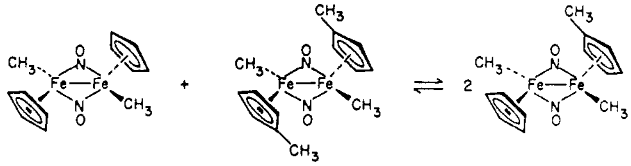
Scheme II



2 5 6

The dimers 1 and 2 are the observed organometallic products of the reaction of 3 with methyl iodide at room temperature in DME. By integration against a known amount of internal standard, the amount of iron in salt 3 is completely accounted for in the quantity of 1 and 2 formed. Thus the total yield of these products is essentially quantiative, and in order for this to be true the sample of 3 used cannot contain substantial impurities, unless they are paramagnetic and lead to the same products. A bit more 1 than 2 (52:48 ratio) was formed, indicating that a small amount of 3 is simply oxidized directly to dimer 2, rather than forming dialkyl complex as well. After a number of unsuccessful attempts at reducing and methylating 2, it was discovered that simple thermolysis of 2 at 45 °C gives 4, along with 1 and an as yet uncharacterized organometallic product with a single ^{1}H NMR resonance at δ 4.40 in benzene-d_6 (Scheme I).

Complex 4 decomposes at a rate comparable to that of its formation (we believe by migratory insertion; see below), and this complicates its isolation. By working rapidly, 4 can be isolated as a green, air-sensitive, and highly volatile solid in analytically pure form in 7.4% yield.[12] Upon following the disappearance of 2 in C_6D_6 at 23.8 °C, its conversion to 4 was found to be cleanly first order over 3 half-lives with an observed rate constant of 1.2×10^{-6} s^{-1}. To determine whether or not 2 also dissociates into monomeric CpFe(NO)Me fragments under these reaction conditions, the methylcyclopentadienyl analogue of 2 was prepared from $[\mathrm{MeCpFe(NO)}]_2$[13] in a manner similar to that by which 2 was prepared. Mixtures of 2 and 5 were found to give complete equilibration with the mixed dimer 6 (Scheme II) within seconds at room temperature in C_6D_6 solution, much faster than alkyl transfer.[14] The overall reaction was observed by ^{1}H NMR, and integration of the iron-bound methyl resonances gave $K_{\mathrm{eq}} = ([6]^2/[2][5]) = 4.2$. This is indicative of little, if any, thermodynamic preference for one particular dimer. We presume this interchange reaction occurs by reversible dissociation of 2 and 5 into the paramagnetic $\mathrm{CpFe(NO)CH_3}$ monomers proposed initially by Brunner.

Although monomeric dialkyl complex 4 decomposes slowly at room temperature to give a variety of products, in the presence of excess trimethylphosphine the trapped insertion product 7 (Scheme I) is formed in 60% yield (^{1}H NMR). This sensitive material can be obtained analytically pure, albeit with significant decomposition during chromatography, in 12% yield.[15] A similar adduct can be observed by ^{1}H NMR with dimethylphenylphosphine, but decomposition of 4 is unaffected by the presence of excess triphenylphosphine. It should further be noted that the extent to which the insertion product can be trapped is the same irrespective of the concentration of trimethylphosphine. This is consistent with rate-determiing migratory insertion followed by rapid trapping, as proposed for the migratory insertion observed[2a,b] for CpCo(NO)-$(\mathrm{CH_3})$.

In summary, reduction of Brunner's dimer 1 leads to a dimeric radical anion, rather than a dianion, which upon alkylation provides a route via a dimethyl dimer to a new monomeic dialkylnitrosyliron complex. Furthermore, NO migratory insertion for the latter is quite facile. We are, therefore, confident that other examples of migratory insertion will be observable and that the paucity of such observations will diminish as the number of known alkyl nitrosyl complexes increases.

Acknowledgment. We acknowledge financial support of this work from the National Institutes of Health (Grant No. GM-25459). We are also grateful to Carol A. Balfe for helpful discussion and assistance with the electrochemical experiments and to Professor Kenneth Sauer and the Melvin Calvin Laboratory of Chemical Biodynamics for the use of their ESR facilities. M.D.S. is the holder of a National Science Foundation Predoctoral Fellowship, 1980–1983. R.G.B. acknowledges a Research Professorship (1982–1983) from the Miller Institute for Basic Research at U.C. Berkeley and an unrestricted grant from the Chevron Research Co.

Registry No. 1, 52124-51-3; 2, 87597-73-7; 3, 87597-74-8; 4, 87597-75-9; 5, 87597-76-0; 6, 87597-77-1; 7, 87597-78-2; Na-$[\mathrm{CpCo(CO)}]_2$, 62602-00-0; $[\mathrm{MeCpFe(NO)}]_2$, 87597-79-3.

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(11) Yields determined by ^{1}H NMR. Isolated yields are lower as reported by Brunner and Wachsmann in ref 4.

(12) Data for 4: mp 56 °C dec; IR (benzene) 1785 (s) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 4.31 (s, 5 H), 1.03 (s, 6 H); ^{13}C NMR (benzene-d_6, ^{1}H decoupled) δ 94.64 (Cp), −4.14 ($\mathrm{CH_3}$); MS (CI), m/e 181 (M$^+$), 166 (base). Anal. Calcd for $\mathrm{C_7H_{11}Fe(NO)}$: C, 46.45; H, 6.12; N, 7.74. Found: C, 46.53; H, 6.16; N, 7.58.

(13) Data for 5: mp 70 °C dec; IR (benzene) 1523 (s) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 4.40 (t, 2 H, J = 2.2 Hz), 4.22 (t, 2 H, J = 2.1 Hz), 1.64 (s, 3 H), −0.01 (s, 3 H); MS (EI), m/e 344 (M − CH$_4^+$), 78 (base). Anal. Calcd for $\mathrm{C_{14}H_{20}Fe_2N_2O_2}$: C, 46.71; H, 5.60; N, 7.78. Found: C, 47.47; H, 5.38; N, 7.75. $[\mathrm{MeCpFe(NO)}]_2$ was prepared from $[\mathrm{MeCpFe(CO)_2}]_2$ and N-methyl-N-nitroso-p-toluenesulfonamide in toluene at reflux. Details of the synthesis and characterization of $[\mathrm{MeCpFe(NO)}]_2$ will be published elsewhere.

(14) The ^{1}H NMR resonances assigned to 6 in benzene-d_6 are δ 4.48 (s, 5 H), 4.38 (t, 2 H, J = 2.1 Hz), 4.19 (t, 2 H, J = 2.1 Hz), 1.61 (s, 3 H), 0.06 (s, 3 H), −0.06 (s, 3 H).

(15) Data for 7: mp 69 °C dec; IR (KBr) 1309 (s), 1291 (s), 1277 (s), 960 (s, sh), 950 (s), 817 (s) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 4.27 (s, 5 H), 3.36 (d, 3 H, J = 2.9 Hz), 1.51 (d, 3 H, J = 8.3 Hz), 0.84 (d, 9 H, J = 9.4 Hz); MS (EI), m/e 257 (M$^+$), 61 (base). Anal. Calcd for $\mathrm{C_{10}H_{20}FeNOP}$: C, 46.72; H, 7.84; N, 5.45. Found: C, 47.05; H. 7.69; N, 5.51.

Bis(cyclopentadienyl(1,3-diborolenyl)cobalt)tin. A Stannocene Analogue with a Bent Tetradecker Sandwich Structure[†]

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Summary: The preparation of $[(\mathrm{C_5H_5})\mathrm{Co}(\mathrm{C_2B_2C})]_2\mathrm{Sn}$ (**2**, $\mathrm{C_2B_2C}$, 4,5-diethyl-1,3-dimethyl-1,3-diborolenyl) from the sandwich anion $[(\mathrm{C_5H_5})\mathrm{Co}(\mathrm{C_2B_2C})]^-$ (**1$^-$**) and $\mathrm{SnCl_2}$ is reported. **2** is the first tetradecker sandwich complex containing a non transition metal. It exhibits a bent structure in which the Co–Sn vectors form a 130° angle. The bending angles of the two crystallographically independent molecules are 112 and 114°, respectively.

[†] Dedicated to Professor Dr. Dr. h. c. mult. E. O. Fischer on the occasion of his 65th birthday.

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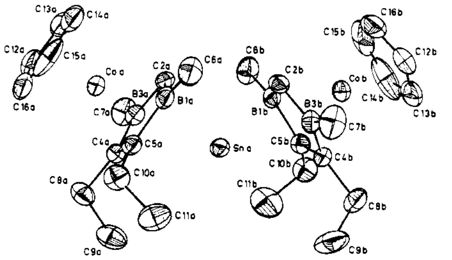
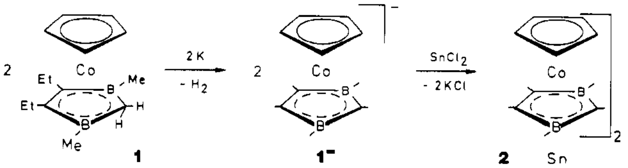


Figure 1. ORTEP plot of one of the two crystallographically independent molecules in the structure of **2**. The thermal ellipsoids are scaled to enclose 30% probability.

Recently we reported the reductive degradation of the tetradecker sandwich complex $[(C_5H_5)Co(C_2B_2C)]_2Ni$ (C_2B_2C, 4,5-diethyl-1,3-dimethyl-1,3-diborolenyl) to elemental nickel and the sandwich anion $[(C_5H_5)Co(C_2B_2C)]^-$ (1^-), which upon addition of transition-metal dihalides led to the formation of the tetradeckers $[(C_5H_5)Co(C_2B_2C)]_2M$ (M = Fe, Co, Zn).[1] The anion 1^- can be conveniently generated by deprotonating the novel sandwich complex[2,3] (C_5H_5)Co(1,3-diborolene) (**1**) which has a three-center, two-electron Co···C···H bond. The complexes $[(C_5H_5)Co(C_2B_2C)]_2M$ (M = Cr, Mn, Fe, Co, Ni, Cu, Zn) were prepared via this route.[4] Our efforts to exploit the unique reactivity of the 18-valence electron sandwich anion 1^- have now led to the preparation and structural characterization of $[(C_5H_5)Co(C_2B_2C)]_2Sn$ (**2**), the first multiple-decker sandwich complex containing a non-transition metal.



At room temperature and under a nitrogen atmosphere a THF solution of **1** (650 mg, 2.34 mmol; 30 mL of THF) readily reacts with a potassium mirror (140 mg of K, 3.58 mmol) to form the yellow-brown anion 1^-. After being stirred for 5 h, the solution is filtered to remove excess potassium. Anhydrous $SnCl_2$ (210 mg, 1.11 mmol) is added, which results in an immediate change in color. Dark orange **2** (507 mg, 69%; mp >140 °C dec) is isolated from the reaction mixture by evaporating the solvent, extracting the residue with petroleum ether, and cooling the extract to −30 °C.

The NMR data[5] for **2** are in accord with a tetradecker sandwich structure that is highly symmetrical on the NMR time scale. The ^{11}B chemical shift is typical for bridging 1,3-diborolenyl ligands. The ^1H resonances of the ethyl groups appear as multiplets of the ABX_3 type. The methylene protons are diastereotopic because the heterocyclic ring bridges two different metal atoms. The resonance of the 1,3-diborolenyl ring proton (δ 4.69) occurs at an unusually low field (in comparison to ^1H NMR δ 2.12 for $[(C_5H_5)Co(C_2B_2C)]_2Zn$).[1] Furthermore, a closer examination of this signal reveals the presence of a pair of poorly resolved satellites separated by 10 Hz. They are the result of a coupling with the spin-active tin isotopes. Individual couplings with the ^{117}Sn and ^{119}Sn nuclei could not be resolved.

For the molecular structure of **2** in the solid state to be established, a single-crystal X-ray diffraction study[6] was carried out. The structure of one of the two crystallographically independent molecules is shown in Figure 1; the structure of the second molecule is similar. Two virtually identical $(C_5H_5)Co(C_2B_2C)$ sandwich units are bound to the central tin atom in an η^5 fashion via the bridging 1,3-diborolenyl ligands. Unlike the transition-metal tetradecker complexes $[(C_5H_5)Co(C_2B_2C)]_2M$ with M = Cr,[4] Mn,[4] Fe,[1] Co,[1] Ni,[1] Cu,[4] and Zn[1] which feature a center of inversion, the tetradecker complex **2** exhibits a bent structure in which the Co–Sn vectors form a 130° angle. The distances and angles within the $(C_5H_5)Co(C_2B_2C)$ units are almost identical with those found in the compounds $[(C_5H_5)Co(C_2B_2C)]_2M$ (M = Cr→Zn). The Co atom occupies a position approximately above and below the centroids of the planar (±0.01 Å) C_2B_2C and C_5H_5 rings. The coordination of the tin atom to the 1,3-diborolenyl ligands is markedly asymmetric. The average Sn–B (2.59, 2.71 Å) and Sn–C(2) (2.43 Å) distances are much shorter than the Sn–C(4,5) distances (2.96, 2.89 Å). For stannocene[7] and decamethylstannocene[8] a similar scatter in the ring carbon–tin bond distances due to "ring slippage" has been observed (2.56–2.85[9] and 2.59–2.78 Å,[8] respectively). In the two independent molecules of **2** the angle between the normals to the planes defined by the 1,3-diborolenyl rings is 112 and 114°, respectively. This unusually small bending angle in comparison to those of stannocene (133, 134°)[10] and decamethylstannocene (144, 145°)[8] suggests that the bending in **2** most likely is controlled by electronic rather than steric factors. The MO consideration of stannocene[8] may be qualitatively applied to the bent tetradecker sandwich because of the isolobal relationship[3,11] $(C_5H_5)^- \underset{\circ}{\longleftrightarrow} [(C_5H_5)Co(C_2B_2C)]^-$. In **2** the negative population overlap between Sn and C is larger than in stannocene. Hence, an optimal decrease in energy of the MO in **2** that corresponds to the $3a_1$ orbital of stannocene ("lone pair")[12] can only be attained at smaller values of the bending angle.

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[1] (1) Tetradecker Complexes. 5. Part 4: W. Siebert, J. Edwin, H. Wadepohl, and H. Pritzkow, *Angew. Chem.*, **94**, 148 (1982); *Angew. Chem., Int. Ed. Engl.*, **21**, 149 (1982).

[2] (2) W. Siebert, J. Edwin, and H. Pritzkow, *Angew. Chem.*, **94**, 147 (1982); *Angew. Chem., Int. Ed. Engl.* **21**, 148 (1982).

[3] (3) J. Edwin, M. C. Böhm, N. Chester, D. Hoffman, R. Hoffmann, H. Pritzkow, W. Siebert, K. Stumpf, and H. Wadepohl, *Organometallics*, **2**, 1666 (1983).

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[5] (5) ^1H NMR (300 MHz, C_6D_6, Me_4Si): δ 4.69 (s, 2, J(SnH) = 10 Hz), 4.10 (s, 10), 2.49 (dq, 4), 2.01 (dq, 4), 1.02 (tr, 12), 0.96 (s, 12). ^{11}B NMR (C_6D_6, $Et_2O\cdot BF_3$): δ 13.

[6] (6) Crystallographic data for **2**: mol wt 660.45; monoclinic, space group $C2/c$; a = 30.860 (5) Å, b = 13.417 (2) Å, c = 31.183 (5) Å, β = 104.63 (2)°, V = 12492.6 Å^3, ρ_{calcd} = 1.407 g cm^{-3}, ρ_{exptl} = 1.40 g cm^{-3}, Z = 16, μ(Mo Kα) = 18.60 cm^{-1}. Diffraction data were collected with a STOE Weissenberg diffractometer (Mo Kα radiation, ω scan) and corrected for absorption (11080 measured reflections ($3 \le \theta \le 25°$); 8686 observed reflections with $I \ge \sigma_I$ were used in the refinement). The structure was solved by Patterson- and difference Fourier maps and refined by blocked-matrix least-squares methods (two C_5H_5 rings showed severe rotational disorder and were refined as rigid groups; all non-hydrogen atoms anisotropic; hydrogen atoms of the CH_2 and C_5H_5 groups in calculated positions, CH_3 groups refined as rigid groups). R = 0.053 and R_w = 0.042 ($w = \sigma_F^{-2}$).

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[8] (8) P. Jutzi, F. Kohl, P. Hofmann, C. Krüger, and Y.-H. Tsay, *Chem. Ber.*, **113**, 757 (1980).

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[10] (10) The values given here correspond to the angles between the normals to the ring planes. In the paper by Atwood et al.[9] the ring centroid–metal–ring centroid angles for Cp_2Sn are given, which differ by about 10°.

[11] (11) J. Edwin, M. Bochmann, M. C. Böhm, D. E. Brennan, W. E. Geiger, C. Krüger, J. Pebler, H. Pritzkow, W. Siebert, W. Swiridoff, H. Wadepohl, J. Weiss, and U. Zenneck, *J. Am. Chem. Soc.*, **105**, 2582 (1983).

[12] (12) It should be noted, however, that SCF Xα-SW calculations revealed a slightly different ordering. See: S. G. Baxter, A. H. Cowley, J. G. Lasch, M. Lattman, W. P. Sharum, and C. A. Stewart, *J. Am. Chem. Soc.* **104**, 4064 (1982).

Stannocenes and **2** exhibit a similar chemical behavior toward HBF_4, which cleaves the molecules. Analogous to the formation of cation[8] $[(C_5Me_5)Sn]^+$ we obtain a cationic dinuclear species. The constitution of the brown solid

$$\mathbf{2} + HBF_4 \rightarrow [(C_5H_5)Co(C_2B_2C)Sn]^+BF_4^- + \mathbf{1}$$

follows from analytical and ^1H NMR data.[13] It exhibits a large high-field shift for the proton of the 1,3-diborolenyl ring in comparison to that of **2**. An excess of HBF_4 destroys the sandwich **1**.

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Registry No. **2**, 87711-03-3.

Supplementary Material Available: Tables of positional and thermal parameters and structure factors and details of the structure analysis (49 pages). Ordering information is given on any current masthead page.

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(13) ^1H NMR (THF-d_8, Me_4Si): δ 4.41 (s, 5), 2.3 (m, 2), 1.8 (m, overlap with THF-d_8), 1.08 (tr, 6), 0.90 (s, 6), 0.05 (s, 1).

Possibilities of 1,1-Dimethylsilole as a Ligand in Transition-Metal Chemistry

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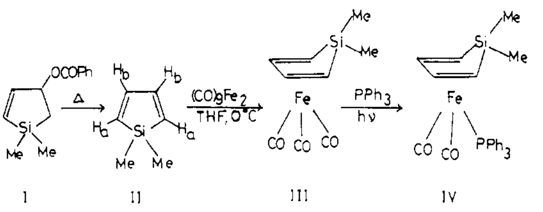
Summary: 1,1-Dimethylsilole is an effective ligand for transition-metal complexes. Direct displacement of carbonyl ligands from $Fe_2(CO)_9$ and $Co_2(CO)_8$ results in the stable complexes $(\eta^4\text{-}C_4H_4SiMe_2)Fe(CO)_3$ and $[(\eta^4\text{-}C_4H_4SiMe_2)(CO)_2Co]_2$, respectively. $(\eta^4\text{-}C_4H_4SiMe_2)(CO)_3Fe$ undergoes carbonyl replacement with PPh_3. Cleavage of the cobalt–cobalt bond is achieved with both iodine and sodium amalgam. The anion obtained from the reduction with sodium amalgam displaces chloride in Ph_3SnCl. Displacement of 1,5-cyclooctadiene in (1,5-COD)$_2$Ni and (1,5-COD)Mo(CO)$_4$ affords the Ni^0 sandwich complex $(\eta^4\text{-}C_4H_4SiMe_2)_2Ni$ and the molybdenum complex $(\eta^4\text{-}C_4H_4SiMe_2)_2Mo(CO)_2$, respectively.

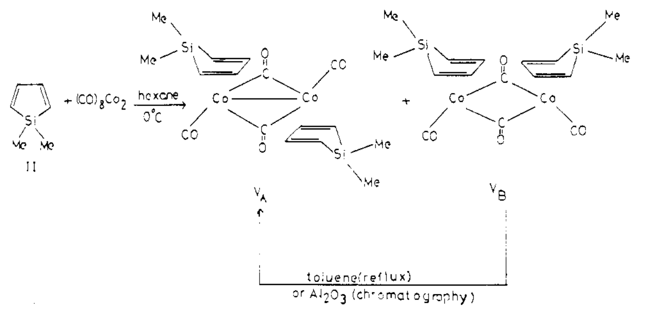
Transition-metal complexes of substituted siloles are well-known[1] and are interesting as potential sources of the unknown (η^5-silacyclopentadienyl)metal complexes.

Recently two groups reported the synthesis of 1,1-dimethylsilole[2,3] from the readily available 3,3-dimethyl-3-silacyclopentene, thus potentially allowing access into C-unsubstituted silole–transition-metal complexes. The recent report by Dubac and co-workers on the trapping of 1,1-dimethylsilole with iron carbonyl[4] prompts us to report our results concerning the complexation of 1,1-dimethylsilole with iron, cobalt, molybdenum, and nickel.

Scheme I



Scheme II



1,1-Dimethylsilole (prepared from the benzoate ester I[3] was collected in THF at −196 °C. After being warmed to 0 °C, the solution was transferred to a flask containing an excess (twice the equimolar amount) of $Fe_2(CO)_9$ and stirred at 0 °C for 40 min. After this time the solution was warmed to room temperature and allowed to stir for 2 h. Removal of the solvent afforded an oil that was chromatographed on silica gel with hexane. The yellow band was collected and concentrated to afford a yellow oil that was shown by ^1H NMR to be the silole complex III and the dimer of dimethylsilole[3] in 90:10 ratio. Pure III[5] was obtained by elution with hexane through a short silica gel column containing 10% $AgNO_3$ (52% yield based on I) (Scheme I).

UV irradiation of III with an equimolar amount of Ph_3P in hexane resulted in the substitution of a carbonyl ligand. The complex IV was obtained as yellow-orange crystals after chromatography on silica gel with hexane and crystallization (42% yield)[6] (Scheme I).

In an analogous synthesis of III, an excess of 1,1-dimethylsilole was reacted with $Co_2(CO)_8$ at 0 °C using hexane as the solvent. Careful crystallizations from hexane at −78 °C afforded an orange solid that was shown by ^1H NMR spectroscopy to be a mixture of the two isomers V_A and V_B (32% yield based on $Co_2(CO)_8$)[7] (Scheme II). This is surprising since in the case of the reaction of 1,1-di-

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(1) Abel, E. W.; Blackmore, T.; Whitley, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2484 and references therein.

(2) Laporterie, A.; Mazerolles, P.; Dubac, J.; Iloughmane, H. *J. Organomet. Chem.* 1981, *206*, C25; 1981, *216*, 321.

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(4) Laporterie, A.; Iloughmane, H.; Dubac, J. *J. Organomet. Chem.* **1983**, *244*, C12.

(5) III: orange yellow oil; ^1H NMR (δ relative to $(CH_3)_4Si$ in CCl_4) 5.89 (m, H_b), 1.96 (m, H_a), 0.83 (s, endo-CH_3), −0.18 (s, exo-CH_3); IR (cyclohexane) ν (CO) 2055 (s), 1985 (s) cm^{-1}; mass spectrum, *m/e* (assignment) 250 (molecular peak).

(6) IV: orange crystals; mp 170.5–171.5 °C; ^1H NMR (in C_6D_6, δ) 7.63–6.73 (m, aromatic), 5.00 (m, H_b), 1.17 (m, H_a), 0.70 (s, endo-CH_3), −0.14 (s, exo-CH_3); IR (cyclohexane) ν (CO) 1975 (s), 1920 (s) cm^{-1}; mass spectrum, *m/e* (assignment) 484 (molecular peak). Anal. Calcd for $C_{26}H_{25}FeO_2PSi$: C, 64.46; H, 5.17; P. 6.40. Found: C, 64.61; H, 5.35; P. 6.53.

(7) V (mixture of isomers A and B): ^1H NMR (in C_6D_6, δ) 5.48 (m, H_b), 5.18 (m, H_b), 2.71 (m, H_a), 0.51 (s, endo-CH_3), 0.45 (s, endo-CH_3), −0.22 (s, exo-CH_3), −0.41 (s, exo-CH_3). Isomer V_A: red-orange crystals; mp 161–161.5 °C; ^1H NMR (C_6D_6, δ) 5.18 (m, H_b), 2.71 (m, H_a), 0.51 (s, endo-CH_3), −0.22 (s, exo-CH_3); IR (cyclohexane) ν(CO) 2020 (s), 2000 (s), 1830 (m) cm^{-1}; mass spectrum, *m/e* (assignment)) 450 (molecular peak). Anal. Calcd for $C_{16}H_{20}Co_2O_4Si_2$: C, 42.67; H, 4.44. Found: C, 42.52; H, 4.40.

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