Table III. Important Interatomic Distances and Angles for [V(μ-Cl)(μ-dppm)BH$_4$]$_2$[a]

	Distances, Å		
V–V′	3.112 (3)	V–H(1)	1.78 (8)
Cl	2.426 (3)	H(2)	1.69 (10)
Cl′	2.422 (3)	B–H(1)	1.24 (9)
P(1)	2.570 (4)	H(2)	1.36 (10)
P(2)	2.568 (4)	H(3)	1.25 (11)
B	2.314 (14)	H(4)	0.94 (9)
	Angles, deg		
Cl–V–Cl′	100.1 (1)	P(2)–V–H(1)	94 (3)
P(1)	91.3 (1)	H(2)	92 (3)
P(2)	88.0 (1)	H(1)–V–H(2)	67 (4)
H(1)	162 (3)	V–Cl–V′	79.9 (1)
H(2)	95 (4)	V–H(1)–B	98 (5)
Cl′–V–P(1)	88.0 (1)	V–H(2)–B	98 (6)
P(2)	93.2 (1)	H(1)–B–H(2)	95 (6)
H(1)	98 (3)	H(3)	105 (6)
H(2)	164 (4)	H(4)	105 (8)
P(1)–V–P(2)	178.7 (1)	H(2)–B–H(3)	115 (7)
H(1)	86 (3)	H(4)	103 (7)
H(2)	87 (3)	H(3)–B–H(4)	128 (7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

other relatively unimportant hydrogen atoms in the refinement.

A table of observed and calculated structure factors is available as supplementary material.

Results and Discussion

The final atomic parameters are listed in Table II. Important interatomic distances and angles are presented in Table III. Less important interatomic dimensions as well as a table of anisotropic thermal parameters are included in the supplementary material.

The molecule of [V(μ-Cl)(μ-dppm)BH$_4$]$_2$, which is represented by its ORTEP drawing in Figure 1, resides on a crystallographic inversion center. Formally, its geometry can be considered as an edge-sharing bioctahedron. The central core, $V_2Cl_2P_4(BH_4)_2$, has effectively D_{2h} symmetry. The chlorine bridges are symmetric, and all equivalent bonds in the coordination sphere have, within the limits of error, the same length. The B, H(1), and H(2) atoms deviate only slightly from coplanarity with the V(μ-Cl)$_2$V′ unit, since they are located 0.034, 0.090, and 0.129 Å, respectively, from the plane. The bridging C(1) carbon atom, which is puckered away from the V_2P_2 plane, and the phenyl groups are not positioned in accord with D_{2h} symmetry.

V–Cl distance is significantly shorter than in the confacial-bioctahedral [V$_2$(μ-Cl)$_3$(THF)$_6$]$^+$ cation,[2] where it is 2.478 [3] Å. The V–V separation is equal to 3.112 (3) Å, which argues against any significant direct metal–metal interaction.

Although problems with the preparation have not yet allowed isolation of bulk samples of the pure compound, so that it has been impossible to carry out characterization by methods other than crystallography, the existence of this complex is of considerable importance. First of all, it shows that the mixed vanadium–zinc starting material can react in a nonredox manner with retention of a divanadium unit and without incorporation of zinc atoms into the product. Second, the compound has a potential for being a precursor to a variety of dinuclear vanadium species since bridging dppm ligands have shown a tendency to stabilize dimers against cleavage,[7] although they do not always do so. Thus, we found that addition of excess pyridine to a post-reaction mixture containing [V(μ-Cl)(μ-dppm)BH$_4$]$_2$ precipitates monomeric VCl$_2$(py)$_4$.[8] This process has a noteworthy feature, namely in spite of the complex composition of the mixture a pure product can be isolated readily (recrystallization from benzene by addition of hexane). Finally we point out that no dimeric vanadium complexes with diphosphines have been reported previously nor have any structural data concerning rare V–BH$_4$ species been available.[9,10]

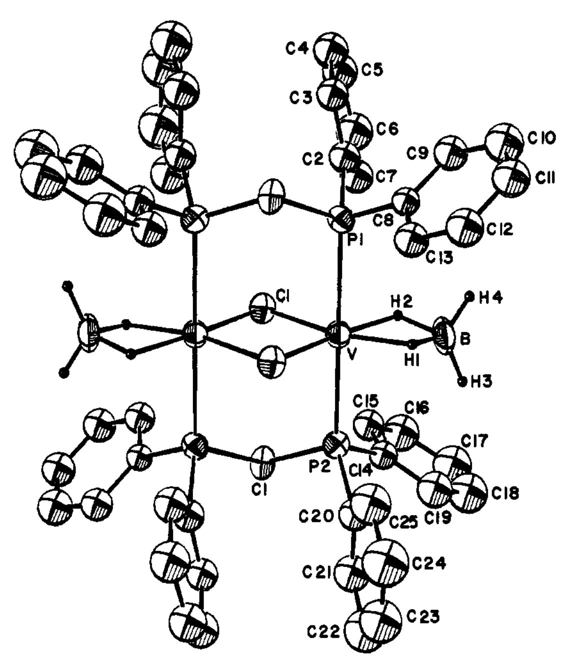

Figure 1. Molecular structure and atom-labeling scheme for [V(μ-Cl)(μ-dppm)BH$_4$]$_2$. The thermal ellipsoids are of 50% probability. Arbitrary radii have been assigned to the hydrogen atoms.

Acknowledgment. We thank the National Science Foundation for financial support and Dr. Willi Schwotzer for his help with the collection of low-temperature data.

Registry No. [V(μ-Cl)(μ-dppm)BH$_4$]$_2$, 92545-24-9; [V$_2$Cl$_3$(THF)$_6$]$_2$(Zn$_2$Cl$_6$), 89172-48-5; NaBH$_4$, 16940-66-2.

Supplementary Material Available: Tables of observed and calculated structure factors, less important bond distances and angles, and anisotropic thermal parameters, *B*'s (9 pages). Ordering information is given on any current masthead page.

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Steric Factors Controlling the Formation of Allenyl- vs. Propargylcobaloxime Complexes

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Recent interest in our laboratories has focused on the reactions of low-valent-state transition-metal complexes with propargyl halides to form allenyl and/or propargyl transition-metal complexes. Such complexes have been proposed as highly reactive intermediates in the iron, cobalt, nickel, and copper salt catalyzed coupling reactions of Grignard reagents with propargyl halides to form substituted allenes.[1] It was

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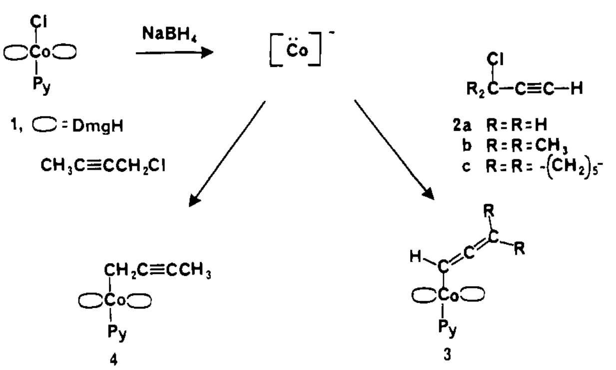
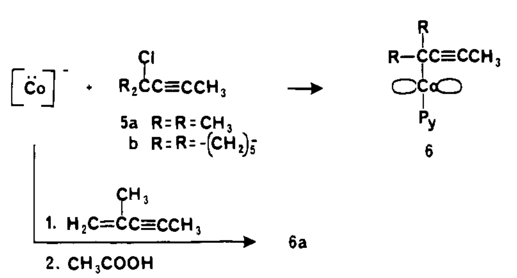
(1) Pasto, D. J.; Chou, S.-K.; Waterhouse, A.; Shults, R. H.; Hennion, G. F. *J. Org. Chem.* **1978**, *43*, 1385.

of interest to prepare more stable, isolable allenyl and propargyl transition-metal complexes for study of their physical and chemical properties. Initial studies have been devoted to nickel- and cobalt-based systems. Preliminary studies on the reactions of propargyl halides with triphenylphosphine complexes of Ni(0) have resulted in the discovery of a remarkable reductive cyclodimerization reaction resulting in the formation of 3,4-bis(alkylidene)cyclobutenes.[2] In the present note we wish to report results derived with cobaloxime complexes.

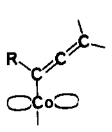
Collman and co-workers had earlier reported that the reduced form of bis(dimethylglyoxamato)(pyridine)cobalt chloride (**1**, pyCo(dmgH)$_2$) reacted with the propargyl chlorides **2a–c** to form the allenyl complexes **3a–c**, while reaction with 1-chloro-2-butyne afforded the propargyl complex **4**.[3] The data available did not provide for an understanding of the factor(s) that determine which type of complex would be formed.



We have extended the Collman studies to include the two nonterminal propargyl chlorides **5a** and **5b**. Surprisingly, **5a** and **5b** react to produce only the tertiary propargyl complexes **6a** and **6b**. The structures of the complexes are readily assigned on the basis of their ^{1}H and ^{13}C NMR (see Experimental Section) and IR spectra (transparent in the 1910-cm^{-1} ($\nu_{C=C=C}$) region[3]). The NMR spectra of the crude complexes indicated that in no case was a mixture of allenyl and propargyl complexes formed. The complex **6a** can also be conveniently prepared by the hydrocobaltation of 2-methylpent-1-en-3-yne.



Tertiary alkylcobaloxime complexes are rarely isolable; the only previously reported tertiary alkyl complexes being those containing the 1-adamantyl[4] and 1-norbornyl[4] (both bridgehead alkyls) and 1-(1-methyl-2,2-diphenylcyclopropyl)[5] complexes. In this study the results show that the type of complex formed depends critically on the degree of substitution on the allenyl carbon atom bonded to cobalt. When the substituent R in **7** is hydrogen, the allenyl complex is isolated, but when R is a larger alkyl group, the allenyl complex is not isolated. This suggests that steric effects in the complexes are the major factors that determine the type of complex isolated. X-ray structural data have shown that the Co–C bond lengths in isopropylcobaloxime complexes is considerably longer (~0.1 up to ~0.24 Å) than in similar methylcobaloxime complexes, the lengthening being attributed primarily to increased steric congestion in the complex.[6,7] In **9** the Co–C bond length is expected to be somewhat shorter than that between Co and sp^3-hybridized C in the alkyl complexes, thereby increasing the magnitude of the steric effects. Apparently, when R = CH$_3$ in **9**, the steric factors becomes severe enough to cause the favoring of the propargyl complex due to the longer Co–C bond.



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The present study does not provide any information concerning the mechanisms of formation of the complexes. Although mixtures of allenyl and propargyl complexes were never formed under the reaction conditions used, it does not preclude a rapid interconversion of the forms as suggested by Johnson and co-workers.[8]

Experimental Section

Propargyl chlorides 5a and **5b** were prepared as described previously.[1]

Preparation of the Propargylcobalt Complexes 6a and 6b. The reduction of **1** followed by reaction with **5a** and **5b** was carried out as described by Collman and co-workers.[3] The orange complexes were recrystallized from aqueous ethanol.[9]

6a: ^{1}H NMR (CDCl$_3$) δ 1.24 (s, 6 H), 1.30 (s, 3 H), 2.12 (s, 12 H), 7.32 (m, 2 H), 7.75 (m, 1 H), 8.60 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ −1.3 (dmgH CH$_3$), 11.4 (≡C*C*H$_3$), 18.0 [(*C*H$_3$)$_2$CCo], 99.1 (≡*C*CH$_3$), 135.2, 150.3, and 165.3 (pyridine ring C's), 164.6 (dmgH ring C).[10] Anal. Calcd for CoC$_{19}$H$_{28}$N$_5$O$_4$: C, 50.78; H, 6.28; N, 15.58. Found: C, 50.43; H, 6.37; N, 15.01.

6b: ^{1}H NMR (CDCl$_3$) δ 1.34 (s, 3 H), 1.36–1.87 (br m, 10 H), 2.12 (s, 12 H), 7.31 (m, 2 H), 7.77 (m, 1 H), 8.61 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ −0.6 (dmgH CH$_3$), 14.3, 15.0, and 24.2 (cyclohexyl C's), 19.8 (≡C*C*H$_3$), 135.0, 150.9, and 166.9 (pyridine ring C's), 165.4 (dmgH ring C). Anal. Calcd for CoC$_{22}$H$_{32}$N$_5$O$_4$: C, 53.99; H, 6.59; N, 14.31. Found: C, 53.97; H, 7.39; N, 14.06.

Hydrocobaltation of 2-Methylpent-1-en-3-yne. To a solution of 1 g of sodium hydroxide in 200 mL of nitrogen-degassed methanol was added 3.0 g (7.5 mmol) of bis(dimethylglyoximato)(pyridine)cobalt chloride (**1**) followed by 0.5 g of sodium borohydride. The reaction mixture was stirred for 20 min, and 0.55 g (8.1 mmol) of 2-methylpent-1-en-3-yne was added. Glacial acetic acid was cautiously added dropwise with vigorous stirring until the reaction mixture turned orange. Water (200 mL) was added, and the reaction mixture was cooled in an ice bath, whereupon gold platelets formed. The crystals were filtered (1.7 g, 46%) and quickly recrystallized[9] from 50% aqueous ethanol, giving very thin gold platelets.

Registry No. 1, 23295-32-1; **5a**, 999-79-1; **5b**, 60820-36-2; **6a**, 92490-51-2; **6b**, 92490-52-3; 2-methylpent-1-en-3-yne, 926-55-6.

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(9) Attempts to recrystallize **6a** and **6b** from aprotic solvents or prolonged heating at reflux in aqueous ethanol resulted in an irreversible transformation to slightly soluble green compounds whose structures have not yet been determined.

(10) The ^{13}C resonances of the propargyl carbon attached to cobalt and the alkynyl carbon attached to the propargyl carbon could not be detected. Apparently the relaxation times of these carbon atoms are quite long. Similarly, the ^{13}C resonances of the carbon atom attached to cobalt in the allenyl complexes could *not* be detected. The central allenyl carbon atoms could be detected by employing a 5-s delay and appear in the δ 199–210 region. The remote allenyl carbon atoms are readily detected and appear in the δ 70 region.