Cobalt(I) complexes: synthesis and molecular and x-ray structures of group 14 (.eta.4-metallole)tris(trimethylphosphine)cobalt tetraphenylborate complexes

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displacement of the chloro and cycloocta-1,5-diene ligands such that the entire one face of the complex is receptive to entering ligand systems. These patterns of reactivity are in marked contrast to those of the traditional synthetic precursors in cyclopentadienyl–ruthenium(II) chemistry and will be elaborated upon in greater detail in future publications.[35]

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Cobalt(I) Complexes: Synthesis and Molecular and X-ray Structures of Group 14 (η^4-Metallole)tris(trimethylphosphine)cobalt Tetraphenylborate Complexes

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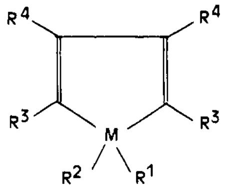
Reaction of $CoBr(PMe_3)_3$ (**4**) with 1,1,3,4-tetramethylmetalloles (Si, **2**; Ge, **3**) in presence of $NaBPh_4$ yielded $[Co(metallole)(PMe_3)_3]BPh_4$ complexes (Si, **5**; Ge, **6**). The crystal structures of **5** and **6** have been determined by X-ray diffraction techniques. They are isomorphous and crystallize in the orthorhombic system $P2_12_12_1$. Crystal data: for **5**, a = 16.064 (2) Å, b = 10.304 (2) Å, c = 25.680 (4) Å; for **6**, a = 16.088 (2) Å, b = 10.272 (2) Å, c = 25.805 (3) Å, Z = 4. R = 0.050 in **5** for 2726 "observed" reflections, while R = 0.056 in **6** for 2911 "observed" reflections. The structures consist of independent BPh_4 anions and Co cations. In both complexes the cobalt is in a distorted square-pyramidal environment with an apical and two basal PMe_3 ligands. The difference between the apical and basal Co–P bond lengths is greater in **5** ($Co–P_a$ = 2.298 (1) Å compared to $Co–P_b$ = 2.229 (2) and 2.230 (2) Å) than in **6** (2.251 (3) Å compared to 2.206 (3) and 2.225 (3) Å). The metalloles are η^4-coordinated by their dimethylbutadiene moiety, which is roughly planar and makes an angle of 77.1° in **5** and of 78.5° in **6** to the basal plane. Bending of the metallole ring after coordination is 41.2° in **5** and 44.5° in **6**. Co is located 0.706 Å above the equatorial plane in **5** and 0.664 Å in **6**. The Co–metallole double-bond distance is shorter in **6** (average 2.059 (10) Å) than in **5** (average 2.102 (7) Å). Multinuclear NMR spectra (183–297 K) indicate that both complexes are stereononrigid.

The reaction of group 14 metalloles (siloles and germoles) with transition-metal complexes have already afforded several coordination compounds. But these reactions have so far been limited to the C-phenylated metalloles (**1**: $R^3 = R^4 = Ph$; $R^3 = Ph$, $R^4 = H$). Coordination occurs through the butadiene part of the ring, and compounds with Fe, Co, Ru, Mo, Ni, Cr, or Rh and 2,3,4,5-tetraphenyl- or 2,5-diphenylmetalloles bearing different groups on Si and Ge have been reported[1,2] (Chart I).

The unstable C-unsubstituted siloles[3-6] or germoles[6,7] ($R^3 = R^4 = H$) were identified as monomers in 1981[4,7] and stabilized as carbonyl iron, nickel, or molybdenum complexes.[8,9] The chemistry of these complexes is still not well-developed despite their interest as (i) cyclic conjugated dienes and (ii) sources of η^5-metallacyclopentadienyl species.[10]

Chart I



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(10) Transients free of η^5-silacyclopentadienyl species are formed in the mass spectrometer during the fragmentation of η^4-complexes of siloles.[1] The C-unsubstituted silacyclopentadienide anion[11] is still not identified although benzo or C-phenylated forms are known.[12]

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To gain more information about their chemistry, we have recently studied the synthesis[13,14] and the electronic structure[15] of the 3,4-dimethylsiloles and -germoles ($R^1 = R^2$ = Me or Ph, R^3 = H, R^4 = Me), which are stable as monomers. We describe here the reactivity of the 1,1,3,4-tetramethylsilole (**2**) and 1,1,3,4-tetramethylgermole (**3**) toward the cobalt(I) complex $CoBr(PMe_3)_3$ (**4**) which reacts specifically with conjugated dienes.[16] The two complexes $[Co(1,1,3,4\text{-}Me_4H_2C_4Si)(PMe_3)_3]BPh_4$ (**5**) and $[Co(1,1,3,4\text{-}Me_4H_2C_4Ge)(PMe_3)_3]BPh_4$ (**6**) have been isolated and their crystal structures determined. This is the first pair of complexes which allow direct comparison of a silole and germole coordinated to the same metal.

Experimental Section

Procedure for Reagents and Solvents. All reactions were performed following the procedures reported in ref 16. $CoBr(PMe_3)_3$ was synthesized following Klein and Karsch.[17] The 1,1,3,4-tetramethylsilole (**2**) and 1,1,3,4-tetramethylgermole (**3**) were prepared as reported in ref 14b, i.e., by the one-pot synthesis from 1,1,3,4-tetramethyl-1-sila(germa)cyclopent-4-en-3-ol and phenyl isocyanate in carbon tetrachloride. The isomeric purity of these metalloles containing their transoid is about 90%.[14]

Synthesis of $[Co(1,1,3,4\text{-}Me_4H_2C_4Si)(PMe_3)_3]BPh_4$ (5). To a solution of $CoBr(PMe_3)_3$ (0.88 g, 2.4 mmol) in acetone (10 mL) was added an excess of **2** (0.89 g, 6.4 mmol) while the solution was stirred. The color of the solution changed from blue-violet to yellow-brown. $NaBPh_4$ (2.4 mmol) dissolved in 10 mL of acetone was added. The yellow powder that precipitated after concentration was filtered, dried, and stored under argon (yield 80%). Recrystallization overnight in acetone at 0 °C gave orange crystals. Anal. Calcd for $C_{41}H_{61}BP_3SiCo$: C, 66.13; H, 8.26; Co, 7.91; P, 12.48; B, 1.45; Si, 3.77. Found: C, 66.18; H, 8.14; Co, 8.05; P, 12.17; B, 1.26; Si, 3.80.

Synthesis of $[Co(1,1,3,4\text{-}Me_4H_2C_4Ge)(PMe_3)_3]BPh_4$ (6). The same procedure was followed. The solution changed color only after addition of $NaBPh_4$. The yield was 50%. Yellow crystals suitable for X-ray determination were obtained by recrystallization from acetone at 0 °C. Anal. Calcd for $C_{41}H_{61}BP_3GeCo$: C, 62.40; H, 7.79; Co, 7.47; P, 11.77; B, 1.37; Ge, 9.20. Found: C, 62.38; H, 7.65; Co, 7.50; P, 12.03; B, 1.50; Ge, 9.11.

NMR Spectra. Variable-temperature ${}^1H$, ${}^1H\{{}^{31}P\}$, ${}^{31}P$, ${}^{31}P\{{}^1H\}$, ${}^{13}C$, and ${}^{13}C\{{}^1H\}$ FT NMR spectra were recorded at 250 MHz for ${}^1H$, 101.27 HMz for ${}^{31}P$, and 62.9 MHz for ${}^{13}C$ NMR by using a Bruker WM-250 spectrometer equipped with a special probe for observing ${}^1H$ and decoupling ${}^{31}P$ NMR spectra. Field frequency stabilization was achieved on an internal ${}^2D$ signal at 38.39 kG. $SiMe_4$ was used as an external reference for ${}^1H$ and ${}^{13}C$ chemical shifts. For ${}^{31}P$ chemical shifts, H_3PO_4 (85%) in D_2O at 298 K was used as reference. The NMR tubes were filled in a nitrogen-filled glovebox, using $(CD_3)_2CO$ or CD_2Cl_2 as solvents.

X-ray Data Collection and Reduction. 1. Complex 5 (X = Si). The selected crystal, which belongs to the orthorhombic system, was sealed in a Lindemann glass capillary and mounted on an Enraf-Nonius CAD 4 diffractometer. Some equatorial extinctions were obvious in preliminary measurements. Matrix transformation and least-squares fit of the setting angles of 25 reflections led to the cell constants given in Table I. A first data set was recorded out to 2θ(Mo) = 52° in the nonconventional space group *Pmcn* ($h0l$, $l = 2n + 1$, and $hk0$, $h + k = 2n + 1$) by procedures described elsewhere.[18] The $h0l$ and $hk0$ equatorial reflections were then measured again with no imposed extinction condition using the slowest possible scan speed. Odd reflection data were weak, but present. There were no extinctions other than axial ones leading to the space group $P2_12_12_1$. Data reduction was then performed.[19] Intensity standards recorded periodically showed only random, statistical fluctuations. No absorption corrections were made. Equatorial reflections measured two times were merged, using the SHELX76 program[20] (R_{av} = 0.022). All nonzero reflections (2726) were used in subsequent calculations.

Table I. Crystal Data and Details of Data Collection and Structure Refinement

	X = Si	X = Ge
	Crystal Data	
formula	$BC_{41}H_{61}P_3SiCo$	$BC_{41}H_{61}P_3GeCo$
fw	744.8	789.3
cryst system	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	16.064 (2)	16.088 (2)
b, Å	10.304 (2)	10.272 (1)
c, Å	25.680 (4)	25.805 (3)
V, Å^3	4250.6	4264.4
Z	4	4
$F(000)$	1592	1664
D(calcd), g cm^{-3}	1.162	1.228
cryst size, mm	0.500 × 0.400 × 0.250	0.625 × 0.250 × 0.075
μ(Mo Kα), cm^{-1}	5.7	12.2
	Data Collection	
temp, °C	20	20
radiatn, Å	λ = 0.71073 (Mo Kα), graphite monochromatized	λ = 0.71073 (Mo Kα), graphite monochromatized
θ min-max, deg	1.5–26	1.5–26
scan mode	ω–2θ	θ–2θ
scan range, deg	0.85 + 0.35 tan θ	0.80 + 0.35 tan θ
receiving aperture, mm	4.0 × 4.0	4.0 × 4.0
takeoff angle, deg	2.8	2.6
intensity stds	6,2,12, 0,3,13, 5,5,0	6,2,12, 0,3,13, 5,5,0
orientatn reflctns	6,2,12, 0,3,13, 5,5,0	6,2,12, 0,3,13, 5,5,0
collected reflctns	5055	7386
unique nonzero reflctns (n)	2726	2911
	Refinement	
no. of refined parameters (m)	256	256
weighting scheme	$w = 1/\lvert\overline{\Delta F}\rvert^2$ (15 groups of reflctns of similar magnitude); $\lvert\Delta F\rvert = \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert$	$w = 1/\lvert\overline{\Delta F}\rvert^2$ (15 groups of reflctns of similar magnitude); $\lvert\Delta F\rvert = \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert$
$R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.050	0.056
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.057	0.065
$S = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n - m)]^{1/2}$	0.72	0.92

2. Complex 6 (X = Ge). The crystal was sealed in a Lindemann glass capillary and mounted on an Enraf-Nonius CAD 4 diffractometer. Least-squares fit of the setting angles of 25 reflections led to the cell constants given in Table I. Compounds **6** and **5** are isomorphous. Data collection was made as for **5**, but some reflections were measured in octants other than hkl in order to compare observed and calculated values for determination of enantiomers. Data reduction was then performed. Intensity standards showed a linear decrease of about 8%. Intensity data were corrected for this decay.[19] No absorption corrections were made. R_{av} for equatorial reflections measured two times was 0.026.

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Table II. Fractional Atomic Coordinates with Estimated Standard Deviations in Parentheses

	X = Si			X = Ge		
atom	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Co	0.24678 (4)	0.51328 (6)	0.58583 (2)	0.24431 (6)	0.51947 (9)	0.58657 (4)
P(1)	0.28427 (9)	0.5616 (2)	0.50167 (4)	0.2840 (2)	0.5656 (3)	0.50497 (11)
C(1)	0.3052 (4)	0.4209 (7)	0.4611 (2)	0.3053 (8)	0.4238 (12)	0.4639 (5)
C(2)	0.3878 (5)	0.6358 (8)	0.5003 (3)	0.3856 (7)	0.6417 (12)	0.5041 (5)
C(3)	0.2444 (4)	0.6838 (7)	0.4621 (2)	0.2424 (8)	0.6901 (12)	0.4634 (4)
P(2)	0.25100 (9)	0.7094 (1)	0.62232 (5)	0.2429 (2)	0.7149 (2)	0.62200 (9)
C(4)	0.2359 (4)	0.7207 (7)	0.6946 (2)	0.2281 (5)	0.7254 (9)	0.6933 (3)
C(5)	0.1643 (4)	0.8195 (7)	0.6056 (3)	0.1546 (7)	0.8253 (12)	0.6047 (4)
C(6)	0.3385 (4)	0.8158 (6)	0.6059 (3)	0.3290 (7)	0.8228 (13)	0.6059 (4)
P(3)	0.36358 (11)	0.4479 (2)	0.62476 (7)	0.3660 (2)	0.4693 (3)	0.62240 (10)
C(7)	0.3439 (5)	0.4170 (8)	0.6952 (3)	0.3561 (7)	0.4637 (12)	0.6925 (4)
C(8)	0.4590 (4)	0.5362 (8)	0.6210 (3)	0.4634 (7)	0.5596 (13)	0.6134 (5)
C(9)	0.3926 (5)	0.2960 (7)	0.5959 (3)	0.3917 (7)	0.3066 (11)	0.5985 (4)
C(10)	0.1028 (5)	0.5143 (8)	0.5809 (3)	0.1047 (6)	0.5354 (9)	0.5821 (4)
C(11)	0.1395 (4)	0.4656 (8)	0.6255 (2)	0.1360 (6)	0.4820 (11)	0.6289 (4)
C(12)	0.1817 (5)	0.3392 (7)	0.6220 (3)	0.1764 (7)	0.3578 (9)	0.6188 (4)
C(13)	0.2020 (4)	0.3158 (7)	0.5697 (2)	0.2006 (6)	0.3213 (10)	0.5683 (4)
X	0.10390 (10)	0.3715 (2)	0.53706 (6)	0.09804 (6)	0.38387 (9)	0.53684 (4)
C(14)	0.0826 (5)	0.5245 (10)	0.6652 (3)	0.0767 (7)	0.5397 (13)	0.6683 (4)
C(15)	0.1916 (5)	0.2414 (10)	0.6660 (3)	0.1875 (7)	0.2612 (11)	0.6621 (4)
C(16)	0.0204 (6)	0.2482 (9)	0.5471 (4)	0.0158 (7)	0.2450 (10)	0.5482 (4)
C(17)	0.1115 (7)	0.3968 (9)	0.4662 (3)	0.1053 (7)	0.4107 (11)	0.4610 (4)
B	0.7504 (4)	0.5176 (6)	0.6680 (2)	0.7502 (6)	0.5178 (9)	0.6675 (3)
C(18)	0.7502 (2)	0.4809 (6)	0.6050 (2)	0.7495 (4)	0.4852 (9)	0.6035 (3)
C(19)	0.8267 (2)	0.4820 (6)	0.5800 (2)	0.8256 (4)	0.4856 (9)	0.5785 (3)
C(20)	0.8306 (2)	0.4711 (6)	0.5263 (2)	0.8291 (4)	0.4747 (9)	0.5251 (3)
C(21)	0.7580 (2)	0.4591 (6)	0.4976 (2)	0.7565 (4)	0.4634 (9)	0.4966 (3)
C(22)	0.6816 (2)	0.4580 (6)	0.5225 (2)	0.6803 (4)	0.4630 (9)	0.5216 (3)
C(23)	0.6777 (2)	0.4690 (6)	0.5762 (2)	0.6768 (4)	0.4739 (9)	0.5751 (3)
C(24)	0.6610 (2)	0.4724 (3)	0.6957 (1)	0.6628 (4)	0.4630 (5)	0.6962 (2)
C(25)	0.6295 (2)	0.5334 (3)	0.7395 (1)	0.6311 (4)	0.5231 (5)	0.7399 (2)
C(26)	0.5674 (2)	0.4743 (3)	0.7684 (1)	0.5687 (4)	0.4633 (5)	0.7683 (2)
C(27)	0.5368 (2)	0.3542 (3)	0.7536 (1)	0.5381 (4)	0.3434 (5)	0.7528 (2)
C(28)	0.5684 (2)	0.2932 (3)	0.7097 (1)	0.5698 (4)	0.2833 (5)	0.7090 (2)
C(29)	0.6305 (2)	0.3523 (3)	0.6808 (1)	0.6322 (4)	0.3431 (5)	0.6807 (2)
C(30)	0.7622 (2)	0.6771 (3)	0.6735 (1)	0.7576 (3)	0.6789 (5)	0.6732 (2)
C(31)	0.6875 (2)	0.7442 (3)	0.6737 (1)	0.6830 (3)	0.7463 (5)	0.6734 (2)
C(32)	0.6874 (2)	0.8786 (3)	0.6748 (1)	0.6830 (3)	0.8811 (5)	0.6750 (2)
C(33)	0.7620 (2)	0.9459 (3)	0.6758 (1)	0.7576 (3)	0.9485 (5)	0.6764 (2)
C(34)	0.8367 (2)	0.8788 (3)	0.6756 (1)	0.8321 (3)	0.8810 (5)	0.6762 (2)
C(35)	0.8368 (2)	0.7444 (3)	0.6745 (1)	0.8321 (3)	0.7462 (5)	0.6746 (2)
C(36)	0.8274 (2)	0.4413 (3)	0.6978 (1)	0.8286 (4)	0.4429 (5)	0.6982 (2)
C(37)	0.8679 (2)	0.4901 (3)	0.7412 (1)	0.8689 (4)	0.4916 (5)	0.7414 (2)
C(38)	0.9309 (2)	0.4191 (3)	0.7646 (1)	0.9315 (4)	0.4200 (5)	0.7648 (2)
C(39)	0.9534 (2)	0.2993 (3)	0.7445 (1)	0.9538 (4)	0.2998 (5)	0.7449 (2)
C(40)	0.9128 (2)	0.2506 (3)	0.7011 (1)	0.9135 (4)	0.2511 (5)	0.7016 (2)
C(41)	0.8499 (2)	0.3216 (3)	0.6778 (1)	0.8509 (4)	0.3227 (5)	0.6782 (2)

All nonzero reflections (2911) of the asymmetric unit were used in subsequent calculations.

Structure Solution and Refinement. 1. Complex 5 (X = Si). The structure was solved by the heavy-atom method. The position of the Co atom was revealed from a Patterson map. The P and Si atoms appeared on the subsequent Fourier map, but refinement diverged. Successive difference Fourier syntheses calculations revealed C and B atoms. Least-squares refinement was performed when all the non-hydrogen atoms were located. Hydrogen atoms were calculated (C–H = 0.95 Å) and given an isotropic temperature factor, $U_H = 0.09$ Å^2, kept fixed. Phenyl rings were refined as isotropic rigid groups (C–C = 1.385 Å). All other atoms were refined anisotropically.

The atomic scattering factors used were those proposed by Cromer and Waber[21] with anomalous dispersion effects.[22] Scattering factors for the hydrogen atoms were those of Stewart et al.[23]

The presence of numerous weak reflections, especially the equatorial ones, led us to adopt an unusual weight scheme in order to improve shift parameters. The σ values derived from counting statistics were ignored. Data reflections were ranged by increasing $|F_o|$ and set off in 15 groups of similar magnitude. A structure factor calculation gave $|\Delta F| = ||F_o| - |F_c||$ values. The plot of $|\overline{\Delta F}|$ vs. $|\overline{F_o}|$ was nearly linear, as for photographic data rather than for diffractometer data.[24] Each group was given a σ value equal to $|\overline{\Delta F}|$. The last refinement cycle led to $R = 0.050$ and $R_w = 0.057$. A test of enantiomeric forms was not significant (only asymmetric unit data were recorded). All parameter shifts were less than 0.5σ (mean value 0.06σ). An analysis of variance showed a slight overweighting of weak reflections. A final difference Fourier map showed a residual electron density of 0.3 e/Å^3.

2. Compound 6 (X = Ge). Least-squares refinement was performed as for **5**. Atomic scattering factors were those of ref 21, 22, and 23. A similar ponderation scheme was used. Both enantiomeric forms were tested, and the best one was kept ($R_1 = 0.056$; $R_2 = 0.058$).

The last refinement cycle led to $R = 0.056$ and $R_w = 0.065$. All parameter shifts were less than 0.7σ (mean value 0.08σ). As for compound **5**, an analysis of variance showed a slight overweighting of weak reflections. The final difference Fourier map showed a residual electron density of 0.4 e/Å^3.

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(21) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.B, p 99.

(22) Cromer, D. T., ref 21, Table 2.3.1, p 149.

(23) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(24) Stout, G. H.; Jensen, L. H. *X-ray Structure Determination*; Macmillan: New York, 1900; Appendix H, p 454.

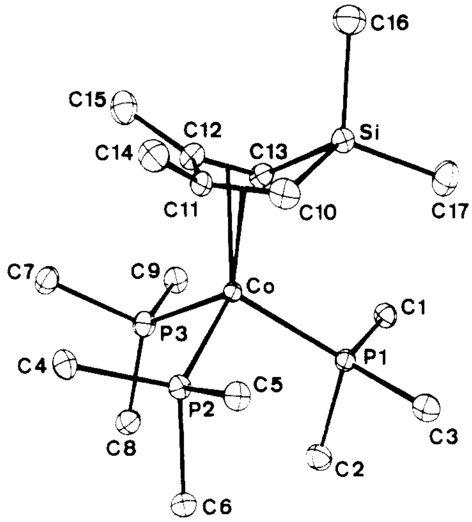


Figure 1. ORTEP drawing of the $[Co(C_8H_{14}Si)(PMe_3)_3]^+$ cation **5**.

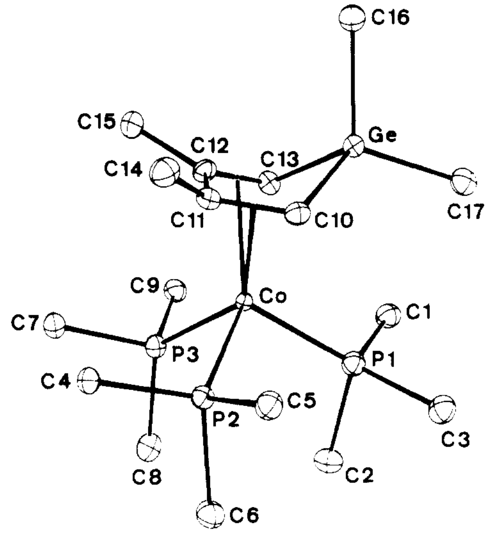


Figure 2. ORTEP drawing of the $[Co(C_8H_{14}Ge)(PMe_3)_3]^+$ cation **6**.

Details of crystal data and structures refinement are given in Table I. Final atomic coordinates with estimated standard deviations are listed in Table II.

Results

$[Co(1,1,3,4\text{-}Me_4H_2C_4M)(PMe_3)_3]BPh_4$ precipitates as the major compound at room temperature when the ligands **2** and **3** are allowed to react with $CoBr(PMe_3)_3$ in acetone in the presence of $NaBPh_4$ (reaction 1).

$$CoBr(PMe_3)_3 + \underset{\substack{\mathbf{2},\ M = Si \\ \mathbf{3},\ M = Ge}}{1,1,3,4\text{-}Me_4H_2C_4M} + NaBPh_4 \rightarrow \underset{\substack{\mathbf{5},\ M = Si \\ \mathbf{6},\ M = Ge}}{[Co(1,1,3,4\text{-}Me_4H_2C_4M)(PMe_3)_3]BPh_4} + NaBr \quad (1)$$

Crystal Structures. The structures of the two cations are pictured in Figures 1 and 2. Selected interatomic distances and angles are given in Table III.

Table III. Selected Interatomic Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses

	X = Si	X = Ge
	Bond Distances	
Co-P(1)	2.298 (1)	2.251 (3)
Co-P(2)	2.229 (2)	2.206 (3)
Co-P(3)	2.230 (2)	2.225 (3)
Co-C(10)	2.316 (8)	2.255 (9)
Co-C(11)	2.062 (6)	2.092 (10)
Co-C(12)	2.274 (7)	2.155 (10)
Co-C(13)	2.197 (7)	2.204 (10)
Co-M(1)[a]	2.081 (7)	2.056 (10)
Co-M(2)[a]	2.123 (7)	2.062 (10)
Co···X	2.995 (2)	3.021 (1)
C(10)-C(11)	1.382 (10)	1.419 (14)
C(11)-C(12)	1.472 (11)	1.454 (15)
C(12)-C(13)	1.403 (9)	1.412 (15)
X-C(10)	1.854 (8)	1.948 (10)
X-C(13)	1.875 (7)	1.948 (10)
X-C(16)	1.865 (9)	1.967 (11)
X-C(17)	1.843 (7)	1.979 (10)
C(11)-C(14)	1.497 (10)	1.516 (15)
C(12)-C(15)	1.523 (11)	1.505 (15)
	Bond Angles	
P(1)-Co-P(2)	101.01 (6)	101.5 (1)
P(1)-Co-P(3)	105.46 (6)	100.8 (1)
P(1)-Co-M(1)[a]	118.8 (2)	120.6 (3)
P(1)-Co-M(2)[a]	114.7 (2)	113.2 (3)
P(2)-Co-P(3)	93.44 (7)	92.7 (1)
P(2)-Co-M(1)[a]	92.5 (2)	86.6 (3)
P(2)-Co-M(2)[a]	141.2 (2)	140.8 (3)
P(3)-Co-M(1)[a]	133.2 (2)	137.9 (3)
P(3)-Co-M(2)[a]	91.3 (2)	98.0 (3)
M(1)-Co-M(2)[a]	57.8 (3)	60.6 (4)
P(1)-Co-C(10)	102.1 (2)	102.7 (3)
P(1)-Co-C(11)	137.4 (2)	139.7 (3)
P(1)-Co-C(12)	132.5 (2)	131.8 (3)
P(1)-Co-C(13)	96.2 (2)	94.8 (3)
P(2)-Co-C(10)	92.8 (2)	86.9 (3)
P(2)-Co-C(11)	91.9 (2)	86.7 (3)
P(2)-Co-C(12)	123.9 (2)	122.4 (3)
P(2)-Co-C(13)	158.3 (2)	157.8 (3)
P(3)-Co-C(10)	150.0 (2)	156.1 (3)
P(3)-Co-C(11)	114.2 (2)	118.2 (3)
P(3)-Co-C(12)	88.0 (2)	96.2 (3)
P(3)-Co-C(13)	94.6 (2)	99.0 (3)
C(10)-Co-C(11)	36.2 (2)	37.9 (4)
C(12)-Co-C(13)	36.5 (2)	37.8 (4)
X-C(10)-C(11)	102.2 (6)	102.7 (7)
C(10)-C(11)-C(12)	117.8 (6)	110.2 (9)
C(11)-C(12)-C(13)	108.6 (6)	121.4 (9)
C(12)-C(13)-X	100.3 (5)	93.6 (7)
C(10)-X-C(13)	88.8 (3)	88.1 (4)
C(10)-C(11)-C(14)	99.0 (6)	101.4 (9)
C(12)-C(11)-C(14)	133.1 (6)	138.1 (10)
C(11)-C(12)-C(15)	126.0 (6)	119.9 (9)
C(13)-C(12)-C(15)	125.0 (7)	118.5 (9)
C(10)-X-C(16)	116.8 (4)	121.8 (4)
C(10)-X-C(17)	119.3 (4)	118.5 (4)
C(13)-X-C(16)	109.6 (4)	105.6 (4)
C(13)-X-C(17)	115.4 (4)	114.0 (4)
C(16)-X-C(17)	106.3 (4)	106.7 (4)

[a] M(1) and M(2) are the midpoints of the C(10)-C(11) and C(12)-C(13) bonds, respectively.

These structures bear a striking similarity to those of $[Co(\eta^4\text{-}C_4H_6)(PMe_3)_3]^+$ and $[Co(\eta^4\text{-}C_7H_8)(PMe_3)_3]^+$.[16] The geometry at the cobalt center can best be considered in terms of a square pyramid with P(1) occupying the apical position. P(2) and P(3) and the dimethylbutadiene part of the metallole ring lie in the basal positions. The cobalt atom is located 0.7064 (5) Å (Si) and 0.664 (1) Å (Ge) above this plane, which is the range usually observed in these complexes. Thus, the metallole is η^4-coordinated to the cobalt center through its dimethylbutadiene moiety. This moiety is roughly planar and makes an angle of 77.1° in **5** and 78.5° in **6** to the basal plane P(2),P(3),M(1),M(2).

The silicon complex is more distorted than the germanium one. This is apparent in the three $Co\text{-}PMe_3$ and the Co-M(1) and Co-M(2) distances (M(1) and M(2) are the midpoints of the C(10)-C(11) and C(12)-C(13) double bonds), which have different values. In the silole com-

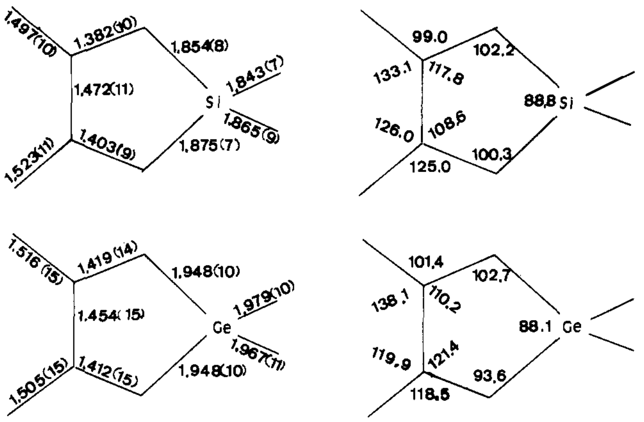


Figure 3. Comparison of the bond lengths (Å) and angles (deg) in the coordinated ligands in **5** (Si) and in **6** (Ge).

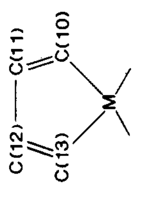
pound, Co–P(1) = 2.298 (1) Å is significantly longer than the two other Co–P(2) and Co–P(3) distances, which are respectively 2.229 (2) and 2.230 (2) Å, as already observed in square-pyramidal d^8 complexes. Moreover, Co–M(1) (2.081 (7) Å) is also shorter than Co–M(2) (2.123 (7) Å). Such differences are not uncommon in five-coordinate complexes, which are known to distort to accommodate ligands.

Consequently, five-coordinate complexes often depart from both the trigonal-bipyramidal (TBP) and square-pyramidal (SP) geometries. Different procedures have been developed to determine which one approximates the actual structure.[25a] We have used a procedure described earlier whereby the M–L bonds, normalized to unit length, are fitted by a least-squares techniques described by Dollase,[26] so as to minimize $\sum_i d_i^2$, 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$_a$–Co–L$_b$ is not fixed by symmetry, provision is made to adjust this angle as well in the minimization procedure. Values of the figure of merit (FOM = $(\sum d_i/5)^{1/2}$) are very similar in both complexes and definitely less favorable for a TBP (0.261 Å (14.9°) for **5** and 0.262 Å (15.0°) for **6**) than for a SP (0.159 Å (9.1°) for **5** and 0.161 Å (9.2°) for **6**).[25b]

However, the silole complex has longer Co–PMe$_3$ and Co–metallole distances than the germole complex. This was unexpected since the Si covalent radius (1.17 Å) is smaller than the Ge one (1.22 Å).[27] It may result, however, from a packing effect in the cobalt coordination sphere, the angles around Co being slightly different in the two complexes. M(1)–Co–M(2) is larger for Ge (60.6 (4)°) than for Si (57.8 (3)°). The angles belonging to the [Co(PMe$_3$)$_3$]$^+$ fragment are also slightly smaller in the Ge compound (Table III). However, all the Co–P and Co–M distances lie in the usual range.

Bond distances and angles in the coordinated metalloles are given in Figure 3, and comparisons with their analogues Ru(Ph$_2$Me$_2$H$_2$C$_4$Si)(CO)$_3$[28] and Fe(Ph$_4$FMeC$_4$Ge)(CO)$_3$[2]

Table IV. Selected Bond Distances and Angles in Silole and Germole Metal Complexes



	M–C(10) [M–C(13)]	M–C(11) [M–C(12)]	C(10)–C(11) [C(12)–C(13)]	C(11)–C(12)	Si–C(10),C(13) [Ge–C(10),C(13)]	angles between C(10),Si,C(13)/ C(10),C(11), C(12),C(13)	ref
[Co(C$_8$H$_{14}$Si)(PMe$_3$)$_3$]BPh$_4$	2.316 (8) [2.197 (7)]	2.062 (6) [2.274 (7)]	1.382 (10) [1.403 (9)]	1.472 (11)	1.854 (5) [1.875 (7)]	41.3	this work
[Co(C$_8$H$_{14}$Ge)(PMe$_3$)$_3$]BPh$_4$	2.255 (9) [2.204 (10)]	2.092 (10) [2.155 (10)]	1.419 (4) [1.412 (15)]	1.454 (15)	1.948 (10) [1.948 (10)]	44.5	this work
Ru(C$_{18}$H$_{18}$Si)(CO)$_3$	2.293 (4)	2.189 (3)	1.453 (4)	1.406 (7)	1.880 (7)	32	28
Fe(C$_{29}$H$_{23}$FGe)(CO)$_3$	2.18 (1) [2.16 (1)]	2.12 (1) [2.09 (1)]	1.44 (2) [1.45 (2)]	1.43 (2)	1.95 (1) [1.93 (1)]	31.1	26
[Co(C$_4$H$_6$)(PMe$_3$)$_3$]BPh$_4$	2.100 (14) [2.081 (13)]	2.083 (16) [2.031 (14)]	1.44 (2) [1.42 (2)]	1.48 (2)			16
C$_{30}$H$_{26}$Si[a]			1.358 (2)	1.511 (2)	1.868 (3)		29
C$_{18}$H$_{18}$Si			1.345 (4)	1.466 (6)	1.878 (3)		28

[a] Mean bond distances.

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[25] (a) Beauchamp, A. L.; Belanger-Gariepy, F.; Arabi, S. *Inorg. Chem.* **1985**, *24*, 1861. (b) FOM indicates the average distances (Å) between corresponding apices of the ideal and actual polyhedra in which all the M–L bonds are normalized to 1 Å. The average angle (deg) between corresponding bonds in the ideal and the actual polyhedra is given within brackets.

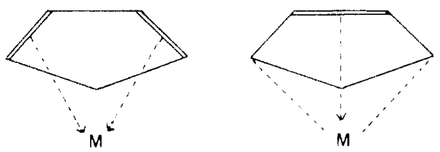
[26] Dollase, W. A. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 513.

[27] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 224.

[28] Muir, K. W.; Walker, R.; Abel, E. W.; Blackmore, T.; Whitley, R. J. *J. Chem. Soc., Chem. Commun.* **1975**, 698.

[29] Parkanyi, L. *J. Organomet. Chem.* **1981**, *216*, 9.

Chart II



are made in Table IV. The C–C distances corresponding to the two double bonds C(10)–C(11) and C(12)–C(13) remain significantly shorter than the third one C(11)–C(12). This was also observed in the butadiene cobalt complex. The ruthenium complex indicates an opposite effect, while in the iron complex similar distances are observed. Thus, the metallole ligand is bonded to the positive cobalt center as a η^4-ligand through its dimethylbutadiene fragment (isomer **1**—Chart I) while in the ruthenium complex, isomer **2** with Ru–C σ bonds is present (Chart II).

Loss of planarity of the metallole ring is observed, as expected. It results from the distortion of the p orbitals of the diene carbon atoms such as to increase their overlap with the metal d orbitals. No Co–Si or Co–Ge interaction is apparent as indicated by the distances: 2.995 (2) Å for Si and 3.021 (1) Å for Ge. The dihedral angle between the two parts of the ring, described by the C(10)–C(11)–C(12)–C(13) and C(10)–Si(Ge)–C(13) planes, respectively, is 41.2° for **5** and 44.5° for **6**. These values are slightly greater than usually observed (average 30°) and may result from the steric effect of the phosphine ligand. The angles at Si (88.8 (3)°) and at Ge (88.1 (4)°) in the ring are only slightly different from the 92.7 (1)° value observed in the free 2,3,4,5-tetraphenyl-1,1-dimethylsilole. Significantly, different values are observed for the angles at the carbon atoms C(11) and C(12) in the two metalloles (Table III; Figure 3), but surprisingly, in both complexes the some of the angles around C(12) is 360°, while it is only 350° around C(11). As a consequence, the dimethylbutadiene part of the ring is also distorted from planarity.

The coordinated PMe_3 ligands show the expected tetrahedral coordination. However, they are more distorted than usual because of the proximity of P(1) and the endo methyl group C(17). The geometry of the BPh_4 anion is normal: mean B–C distances being 1.659 (7) Å for **5** and 1.678 (11) Å for **6**; mean C–B–C angles having 109.5° value in both cases.

NMR Spectra of Complexes 5 and 6. The ^1H, ^{13}C, and ^{31}P NMR data, in dichloromethane-d_2 or acetone-d_6, are shown in Table V. The resonances corresponding to various carbon nuclei are assigned on the basis of their ^{13}C–^1H coupling and comparison with the free ligands. Some dissociation of the silole and germole ligands is observed at 293 K, but lowering the temperature prevents this dissociation and decreases the broadness of the signals.[30]

The $^{13}C\{^1H\}$ NMR spectra consist of (i) a single broad line at 20.0 ppm which is attributed to the PMe_3 carbons, (ii) four lines corresponding to BPh_4 (121.3, 125.3, 134.8, 162.8 ppm (J_{C-B} = 48 Hz)), and (iii) five lines which are assigned to the metallole ring carbons C(10) and C(11) and to the three methyl carbons C(14), C(16), and C(17). C(10) and C(11) are both markedly shifted upfield relative to the free ligand; these shifts are $\Delta\delta$ = 85.6 ppm for C(10) and 54.4 ppm for C(11) in complex **5** and $\Delta\delta$ = 68.8 ppm for C(10) and 41.8 ppm for C(11) in complex **6**. These values

Table V. $^{13}C\{^1H\}$ and $^1H\{^{31}P\}$ NMR Data (δ (J, Hz))[a,b]

	$^{13}C\{^1H\}$							$^1H\{^{31}P\}$					
	T, K	C_1 exo	C_1 endo	C_2	C_3	C_4	ref	T, K	Me_1 exo	Me_1 endo	H(C=)	Me_4	ref
2, $C_8H_{14}Si$		−5.1		126.5	157	20.6	14b		0.10		5.46	1.96	14b
5, $[Co(C_8H_{14}Si)(PMe_3)_3]BPh_4$	193	1.3	6.9	40.9 (155)	102.5	17.3 (127)	this work	223	−0.12	0.61	1.50	2.34	this work
7, $Fe(C_8H_{14}Si)(CO)_3$		−2.8	8.3	49.2	106.7	17.4	this work		−0.23	0.45	1.90	1.48	14b
3, $C_8H_{14}Ge$		−4.6		127	153.3	20.6	this work		0.30		5.71	1.97	15
6, $[Co(C_8H_{14}Ge)(PMe_3)_3]BPh_4$	178	2.8 (128)	7.1 (124)	43.7 (157)	101.9	17.3 (128)	this work	183	−0.10	0.59	2.10	1.60	this work
8, $Fe(C_8H_{14}Ge)(CO)_3$	177	−2.8 (122)	8.3 (117)	49.2 (156)	106.9	17.4 (127)	this work		0.00	0.63	2.30	1.86	15

[a] ^{13}C in CD_2Cl_2 for **2**, **5**, **6**, **7**, and **8** and in $CDCl_3$ for **3**. [b] ^1H in CD_2Cl_2 for **6**, in CCl_4 for **2** and **3** in C_6D_6 for **7** and **8**, and in $(CD_3)_2(CO)$ for **5**.

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[30] Fellmann, J. D.; Garrou, P. E.; Withers, H. P.; Seyferth, D.; Traficante, D. D. *Organometallics* **1983**, *2*, 818. Jesson, J. P.; Meakin, P. *J. Am. Chem. Soc.* **1974**, *96*, 5760.

are slightly larger than those obtained in the dimethylbutadiene analogue [Co(C_8H_{10})(PMe$_3$)$_3$]BPh$_4$ ($\Delta\delta$ = 68.8 ppm for C(10) and 41.8 ppm for C(11)) but are still typical of η^4-coordinated dienes. Consequently, in solution the silole and the germole ligands are also η^4-bonded to the [Co(PMe$_3$)$_3$]$^+$ fragment. No spectacular influence of the heteroatom on the chemical shifts is apparent. In both complexes, the exo CH_3 carbon is less deshielded than the endo one. Comparisons with the isoelectronic molecular Fe(C_8H_{14}Si)(CO)$_3$ and Fe(C_8H_{14}Ge)(CO)$_3$ complexes indicate that the metallole behaves similarly in complexes **5** and **6**.

The ^{1}H NMR spectrum confirms this conclusion. Four lines are observed for the exo CH_3, endo CH_3, CH_3, and CH protons of the metallole ring. The higher field signal corresponds to the exo methyl group.[1] Upon coordination the α-alkene hydrogens H–C(10,13) are significantly shifted to higher field ($\Delta\delta$ = 3.96 ppm for **5** and 3.61 ppm for **6**), which is characteristic of η^4-diene to metal bonding. Coupling between P atoms and the H and C atoms of the metallole ring is observed, together with coupling between Si and endo and exo CH_3 protons (J^{29}Si–^{1}H) = 3 Hz). Such coupling between the C atoms of the diene and the P atom of a phosphine ligand through the metal center has already been observed.[16]

^{31}P{^{1}H} NMR spectra of the two complexes consist of a single broad phosphine resonance down to 178 K at 3.8 (**5**) and 4.2 ppm (**6**) which indicates that the complexes are still stereononrigid at low temperature. Such a result has been reported for [Co(NBD)(PMe$_3$)$_3$]BPh$_4$[31] (NBD = norbornadiene), but stereorigidity is observed at room temperature for the acyclic dienes: butadiene, isoprene, and dimethylbutadiene.[16] Thus, stereononrigidity in the metallole complexes shows that a low-energy exchange process equilibrating the phosphorus ligands is present and is not hindered by a steric interaction between the endo methyl group and the axial PMe$_3$ ligand. Variations in the diene rearrangement barrier energy have already been observed in Fe(diene)(CO)$_3$ complexes.[32] Tentative explanations have been proposed including the bonding between the ML$_3$ moiety and the diene (π or $\sigma + \pi$), influence of the LUMO, and mixing of five-coordination (fluxional) with six-coordination (rigid). We hope to obtain more information from a study, now in progress, of complexation of metallole rings bearing different substituents.

In summary, tetramethylsilole and tetramethylgermole react similarly with CoBr(PMe$_3$)$_3$ to give isomorphous cationic complexes: [Co(C_8H_{14}Si)(PMe$_3$)$_3$]BPh$_4$ and [Co(C_8H_{14}Ge)(PMe$_3$)$_3$]BPh$_4$, both of which are best described as square pyramids, the silole compound being more distorted than the germole one. The metallole ligand is η^4-bonded to the cobalt through the dimethylbutadiene part of the ring. The complexes are still stereononrigid at 178 K.

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Registry No. **2**, 82763-95-9; **3**, 82763-96-0; **5**, 104439-72-7; **6**, 104439-74-9; CoBr(PMe$_3$)$_3$, 53432-07-8.

Supplementary Material Available: Tables of thermal parameters and hydrogen parameters as well as least-squares plane equations for **5** and **6** (6 pages); listings of observed and calculated structure factors for **5** and **6** (28 pages). Ordering information is given on any current masthead page.

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(31) Ananias de Carvalho, L. C.; Dartiguenave, M.; Dartiguenave, Y.; Beauchamp, A. L, work in progress.

(32) Kruczynski, L.; Takats, J. *Inorg. Chem.* **1976**, *15*, 3140.