1)-C(6)	2.090(2)	C(6)#1-Co(1)-C(7)	54.29(13)
Co(1)-C(5)	2.098(2)	C(6)-Co(1)-C(7)	39.5
Co(1)-C(5)#1	2.098(2)	C(5)-Co(1)-C(7)	66.18(6)
Co(1)-C(7)#1	2.109(2)	C(5)#1-Co(1)-C(7)	19.54(15)
Co(1)-C(7)	2.109(2)	C(7)#1-Co(1)-C(7)	68.91(12)
Co(1)-C(4)#1	2.122(2)	C(1)-Co(1)-C(4)#1	122.32(15)

Co(1)-C(4)	2.122(2)	C(1)#1-Co(1)-C(4)#1	111.62(15)
Si(1)-C(2)	1.831(3)	C(2)-Co(1)-C(4)#1	158.47(4)
Si(1)-Cl(1)	2.025(2)	C(2)#1-Co(1)-C(4)#1	102.66(10)
Si(1)-Cl(3)	2.0276(16)	C(6)#1-Co(1)-C(4)#1	66.08(6)
Si(1)-Cl(2)	2.0371(15)	C(6)-Co(1)-C(4)#1	20.65(14)
C(1)-C(2)	1.379(5)	C(5)-Co(1)-C(4)#1	56.04(12)
C(3)-C(7)	1.4195	C(5)#1-Co(1)-C(4)#1	39.3
C(3)-C(4)	1.4196	C(7)#1-Co(1)-C(4)#1	65.75(6)
C(4)-C(5)	1.4196	C(7)-Co(1)-C(4)#1	20.75(16)
C(5)-C(6)	1.4195	C(1)-Co(1)-C(4)	111.62(15)
C(6)-C(7)	1.4196	C(1)#1-Co(1)-C(4)	122.32(15)
C(1)-Co(1)-C(1)#1	112.8(3)	C(2)-Co(1)-C(4)	102.66(10)
C(1)-Co(1)-C(2)	39.74(15)	C(2)#1-Co(1)-C(4)	158.47(4)
C(1)#1-Co(1)-C(2)	89.41(15)	C(6)#1-Co(1)-C(4)	20.65(14)
C(1)-Co(1)-C(2)#1	89.41(15)	C(6)-Co(1)-C(4)	66.08(6)
C(1)#1-Co(1)-C(2)#1	39.74(15)	C(5)-Co(1)-C(4)	39.3
C(2)-Co(1)-C(2)#1	90.48(12)	C(5)#1-Co(1)-C(4)	56.04(12)
C(1)-Co(1)-C(6)#1	131.77(15)	C(7)#1-Co(1)-C(4)	20.75(16)
C(1)#1-Co(1)-C(6)#1	104.08(16)	C(7)-Co(1)-C(4)	65.75(6)
C(2)-Co(1)-C(6)#1	114.60(4)	C(4)#1-Co(1)-C(4)	70.61(13)
C(2)#1-Co(1)-C(6)#1	137.82(14)	C(2)-Si(1)-Cl(1)	115.13(11)
C(1)-Co(1)-C(6)	104.08(16)	C(2)-Si(1)-Cl(3)	112.61(11)
C(1)#1-Co(1)-C(6)	131.77(15)	Cl(1)-Si(1)-Cl(3)	107.18(8)
C(2)-Co(1)-C(6)	137.82(14)	C(2)-Si(1)-Cl(2)	108.99(8)
C(2)#1-Co(1)-C(6)	114.59(4)	Cl(1)-Si(1)-Cl(2)	105.56(8)
C(6)#1-Co(1)-C(6)	69.48(14)	Cl(3)-Si(1)-Cl(2)	106.85(7)
C(1)-Co(1)-C(5)	88.65(16)	C(2)-C(1)-Co(1)	70.3(2)
C(1)#1-Co(1)-C(5)	157.98(16)	C(1)-C(2)-Si(1)	125.1(2)
C(2)-Co(1)-C(5)	105.46(10)	C(1)-C(2)-Co(1)	70.0(2)
C(2)#1-Co(1)-C(5)	152.03(3)	Si(1)-C(2)-Co(1)	119.90(11)
C(6)#1-Co(1)-C(5)	55.15(15)	C(7)-C(3)-C(4)	108.0
C(6)-Co(1)-C(5)	39.6	C(7)-C(3)-Co(1)	69.67(7)
C(1)-Co(1)-C(5)#1	157.98(16)	C(4)-C(3)-Co(1)	70.24(6)
C(1)#1-Co(1)-C(5)#1	88.65(16)	C(3)-C(4)-C(5)	108.0
C(2)-Co(1)-C(5)#1	152.03(3)	C(3)-C(4)-Co(1)	70.75(7)
C(2)#1-Co(1)-C(5)#1	105.46(10)	C(5)-C(4)-Co(1)	69.44(8)
C(6)#1-Co(1)-C(5)#1	39.6	C(6)-C(5)-C(4)	108.0
C(6)-Co(1)-C(5)#1	55.15(15)	C(6)-C(5)-Co(1)	69.87(7)
C(5)-Co(1)-C(5)#1	70.55(13)	C(4)-C(5)-Co(1)	71.26(8)
C(1)-Co(1)-C(7)#1	96.53(15)	C(5)-C(6)-C(7)	108.0
C(1)#1-Co(1)-C(7)#1	143.02(16)	C(5)-C(6)-Co(1)	70.51(6)
C(2)-Co(1)-C(7)#1	100.468(13)	C(7)-C(6)-Co(1)	70.97(7)
C(2)#1-Co(1)-C(7)#1	168.40(13)	C(3)-C(7)-C(6)	108.0
C(6)#1-Co(1)-C(7)#1	39.5	C(3)-C(7)-Co(1)	71.19(7)
C(6)-Co(1)-C(7)#1	54.29(13)	C(6)-C(7)-Co(1)	69.51(8)

C(5)-Co(1)-C(7)#1	19.54(15)		
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Symmetry transformations used to generate equivalent atoms: #1 -x, y, -z+1/2

Table S7. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **7**.

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U₁₁	U₂₂	U₃₃	U₂₃	U₁₃	U₁₂
Co(1)	38(1)	24(1)	35(1)	0	5(1)	0
Si(1)	43(1)	46(1)	48(1)	5(1)	16(1)	0(1)
Cl(2)	86(1)	68(1)	87(1)	-6(1)	48(1)	17(1)
Cl(3)	52(1)	85(1)	114(1)	-5(1)	25(1)	-23(1)
Cl(1)	97(1)	99(1)	46(1)	14(1)	11(1)	16(1)
C(1)	42(2)	69(3)	48(2)	17(2)	7(2)	15(2)
C(2)	41(2)	32(2)	52(2)	2(2)	18(2)	2(1)
C(3)	44(3)	34(3)	76(4)	21(3)	31(3)	6(2)
C(4)	37(3)	23(2)	68(4)	9(3)	18(3)	-8(2)
C(5)	74(4)	38(3)	74(5)	-1(3)	13(3)	-22(3)
C(6)	88(4)	44(3)	78(4)	-9(3)	27(4)	-13(3)
C(7)	76(4)	40(3)	78(5)	7(3)	36(3)	6(3)

Table S8. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **7**.

	x	y	z	U(eq)
H(1A)	850(30)	140(70)	3430(30)	64(13)
H(1B)	1530(30)	1920(60)	3080(30)	60(12)
H(2)	430(20)	-510(50)	1930(20)	35(9)
H(3)	-951	5179	1376	59
H(4)	629	5137	1310	50
H(5)	1346	5088	2873	74
H(6)	209	5099	3905	82
H(7)	-1210	5156	2980	75

Figure 3. Numbering scheme of **8**.

Table S9. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **8**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	6845(2)	272(3)	2422(2)	29(1)
C(2)	6698(2)	847(2)	3501(2)	28(1)
C(3)	7123(2)	-230(3)	4618(2)	35(1)
C(4)	5588(2)	-2401(3)	4332(2)	36(1)
C(5)	4730(2)	-1887(2)	3142(2)	30(1)
C(6)	4946(2)	-2318(2)	2066(2)	32(1)
C(7)	4762(2)	2800(3)	1441(2)	51(1)
C(8)	4103(2)	1504(2)	676(2)	46(1)
C(9)	3277(2)	777(3)	1214(2)	53(1)
C(10)	3403(2)	1642(3)	2285(2)	59(1)
C(11)	4321(2)	2901(3)	2419(2)	58(1)
O(1)	6848(1)	-2078(2)	4477(1)	34(1)
Co(1)	5041(1)	352(1)	2305(1)	21(1)

Table S10. Bond lengths [$\text{\AA}$] and angles [deg] for **8**.

C(1)-C(2)	1.396(3)	Co(1)-C(6)-H(6B)	110.6(12)
C(1)-Co(1)	2.018(2)	H(6A)-C(6)-H(6B)	112.4(2)
C(1)-H(1A)	0.92(2)	C(11)-C(7)-C(8)	108.69(2)
C(1)-H(1B)	0.93(2)	C(11)-C(7)-Co(1)	71.39(11)
C(2)-C(3)	1.497(2)	C(8)-C(7)-Co(1)	71.20(10)
C(2)-Co(1)	2.0316(16)	C(11)-C(7)-H(7)	125.7
C(2)-H(2)	0.93(2)	C(8)-C(7)-H(7)	125.7

C(3)-O(1)	1.417(2)	Co(1)-C(7)-H(7)	123.4
C(3)-H(3A)	0.9900	C(7)-C(8)-C(9)	106.69(16)
C(3)-H(3B)	0.9900	C(7)-C(8)-Co(1)	69.94(10)
C(4)-O(1)	1.414(2)	C(9)-C(8)-Co(1)	69.62(10)
C(4)-C(5)	1.505(3)	C(7)-C(8)-H(8)	126.7
C(4)-H(4A)	0.9900	C(9)-C(8)-H(8)	126.7
C(4)-H(4B)	0.9900	Co(1)-C(8)-H(8)	125.4
C(5)-C(6)	1.397(3)	C(10)-C(9)-C(8)	109.1(2)
C(5)-Co(1)	2.026(2)	C(10)-C(9)-Co(1)	71.46(11)
C(5)-H(5)	0.92(2)	C(8)-C(9)-Co(1)	71.41(11)
C(6)-Co(1)	2.016(2)	C(10)-C(9)-H(9)	125.4
C(6)-H(6A)	0.97(2)	C(8)-C(9)-H(9)	125.4
C(6)-H(6B)	0.98(2)	Co(1)-C(9)-H(9)	123.3
C(7)-C(11)	1.384(2)	C(11)-C(10)-C(9)	107.2(2)
C(7)-C(8)	1.3856(16)	C(11)-C(10)-Co(1)	70.85(12)
C(7)-Co(1)	2.074(2)	C(9)-C(10)-Co(1)	69.58(11)
C(7)-H(7)	0.9500	C(11)-C(10)-H(10)	126.4
C(8)-C(9)	1.387(2)	C(9)-C(10)-H(10)	126.4
C(8)-Co(1)	2.090(2)	Co(1)-C(10)-H(10)	124.8
C(8)-H(8)	0.9500	C(10)-C(11)-C(7)	108.2(2)
C(9)-C(10)	1.387(2)	C(10)-C(11)-Co(1)	70.64(11)
C(9)-Co(1)	2.067(2)	C(7)-C(11)-Co(1)	69.82(11)
C(9)-H(9)	0.9500	C(10)-C(11)-H(11)	125.9
C(10)-C(11)	1.380(2)	C(7)-C(11)-H(11)	125.9
C(10)-Co(1)	2.091(2)	Co(1)-C(11)-H(11)	125.2
C(10)-H(10)	0.9500	C(4)-O(1)-C(3)	111.26(14)
C(11)-Co(1)	2.094(2)	C(6)-Co(1)-C(1)	89.52(9)
C(11)-H(11)	0.9500	C(6)-Co(1)-C(5)	40.43(7)
C(2)-C(1)-Co(1)	70.36(10)	C(1)-Co(1)-C(5)	105.06(8)
C(2)-C(1)-H(1A)	120.3(13)	C(6)-Co(1)-C(2)	106.16(8)
Co(1)-C(1)-H(1A)	108.1(12)	C(1)-Co(1)-C(2)	40.34(7)
C(2)-C(1)-H(1B)	118.6(12)	C(5)-Co(1)-C(2)	94.10(7)
Co(1)-C(1)-H(1B)	112.9(12)	C(6)-Co(1)-C(9)	93.62(8)
H(1A)-C(1)-H(1B)	117(2)	C(1)-Co(1)-C(9)	146.17(8)
C(1)-C(2)-C(3)	122.7(2)	C(5)-Co(1)-C(9)	98.90(8)
C(1)-C(2)-Co(1)	69.30(9)	C(2)-Co(1)-C(9)	159.92(8)
C(3)-C(2)-Co(1)	120.54(12)	C(6)-Co(1)-C(7)	144.30(8)
C(1)-C(2)-H(2)	117.1(12)	C(1)-Co(1)-C(7)	93.85(9)
C(3)-C(2)-H(2)	113.5(12)	C(5)-Co(1)-C(7)	160.96(8)
Co(1)-C(2)-H(2)	105.1(12)	C(2)-Co(1)-C(7)	99.07(8)
O(1)-C(3)-C(2)	114.70(14)	C(9)-Co(1)-C(7)	64.98(8)
O(1)-C(3)-H(3A)	108.6	C(6)-Co(1)-C(8)	106.75(7)
C(2)-C(3)-H(3A)	108.6	C(1)-Co(1)-C(8)	108.20(8)
O(1)-C(3)-H(3B)	108.6	C(5)-Co(1)-C(8)	132.27(7)
C(2)-C(3)-H(3B)	108.6	C(2)-Co(1)-C(8)	133.12(7)

H(3A)-C(3)-H(3B)	107.6	C(9)-Co(1)-C(8)	38.98(5)
O(1)-C(4)-C(5)	115.38(15)	C(7)-Co(1)-C(8)	38.87(5)
O(1)-C(4)-H(4A)	108.4	C(6)-Co(1)-C(10)	116.41(9)
C(5)-C(4)-H(4A)	108.4	C(1)-Co(1)-C(10)	154.05(9)
O(1)-C(4)-H(4B)	108.4	C(5)-Co(1)-C(10)	96.12(8)
C(5)-C(4)-H(4B)	108.4	C(2)-Co(1)-C(10)	124.56(8)
H(4A)-C(4)-H(4B)	107.5	C(9)-Co(1)-C(10)	38.96(5)
C(6)-C(5)-C(4)	123.2(2)	C(7)-Co(1)-C(10)	65.05(9)
C(6)-C(5)-Co(1)	69.38(10)	C(8)-Co(1)-C(10)	65.43(8)
C(4)-C(5)-Co(1)	120.41(13)	C(6)-Co(1)-C(11)	154.85(9)
C(6)-C(5)-H(5)	121.2(13)	C(1)-Co(1)-C(11)	115.54(9)
C(4)-C(5)-H(5)	109.1(13)	C(5)-Co(1)-C(11)	126.54(8)
Co(1)-C(5)-H(5)	107.0(12)	C(2)-Co(1)-C(11)	95.21(8)
C(5)-C(6)-Co(1)	70.18(10)	C(9)-Co(1)-C(11)	64.73(8)
C(5)-C(6)-H(6A)	120.6(11)	C(7)-Co(1)-C(11)	38.78(5)
Co(1)-C(6)-H(6A)	115.7(12)	C(8)-Co(1)-C(11)	65.07(8)
C(5)-C(6)-H(6B)	119.9(12)	C(10)-Co(1)-C(11)	38.51(5)

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
C(1)	22(1)	31(1)	35(1)	3(1)	8(1)	-2(1)
C(2)	23(1)	26(1)	31(1)	-1(1)	0(1)	-4(1)
C(3)	33(1)	35(1)	28(1)	-4(1)	-2(1)	-1(1)
C(4)	43(1)	32(1)	33(1)	8(1)	10(1)	-3(1)
C(5)	26(1)	27(1)	36(1)	3(1)	8(1)	-5(1)
C(6)	35(1)	22(1)	33(1)	-5(1)	3(1)	-5(1)
C(7)	42(1)	31(1)	73(2)	25(1)	6(1)	9(1)
C(8)	58(1)	53(1)	23(1)	8(1)	6(1)	32(1)
C(9)	28(1)	41(1)	72(2)	8(1)	-15(1)	6(1)
C(10)	50(1)	80(2)	55(1)	31(1)	29(1)	45(1)
C(11)	81(2)	39(1)	39(1)	-8(1)	-9(1)	37(1)
O(1)	36(1)	29(1)	31(1)	4(1)	3(1)	7(1)
Co(1)	21(1)	20(1)	20(1)	-1(1)	3(1)	1(1)

Table S12. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **8**.

	x	y	z	U(eq)
H(3A)	8024	-88	4947	41
H(3B)	6741	264	5207	41
H(4A)	5345	-1736	4955	44
H(4B)	5478	-3690	4462	44
H(7)	5408	3503	1316	61
H(8)	4198	1177	-72	55
H(9)	2715	-163	900	64
H(10)	2944	1412	2826	71
H(11)	4603	3698	3069	70
H(1A)	699(2)	109(3)	189(2)	31(5)
H(1B)	713(2)	-88(3)	237(2)	33(5)
H(2)	671(2)	207(3)	363(2)	32(5)
H(5)	3950(2)	-180(3)	320(2)	34(5)
H(6A)	571(2)	-290(3)	205(2)	32(5)
H(6B)	426(2)	-263(3)	138(2)	38(5)

Figure 4. Numbering scheme of **9**.

Table S13. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	3810(20)	7358(5)	11324(12)	48(1)
C(2)	1540(20)	7766(4)	11408(11)	49(1)
C(5)	1480(20)	8755(3)	7863(10)	52(1)
C(6)	3530(20)	8282(4)	7294(12)	51(1)
C(7)	-1590(20)	6369(4)	8035(14)	57(1)
C(8)	-920(20)	6647(4)	6215(12)	50(1)
C(9)	1340(20)	6169(4)	6180(11)	41(1)
C(10)	2070(20)	5585(5)	7942(14)	44(1)
C(11)	260(20)	5729(5)	9092(15)	52(2)
Co(1)	1634(18)	7202(1)	8635(9)	28(1)
C(3A)	760(20)	8919(4)	11333(13)	53(2)
C(4A)	1915(16)	9442(6)	9733(10)	55(2)
C(3B)	2030(70)	8950(8)	11550(40)	67(11)
C(4B)	770(60)	9400(30)	9550(20)	72(12)

Table S14. Bond lengths [$\text{\AA}$] and angles [deg] for **9**.

C(1)-C(2)	1.388(8)	C(9)-C(10)-Co(1)	69.7(3)
C(1)-Co(1)	2.001(5)	C(11)-C(10)-Co(1)	68.1(4)
C(2)-C(3A)	1.513(5)	C(10)-C(11)-C(7)	109.9(6)
C(2)-C(3B)	1.513(5)	C(10)-C(11)-Co(1)	72.6(4)
C(2)-Co(1)	2.013(4)	C(7)-C(11)-Co(1)	70.8(3)
C(5)-C(6)	1.409(8)	C(1)-Co(1)-C(2)	40.4(2)
C(5)-C(4A)	1.512(5)	C(1)-Co(1)-C(5)	97.4(2)
C(5)-C(4B)	1.513(5)	C(2)-Co(1)-C(5)	83.8(2)
C(5)-Co(1)	2.019(4)	C(1)-Co(1)-C(6)	93.2(2)

C(6)-Co(1)	2.039(5)	C(2)-Co(1)-C(6)	106.6(2)
C(7)-C(8)	1.398(9)	C(5)-Co(1)-C(6)	40.6(2)
C(7)-C(11)	1.403(10)	C(1)-Co(1)-C(11)	97.8(3)
C(7)-Co(1)	2.069(5)	C(2)-Co(1)-C(11)	95.9(2)
C(8)-C(9)	1.409(7)	C(5)-Co(1)-C(11)	155.9(3)
C(8)-Co(1)	2.084(5)	C(6)-Co(1)-C(11)	155.5(2)
C(9)-C(10)	1.393(8)	C(1)-Co(1)-C(7)	126.3(3)
C(9)-Co(1)	2.088(4)	C(2)-Co(1)-C(7)	100.7(2)
C(10)-C(11)	1.402(8)	C(5)-Co(1)-C(7)	116.5(3)
C(10)-Co(1)	2.111(7)	C(6)-Co(1)-C(7)	139.6(3)
C(11)-Co(1)	2.051(5)	C(11)-Co(1)-C(7)	39.8(3)
C(3A)-C(4A)	1.513(5)	C(1)-Co(1)-C(8)	163.7(2)
C(3B)-C(4B)	1.513(5)	C(2)-Co(1)-C(8)	135.6(2)
C(2)-C(1)-Co(1)	70.2(3)	C(5)-Co(1)-C(8)	97.6(2)
C(1)-C(2)-C(3A)	128.2(6)	C(6)-Co(1)-C(8)	102.4(2)
C(1)-C(2)-C(3B)	102(2)	C(11)-Co(1)-C(8)	66.0(3)
C(3A)-C(2)-C(3B)	26.9(15)	C(7)-Co(1)-C(8)	39.3(3)
C(1)-C(2)-Co(1)	69.3(3)	C(1)-Co(1)-C(9)	136.5(2)
C(3A)-C(2)-Co(1)	111.4(4)	C(2)-Co(1)-C(9)	161.1(2)
C(3B)-C(2)-Co(1)	111.8(13)	C(5)-Co(1)-C(9)	113.8(2)
C(6)-C(5)-C(4A)	117.2(6)	C(6)-Co(1)-C(9)	91.8(2)
C(6)-C(5)-C(4B)	141(2)	C(11)-Co(1)-C(9)	65.3(2)
C(4A)-C(5)-C(4B)	24(2)	C(7)-Co(1)-C(9)	66.0(2)
C(6)-C(5)-Co(1)	70.4(3)	C(8)-Co(1)-C(9)	39.5(2)
C(4A)-C(5)-Co(1)	110.2(4)	C(1)-Co(1)-C(10)	102.7(3)
C(4B)-C(5)-Co(1)	109.1(15)	C(2)-Co(1)-C(10)	124.8(2)
C(5)-C(6)-Co(1)	68.9(3)	C(5)-Co(1)-C(10)	151.1(2)
C(8)-C(7)-C(11)	107.0(5)	C(6)-Co(1)-C(10)	116.8(2)
C(8)-C(7)-Co(1)	70.9(3)	C(11)-Co(1)-C(10)	39.3(2)
C(11)-C(7)-Co(1)	69.4(3)	C(7)-Co(1)-C(10)	66.6(2)
C(7)-C(8)-C(9)	107.6(5)	C(8)-Co(1)-C(10)	66.1(2)
C(7)-C(8)-Co(1)	69.8(3)	C(9)-Co(1)-C(10)	38.8(2)
C(9)-C(8)-Co(1)	70.4(3)	C(2)-C(3A)-C(4A)	106.2(5)
C(10)-C(9)-C(8)	109.4(5)	C(5)-C(4A)-C(3A)	109.0(5)
C(10)-C(9)-Co(1)	71.5(3)	C(4B)-C(3B)-C(2)	105(2)
C(8)-C(9)-Co(1)	70.1(3)	C(3B)-C(4B)-C(5)	109(2)
C(9)-C(10)-C(11)	106.1(6)		

Table S15. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9**. The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	42(3)	66(3)	31(2)	-1(2)	-8(2)	-3(2)
C(2)	64(3)	56(3)	29(2)	-6(2)	11(2)	-2(3)
C(5)	75(4)	17(2)	57(3)	12(2)	-4(3)	-2(2)
C(6)	60(3)	46(3)	51(3)	7(2)	18(2)	-15(2)
C(7)	32(2)	50(3)	94(4)	-26(3)	22(2)	-17(2)
C(8)	44(3)	41(3)	57(3)	-16(2)	-15(2)	-2(2)
C(9)	49(3)	34(2)	41(2)	-10(2)	9(2)	1(2)
C(10)	48(3)	26(2)	58(3)	-1(2)	10(3)	-6(2)
C(11)	75(5)	28(3)	63(4)	2(2)	36(4)	-15(3)
Co(1)	27(1)	27(1)	31(1)	1(1)	6(1)	-2(1)

Table S16. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9**.

	x	y	z	U(eq)
H(1A)	4281	6694	12087	58
H(1B)	5151	7878	11411	58
H(2A)	592	7305	12183	59
H(2B)	497	7421	12268	59
H(5A)	139	8974	6749	62
H(5B)	205	8846	6628	62
H(6A)	5128	8498	8061	62
H(6B)	3481	8193	5832	62
H(7)	-3038	6574	8474	69
H(8)	-1821	7079	5187	61
H(9)	2226	6235	5121	49
H(10)	3502	5173	8292	53
H(11)	292	5437	10394	63
H(3A1)	1310	9264	12656	64
H(3A2)	-1028	8973	10979	64
H(4A1)	1203	10156	9412	66
H(4A2)	3676	9527	10232	66
H(3B1)	1362	9266	12674	80
H(3B2)	3789	9094	11772	80
H(4B1)	1240	10151	9435	86
H(4B2)	-1008	9368	9459	86

3. Synthesis and Characterization of New Complexes

3.1. Substitution Reactions

General procedure

To a stirred solution of (η^5 -cyclopentadienyl)-bis-(η^2 -trimethylvinylsilane)cobalt(I) (**6**, 0.2 M, 1.0 mmol) in Et₂O an excess of the appropriate alkene (5 mmol) was added dropwise at – 30 °C over a period of 2 minutes. The resulting solution was stirred for further 5 minutes and finally the solvent was removed under reduced pressure at –20 °C. Drying *in vacuo* yielded the products in quantitative yield.

η^5 -Cyclopentadienyl-bis-(η^2 -trichlorovinyl silane)cobalt(I) (**7**)

Yield: 0.443 g (quant.) of **7**. ¹H NMR (25 °C, C₆D₆, 300 MHz): δ = –1.50 (dd, ³*J*(H,H) = 14.7, ³*J*(H,H) = 10.7 Hz, 2H, CHSi), 2.17 (d, ³*J*(H,H) = 10.6 Hz, 2H, CH₂ *cis*), 2.61 (d, ³*J*_{H,H} = 14.1 Hz, 2H, CH₂ *trans*), 4.53 (s, 5H, C₅H₅) ppm. ¹³C NMR (25 °C, C₆D₆, 75 MHz): δ = 41.40 (s, CH₂), 46.15 (CHSi), 87.00 (s, C₅H₅) ppm. ²⁹Si NMR (–50 °C, CD₂Cl₂, 79 MHz) δ = 5.31 (SiCl₃) ppm.

Crystals suitable for X-ray crystallographic analysis were obtained by cooling a concentrated solution of **7** in diethyl ether to –40 °C.

η^5 -Cyclopentadienyl-[η^4 -(prop-2-enyl)ether]cobalt(I) (**8**)

Yield: 0.222 g (quant.) of **8**. ¹H NMR (20 °C, CD₂Cl₂, 300 MHz): δ = 0.64 (d, ³*J*(H,H) = 12.0 Hz, 2H, CH₂ *trans*), 2.85 (d, ³*J*(H,H) = 7.0 Hz, 2H, CH₂ *cis*), 3.00–3.19 (m, 2H, CH), 3.21–3.36 (m, 2H, CH₂), 3.43–3.61 (m, 2H, CH₂), 4.71 (s, 5H, C₅H₅) ppm. ¹³C NMR (20 °C,

CD₂Cl₂, 75 MHz): δ = 32.85 (s, C=CH₂), 42.39 (s, CH), 69.46 (s, CH₂), 86.12 (s, C₅H₅) ppm. MS (CI, positive, isobutane): 99 [C₆H₁₀O + H⁺], 124 [CpCo + H⁺], 223 [MH⁺].

A concentrated diethyl ether solution of **9** was cooled to -40 °C to receive crystals suitable for X-ray crystallographic analysis.

η^5 -Cyclopentadienyl-(η^4 -hexa-1,5-diene)cobalt(I) (9**)**

Yield: 0.206 g (quant.) of **9**. ¹H NMR (-21 °C, CD₂Cl₂, 300 MHz): δ = 0.85 (d, ³J(H,H) = 12.0 Hz, 2H, CH₂ *trans*), 0.92–1.10 (m, 2H, CH₂), 2.17 (d, ³J(H,H) = 8.3 Hz, 2H, CH₂ *cis*), 3.75–3.91 (m, 2H, CH), 4.51 (s, 5H, C₅H₅) ppm. ¹³C NMR (-21 °C, CD₂Cl₂, 75 MHz): δ = 33.53 (s, CH₂), 39.36 (s, C=CH₂), 63.91 (s, CH), 84.47 (s, C₅H₅) ppm. MS (CI, positive, isobutane): 83 [C₆H₁₀ + H⁺], 207 [MH⁺].

Crystals suitable for X-ray crystallographic analysis were obtained by cooling a concentrated diethyl ether solution of **9** to -40 °C.

η^5 -Cyclopentadienyl-(η^4 -penta-1,4-diene)cobalt(I) (10**)**

Yield: 0.192 g (quant.) of **10**. ¹H NMR (-50 °C, CD₂Cl₂, 400 MHz): δ = 0.16 (d, ³J(H,H) = 10.9 Hz, 2H, CH₂ *trans*), 1.04 (dt, ³J(H,H) = 4.3 Hz, ²J(H,H) = 11.9 Hz, 1H, CH₂), 1.58 (d, ³J(H,H) = 7.0 Hz, 2H, CH₂ *cis*), 2.80–2.90 (m, 1H, CH₂), 2.90–3.02 (m, 2H, CH), 4.69 (s, 5H, C₅H₅) ppm. ¹³C NMR (-50 °C, CD₂Cl₂, 100 MHz): δ = 17.21 (s, (C=CH₂), 28.79 (s, CH), 36.54 (CH₂), 81.68 (s, C₅H₅) ppm. MS (CI, positive, isobutane): 127 [Co(C₅H₈)⁺], 193 [MH⁺].

η^5 -Cyclopentadienyl-(η^4 -1,1,3,3-tetramethyl-1,3-divinyl-disiloxane)cobalt(I) (11**)**

Yield: 0.310 g (quant.) of **11**. ¹H NMR (-50 °C, CD₂Cl₂, 400 MHz): δ = -0.15 (s, 6H, SiCH₃), 0.36 (s, 6H, SiCH₃), 1.08 (d, ³J(H,H) = 15.2 Hz, 2H, CH), 1.34 (dd, ³J(H,H) = 11.9 Hz,

$^2J(\text{H,H}) = 15.7$, 2H, CH_2 *trans*), 3.51 (d, $^3J(\text{H,H}) = 11.9$ Hz, 2H, CH_2 *cis*), 4.63 (s, 5H, C_5H_5) ppm. ^{13}C NMR (-50°C , CD_2Cl_2 , 100 MHz): $\delta = -0.11$ (s, (SiCH_3)), 2.35 (s, (SiCH_3)), 29.38 (s, CHSi), 44.82 ($\text{C}=\text{CH}_2$), 85.16 (s, C_5H_5) ppm. ^{29}Si NMR (-50°C , CD_2Cl_2 , 79 MHz) $\delta = 6.16$ ppm. MS (CI, positive, isobutane): 124 [$\text{CpCo} + \text{H}^+$], 188 [$\text{C}_8\text{H}_{18}\text{OSi}_2 + \text{H}^+$], 311 [MH^+].

η^5 -Cyclopentadienyl-bis-(η^2 -dimethyl fumarate)cobalt(I) (**12**)

Yield: about 15% of **12**.

^1H NMR (25°C , C_6D_6 , 300 MHz): $\delta = 2.07$ (d, $^3J(\text{H,H}) = 11.9$ Hz, 2H, CH), 3.26 (s, 6H, CH_3), 3.62 (s, 6H, CH_3), 4.73 (s, 5H, C_5H_5) ppm. MS (ESI): 435 [$\text{M} + \text{Na}^+$], 291 [$\text{M}-\text{C}_6\text{H}_8\text{O}_4 + \text{Na}^+$].

3.3 Summary and NMR spectra of complexes 6-12

The ^1H and ^{13}C resonances and their relative shift (shift = $\delta_{\text{free alkene}} - \delta_{\text{complex}}$) corresponding to the free alkene are depicted in Table 17.

Table S17. Comparison of NMR data

	complex 6		complex 7		complex 8	
¹ H						
	δ [ppm]	Δδ [ppm]	δ [ppm]	Δδ [ppm]	δ [ppm]	Δδ [ppm]
A	-1.63	7.71	-1.50	7.75	3.08	2.96
B	2.26	3.56	2.17	3.96	2.85	2.34
C	2.49	3.09	2.61	3.77	0.64	4.68
¹³ C						
	δ [ppm]	Δδ [ppm]	δ [ppm]	Δδ [ppm]	δ [ppm]	Δδ [ppm]
1	40.13	92.43	41.40	98.16	32.85	83.52
2	49.25	92.59	46.15	85.43	42.39	93.09

	complex 9		complex 10		complex 11	
¹ H						
	δ [ppm]	Δδ [ppm]	δ [ppm]	Δδ [ppm]	δ [ppm]	Δδ [ppm]
A	3.83	2.07	2.96	2.75	1.08	5.09
B	2.17	2.93	1.58	3.33	3.51	2.45
C	0.85	4.31	0.16	4.75	1.34	4.43
¹³ C						
	δ [ppm]	Δδ [ppm]	δ [ppm]	Δδ [ppm]	δ [ppm]	Δδ [ppm]
1	39.37	75.47	17.21	98.28	44.82	94.36
2	63.92	75.46	28.79	107.92	29.38	101.85

	complex 12	
¹ H		
	δ [ppm]	Δδ [ppm]
A	2.07	4.68
B	-	-
C	4.73	2,02

^1H and ^{13}C NMR spectra of 6:

^1H and ^{13}C NMR spectra of 7:

^1H and ^{13}C NMR spectra of 8:

^1H and ^{13}C NMR spectra of 9:

^1H and ^{13}C NMR spectra of 10:

^1H and ^{13}C NMR spectra of 11 with residues of the free alkene:

¹H NMR spectra of 12:

4. [2+2+2] Cycloaddition Reactions and Reactions of 6 and 9 with Chlorinated Solvents

4.1 [2+2+2] Cycloaddition Reactions

3-Methyl-6,7-dihydro-5H-cyclopenta[c]pyridine (**16**)³

Colorless solid, yield: 77 mg (57%) of **16**. ¹H NMR (CDCl₃, 400 MHz): δ = 2.01 (qt, ³J(H,H) = 7.4 Hz, 2H, CH₂(CH₂)₂), 2.45 (s, 3H, CH₃), 2.79 (t, ³J(H,H) = 7.1 Hz, 2H, CH₂), 2.81 (t, ³J(H,H) = 7.2 Hz, 2H, CH₂), 6.97 (s, 1H, CH), 7.21 (s, 1H, CH=N) ppm. ¹³C NMR (CDCl₃, 100 MHz): 23.9, 25.1, 29.9, 32.6, 119.6, 137.3, 144.2, 154.8, 155.3 ppm. HRMS (ESI): Calcd for [C₉H₁₂N]⁺: 134.0964. Found: 134.0965.

3-Isopropyl-6,7-dihydro-5H-cyclopenta[c]pyridine (**17**)

Yellow oil, yield: 140 mg (86%) of **17**. ^1H NMR (CDCl_3 , 400 MHz): δ = 1.22 (d, $^3J(\text{H,H})$ = 7.0 Hz 6H, $\text{CH}(\text{CH}_3)_2$, 2.02 (qt, $^3J(\text{H,H})$ = 7.4 Hz, 2H, $\text{CH}_2(\text{CH}_2)_2$, 2.82 (t, $^3J(\text{H,H})$ = 7.5 Hz, 4H, CH_2), 2.99 (hp, $^3J(\text{H,H})$ = 6.9 Hz, 1H, CH), 7.01 (s, 1H, CH_{Ar}), 8.30 (s, 1H, $\text{CH}=\text{N}$) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 22.8, 25.1, 29.9, 32.7, 35.9, 116.8, 137.6, 144.2, 154.9, 164.6 ppm. HRMS (ESI): Calcd for $[\text{C}_{11}\text{H}_{16}\text{N}]^+$: 162.1277. Found: 162.1278.

3-*tert*-Butyl-6,7-dihydro-5H-cyclopenta[c]pyridine (**18**)

Yellow oil, yield: 125 mg (71%) of **18**. ^1H NMR (CDCl_3 , 400 MHz): δ = 1.31 (s, 9H, $\text{C}(\text{CH}_3)_3$, 2.04 (qt, $^3J(\text{H,H})$ = 7.4 Hz, 2H, $\text{CH}_2(\text{CH}_2)_2$, 2.84 (t, $^3J(\text{H,H})$ = 7.5 Hz, 4H, CH_2), 7.21 (s, 1H, CH_{Ar}), 8.38 (s, 1H, $\text{CH}=\text{N}$) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 25.1, 29.9, 30.4, 33.0, 37.1, 115.7, 137.5, 143.3, 155.6, 166.2 ppm. HRMS (ESI): Calcd for $[\text{C}_{12}\text{H}_{18}\text{N}]^+$: 176.1434. Found: 176.1435.

3-Phenyl-6,7-dihydro-5H-cyclopenta[c]pyridine (**19**)⁴

Colorless solid, yield: 179 mg (92%) with **6** and 192 mg (98%) with **9** of **19**. ^1H NMR (CDCl_3 , 400 MHz): δ = 2.11 (qt, $^3J(\text{H,H})$ = 7.5 Hz, 2H, $\text{CH}_2(\text{CH}_2)_2$, 2.90-2.97 (m, 4H, CH_2), 7.32-7.43 (m, 3H, CH_{Ar}), 7.58 (s, 1H, CH_{Ar}), 7.89-7.93 (m, 2H, CH_{Ar}), 8.51 (s, 1H, $\text{CH}=\text{N}$) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 25.1, 30.1, 33.0, 117.5, 127.2, 128.9, 129.1, 139.7, 143.9, 154.6, 156.7 ppm. HRMS (ESI): Calcd for $[\text{C}_{14}\text{H}_{14}\text{N}]^+$: 196.1121. Found: 196.1121.

1,4-Di-*tert*-butyl-3-phenyl-6,7-dihydro-5H-cyclopenta[c]pyridine (**20**)

Colorless solid, yield: 162 mg (53%) with **6** and 94 mg (31%) with **9** of **20**. ^1H -NMR (CDCl_3 , 400 MHz): 1.09 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.34 (s, 9H, $\text{N}=\text{C}(\text{CH}_3)_3$), 1.54 (qt, $^3J(\text{H,H})$ = 7.1 Hz, 2H, $\text{CH}_2(\text{CH}_2)_2$, 2.69 (t, 2H, $^3J(\text{H,H})$ = 7.0 Hz, CH_2), 2.75 (t, 2H, $^3J(\text{H,H})$ = 7.0 Hz, CH_2), 6.98-7.10 (m, 3H, CH_{Ar}), 7.34-7.39 (s, 2H, CH_{Ar}) ppm. ^{13}C -NMR (CDCl_3 , 100 MHz): 26.6, 29.6,

31.4, 32.4, 35.8, 36.2, 38.0, 126.8, 127.5, 127.8, 129.7, 135.0, 137.2, 147.4, 154.0, 155.1, 158.9 ppm. HRMS (ESI): Calcd for $[C_{22}H_{30}N]^+$: 308.2373. Found: 308.2372.

3-Phenyl-5,6,7,8-tetrahydro-isoquinoline (**21**)⁴

Yellow oil, yield 96 mg (46%) with **6** and 132 mg (63%) with **9** of **21**. ¹H-NMR (CDCl₃, 400 MHz): δ = 1.73-1.78 (m, 4H, CH₂), 2.66-2.76 (m, 4H, CH₂), 7.25-7.41 (m, 4H, CH_{Ar}), 7.83-7.89 (m, 2H, CH_{Ar}), 8.30 (s, 1H, CH=N) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ = 22.4, 22.7, 26.1, 29.1, 121.0, 126.8, 128.6, 128.7, 132.0, 139.1, 147.6, 149.6, 154.0 ppm. HRMS (ESI): Calcd for (C₁₅H₁₅N)⁺: 209.1199. Found: 209.1196.

4.2 Reactions of **6** and **9** with Chlorinated Solvents

General procedure of the conversion of complex **6** and **9** with chlorinated solvents

The appropriate complex **6** or **9** (0.32 mmol) is dissolved in Et₂O (2 mL) and 4 mL of the chlorinated solvent (CCl₄, CHCl₃, CH₂Cl₂) were added dropwise while stirring at -78 °C. The resulting red solution was allowed to warm to room temperature and slowly turned to green. After 60 minutes of additional stirring the volatile compounds are removed under reduced pressure and drying in vacuum yields [(Cp₂Co)₂(CoCl₄)].

MS (ESI, positive mode): 189.0109 [Cp₂Co]⁺. (ESI, negative mode): 163.8411 [CoCl₃]⁻.

Crystals suitable for X-ray analysis were obtained by cooling a saturated ethanol solution of [(Cp₂Co)₂(CoCl₄)] at -4 °C. The structural features are in correspondence to the ones reported for similar complexes.⁵

5. Computational details

All computations have been carried out with the G03 program package.^[6] The computations were carried out at the DFT/6-311G* level using the hybrid method B3LYP which includes a mixture of Hartree-Fock exchange with DFT exchange-correlation. Becke's three parameter functional where the non-local correlation is provided by the LYP expression (Lee, Yang, Parr correlation functional) was used. Structural parameters of **3-11** and their respective alkene are taken from the geometry optimisation calculations.

It should be emphasized that the computation was carried out for a single, isolated (gasphase) species. There may well be differences among gas-phase, solution, and solid-state data.

Table S18. Calculated energies (ΔH and ΔG) of the free alkenes.

free alkene	ΔH [hartree]	ΔG [hartree]
cycloocta-1,5-diene	-311.886202	-311.925271
ethylene	-78.552122	-78.578288
trimethylvinyl silane	-487.171163	-487.216160
trichlorovinyl silane	-1748.301332	-1748.344285
prop-2-enyl ether	-309.728060	-309.771164
hexa-1,5-diene	-234.513489	-234.552972
penta-1,4-diene	-195.221305	-195.257294
1,1,3,3-tetramethyl-1,3-divinyl-disiloxane	-970.895327	-969.963961
dimethyl fumarate	-534.333039	-534.383061

Table S19. Calculated energies (ΔH and ΔG) of the complexes.

complex	ΔH [hartree]	ΔG [hartree]
CpCo(cycloocta-1,5-diene) (3)	-1888.171133	-1888.222602
CpCo(ethylene) ₂ (4)	-1733.363083	-1733.410876
CpCo(trimethylvinyl silane) ₂ (6)	-2550.589196	-2550.670093
CpCo(trichlorovinyl silane) ₂ (7)	-5072.863040	-5072.939970
CpCo(prop-2-enyl ether) (8)	-1885.984372	-1886.035532
CpCo(hexa-1,5-diene) (9)	-1810.770916	-1810.819682
CpCo(penta-1,4-diene) (10)	-1771.475210	-1771.521361
CpCo(1,1,3,3-tetramethyl-1,3-divinyl-disiloxane) (11)	-2546.147243	-2546.219322
CpCo(dimethyl fumarate) ₂ (12)	-2644.928190	-2645.017059

Energetic parameters of the substitution reaction are given in the following scheme. ΔH and ΔG (in square brackets) are calculated for the reaction below (Figure S5) and given in kcal/mol. ($\Delta G = \Delta H - T\Delta S$). It has to be emphasized that the deformation energy of the olefins are not included.

Figure S5.

Scheme S1.

6. References

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