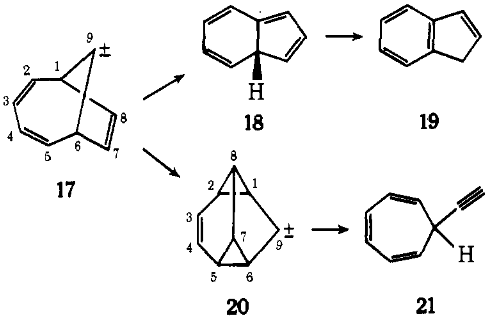
16

conversion to **7** upon protonation. Indeed vacuum pyrolysis of the sodium salt of bicyclo[4.2.2]deca-2,4,9-trien-7-one *p*-tosylhydrazone, reaction of the condensate with sodium dimsyl in dimethyl sulfoxide, and acidification of the product is an advantageous method for preparing **7** (>54% isolated). Such an overall process might be the source of **7** from pyrolysis of **2** in a basic environment.

Bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene (**17**), presumably generated by decomposition of 9-diazobicyclo[4.2.1]nona-2,4,7-triene as derived from thermolysis of the dry sodium salt of the *p*-tosylhydrazone of bicyclo[4.2.1]nona-2,4,7-trien-9-one, has been reported[1] to give indene (**19**, 95%). A simple path for conversion of **17** to **19** (and is analogous to that suggested for conversion of **1** to **5**) is rearrangement to bicyclo[4.3.0]nona-2,4,6,8-tetraene (**18**) which undergoes 1,5-sigmatropic isomerization to **19.** It has now been found that **17,** as generated thermally, also yields 1-ethynyl-2,4,6-cycloheptatriene[16] (**21,** 5%). Acetylene **21** may result from cyclopropylcarbinyl collapse of **20** as formed by cycloaddition of the C_2–C_5 diene and C_7–C_8 monoene moieties within **17** or its precursors.[17] The overall behavior of **1** and **13** is thus formally identical. Study of possible degeneracy and the significance of bicycloaromatic interactions in isomerization of **1** and **17** will be initiated.



Acknowledgment. We should like to acknowledge support of this research by the National Science Foundation, a dissertation year fellowship to T. V. Rajanbabu by the Stauffer Chemical Company, and the initial observations by J. B. Press relative to the properties of **1.**

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(4) Progress in synthesis of bridgehead olefins has been reviewed by G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **12,** 464 (1973).
(5) ^{1}H NMR ($CDCl_3$) δ 2.2 (m, 1 H), 2.7 (m, 1 H), 2.9 (m, 1 H), 5.6 (m, 1 H), 5.9 (m, 4 H), and 6.3 (m, 2 H); ^{13}C NMR ($CDCl_3$, −40 °C) δ 139.3 (1 C), 138.7 (1 C), 135.3 (1 C), 128.0 (1 C), 125.6 (2 C), 121.4 (1 C), 36.4 (1 C), and 32.8 (1 C) (the ^{13}C resonance of C_6 is of too low intensity to be recorded).
(6) (a) Prepared previously by P. Radlick and W. Rosen, *J. Am. Chem. Soc.*, **88,** 3461 (1966). (b) We should like to thank Dr. Radlick and his colleagues for a sample of **7.**
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(8) (a) In the present interpretation **2** is assumed to convert first to **1** which then yields **8.** It cannot be ruled out, however, that sodium bicyclo[4.2.2]deca-2,4,9-trien-7-one *p*-tosylhydrazone or/and **2** undergo intramolecular cycloaddition of their C_2–C_5 diene and C_9–C_{10} monoene bridges before conversion (in part) to **8.** (b) 1,7-Hydrogen migration in **5** to give **8** is symmetry forbidden.
(9) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82,** 1002 (1960).
(10) An alternate, less likely mechanism involves isomerization of **1** to bullvalylidene and then cyclopropylcarbinyl fragmentation to **9.**
(11) M. R. Willcott, J. F. M. Oth, J. Thio, G. Plinke, and G. Schröder, *Tetrahedron Lett.*, 1579 (1971).
(12) G. Schröder, J. Prange, B. Pritze, J. Thio, and J. F. M. Oth, *Chem. Ber.*, **104,** 3406 (1971).
(13) (a) NMR ($CDCl_3$) δ 1.69–2.10 (m, 4 H, H_9 and H_{10}), 2.77 (br m, 1 H, H_1), 3.13 (br m, 1 H, H_6), and 5.80 (m, 6 H, olefinic H); (b) **13**a is also described by M. Fus, University of Koln, West Germany, 1968; (c) NMR ($CDCl_3$) δ 1.69–2.10 (m, 3 H, H_9 and H_{10}, coupling simplified), 3.13 (br m, 1 H, H_6), and 5.80 (m, 6 H, olefinic H). It is noted that the absorption at δ 2.77 has disappeared (bridgehead H_1).
(14) H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc.*, **95,** 1669 (1973).
(15) The adduct is of proper analysis; NMR ($CDCl_3$) δ 7.25 (m, 5 H, aromatic), 6.00 (m, 6 H, H_2, H_3, H_4, H_5, H_8, H_9), 4.45 (dd, 1.5 Hz, 4 Hz, 1 H, H_7), 3.15 (br m, bridgehead H_1), 2.25 (d, 13 Hz, 1 H, H_{10}, endo), 1.6 (dd, 12 Hz, 5 Hz, 1 H, H_{10}, exo). The triazole loses nitrogen readily upon heating and in mass spectral analysis.
(16) R. M. Hoskinson, *Aust. J. Chem.*, **23,** 399 (1970).
(17) (a) An alternate, more complicated mechanism might involve rearrangement of **17** to barbarylidene and subsequent cyclopropylcarbinyl fragmentation similar to that in footnote 10. (b) Pyrolysis of the sodium salt of barbaralone *p*-tosylhydrazone gives **21** (~100%).

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Stereochemical Rigidity and Enantiomerization of Bis(diisopropylamino)dialkylaminoboranes

Sir:

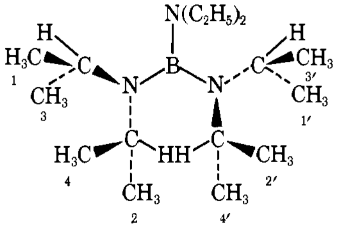
There is considerable interest in the conformational and dynamical behavior of aminoboranes;[1-3] however, with the exception of a brief report and discussion of a B–N torsional barrier in bis(dimethylamino)methylphenylaminoborane, $[(CH_3)_2N]_2BN(CH_3)(C_6H_5)$,[2] little is known of the stereodynamics of tris(amino) boranes. Recently, we have begun an investigation of the properties of these compounds, which are isoelectronic with the biologically important guanidinium ions. This communication reports the detection of stereochemically rigid (on the NMR time scale) bis(diisopropylamino)dialkylaminoboranes and the determination of the barrier to and the permutational mode of a concerted rotation which occurs about the two B–N(i-C_3H_7)$_2$ bonds.

At ambient temperature, the ^{1}H spectrum of bis(diisopropylamino)diethylaminoborane,[4] $[(i\text{-}C_3H_7)_2N]_2BN(C_2H_5)_2$ (I), exhibits four resonances: a septet (δ 3.58, J = 7.0 Hz) arising from the isopropyl methine protons; a quartet (δ 2.93, J = 7.0 Hz) from the ethyl methylene protons; a doublet (δ 1.21, J = 7.0 Hz) from the isopropyl methyl protons; and a triplet (δ 0.95, J = 7.0 Hz) from the ethyl methyl protons. At −110 °C, in contrast, the ethyl resonances are typical of an ABX_3 system ($\delta_{CH_2} \sim 2.73$, J_{AB} = 12 Hz, δ_{CH_3} 0.78), the isopropyl methyl resonances consist of two broad doublets (δ 1.13, J = 6.5 Hz, and δ 0.96, J = 6.0 Hz), and there are two well separated resonances arising from anisochronous isopropyl methine protons ($\delta \sim 3.51$ and 3.27).

The noise-decoupled ^{13}C spectrum at −105 °C exhibits resonances assigned to the isopropyl methine carbon (δ 62.4), the ethyl methylene carbon (δ 53.2), the ethyl methyl carbon (δ 28.2), and four peaks attributable to isopropyl methyl carbons occupying four diastereotopic sites (δ 41.5, 41.2, 37.7, and 37.0). On warming, the ethyl and the isopropyl methine peaks do not change, but the isopropyl methyl resonances undergo coalescence and resharpen to a single peak by −48 °C. Further warming to 30 °C does not affect the spectrum. Chemical shifts at 30 °C are isopropyl methine, δ 61.8; ethyl methylene, δ 53.9; isopropyl methyl, δ 38.7; and ethyl methyl, δ 27.5.

The stereochemical relationships between groups in I cannot be determined unequivocably from either ^{1}H or ^{13}C spectra alone. However, the observation of two separate isopropyl methine proton resonances and four separate isopropyl methyl carbon resonances indicates that there are two distinct isopropyl sites and that within each of these sites, the methyl groups reside in diastereotopic environments. The ethyl groups appear to be isochronous. However, the protons within each ethyl methylene group give rise to the AB portion of the ABX$_3$ pattern seen in the ^{1}H spectrum, and are therefore diastereotopic. Thus anisochronicity is observed in every prochiral group in the molecule. This indicates that I exists in a stereochemically rigid chiral or meso configuration at low temperature.[7-9]

In fact vibrational spectroscopy,[10] molecular orbital calculations,[11] electron diffraction,[12] and photoelectron spectroscopy[13] all indicate that tris(amino)boranes adopt a helically chiral conformation. For I such a chiral structure would lead to an arrangement of the diisopropylamino groups as shown below.[14] Such chiral structures are not unique to aminoboranes, but are also observed in a number of stereochemically correspondent systems.[15-18] Although a meso configuration such as A would also be consistent with the low-temperature NMR data for I, such a conformation has not been observed in other tris(amino)boranes or in similar systems. We therefore conclude that, in all probability, the static conformation of I is the helically chiral one.[19]



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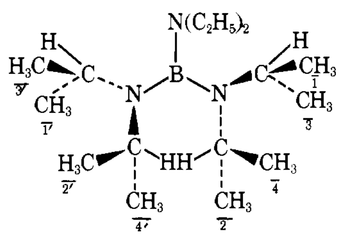

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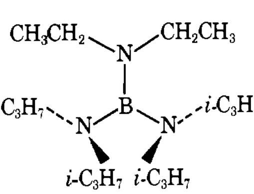

A

These chiral structures possess a C_2 axis through the diethylamino N-B bond. Because of this symmetry element, diisopropyl methyls 1 and 1′ are equivalent, as are 2 and 2′, 3 and 3′, and 4 and 4′. As NMR cannot distinguish enantiomeric groups in an achiral environment, the signals from I and Ī will appear at identical positions and four different isopropyl methyl resonances will be observed when $(i\text{-C}_3\text{H}_7)_2$N-B rotation is slow.[7,20]

As the temperature is increased, the rate of B-N rotation will accelerate. Since all anisochronicity within the prochiral groups in the molecule is observed to disappear upon warming, enantiomerization must be occurring. The only likely pathways for the interchange of enantiomers[21] are: (A) Via a rotation of both N(i-C$_3$H$_7$)$_2$ groups through the BN$_3$ plane. This would exchange methyls 1 with 3 and 2 with 4, but would not interchange the isopropyl methine sites. (B) Via a rotation of both N(i-C$_3$H$_7$)$_2$ groups through planes perpendicular to the BN$_3$ plane. Such a pathway would result in interchange of anisochronous methine groups, but not in complete averaging of the isopropyl methyl groups, since 1 would be exchanged only with 4 and 2 only with 3. (C) Via the rotation of one N(i-C$_3$H$_7$)$_2$ group through the BN$_3$ plane and the other through a plane perpendicular to the BN$_3$ plane. This would lead to averaging of all four isopropyl methyl groups and of the two methine sites. (D) Via nonconcerted rotations which would average all sites. While C and D both can account for the high temperature observations only spectra simulated using the permutations characteristic of C reproduce the experimental ^{13}C isopropyl methyl spectra in the intermediate exchange region.[22] Thus barring the exceedingly unlikely possibility that the activation energies for pathways A and B are identical, enantiomerization must be occurring by C. From the simulated spectra a $\Delta G^{\ddagger}{}_{193\text{K}} = 9.4$ kcal/mol was calculated for this process.

Bis(diisopropylamino)dimethylaminoborane, $\{[(\text{CH}_3)_2\text{CH}]_2\text{N}\}_2\text{BN}(\text{CH}_3)_2$ (II), bis(diisopropylamino)chloroborane, $\{[(\text{CH}_3)_2\text{CH}]_2\text{N}\}_2\text{BCl}$ (III), tris(methylamino)borane $(\text{CH}_3\text{NH})_3\text{B}$ (IV), tris(ethylamino)borane, $(\text{C}_2\text{H}_5\text{NH})_3\text{B}$ (V), and tris(isopropyl)amino)borane, $[(\text{CH}_3)_2\text{CHNH}]_3\text{B}$ (VI) were also investigated by NMR. Neither the ^{1}H of III, IV, V, or VI nor the ^{13}C spectra of III or VI were temperature dependent between 30 and −120 °C. In the case of II, however, ^{1}H and ^{13}C spectral behavior was very similar to that observed in I. The intermediate exchange region of the ^{13}C isopropyl methyl region could again be duplicated assuming that enantiomerization occurs by pathway C. The barrier calculated for this molecule is $\Delta G^{\ddagger}{}_{163\text{K}} = 7.9$ kcal/mol.

The barriers to B-N rotation are, thus, in the order III < II < I. In view of the foregoing discussion this ordering is to be expected if the barriers have predominantly steric origin.

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(11) (a) P. G. Perkins and D. H. Wall, *J. Chem. Soc. A*, 1207–1211 (1966); (b) G. H. King, S. S. Krishnamurthy, M. F. Lappert, and J. B. Pedley, *J. Chem. Soc., Faraday Trans.*, 70–83 (1972).

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(14) Dewar and Rona[2] have suggested that nitrogen may, in fact, be pyramidal in aminoboranes. However, the nitrogen inversional barrier would be quite low due to π stabilization of the planar pyramidal inversion state. Thus the nitrogen would appear to be planar on the NMR time scale.

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(16) J. F. Blount, P. Finocchiaro, D. Gust, and K. Mislow, *J. Am. Chem. Soc.*, **95**, 7019–7029 (1973).

(17) J. P. Hummel, D. Gust, and K. Mislow, *J. Am. Chem. Soc.*, **96**, 3679–3681 (1974).

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(19) A variety of other chiral structures can, of course, be proposed provided motions other than, or in addition to, B-N torsion have ceased. However, we have been unable to propose any other stereochemically resonable conformation which is consistent with the observed spectra unless accidental equivalencies occur in ^{13}C and ^{1}H chemical shifts and/or between the energies of dissimilar exchange processes.

(20) These NMR data do not indicate whether the diethylamino group is skewed to or coplanar with the BN$_3$ plane, or even whether it is or is not rotating rapidly about the B-N bond at low temperature. We believe, however, that its rotation has also slowed and will present evidence for this as well as a detailed discussion of the stereodynamics of these and related compounds in a forthcoming full paper.

(21) A detailed topological analysis for such isomerizations has been presented for stereochemically correspondent systems.[8,15,16]

(22) It should be noted that processes analogous to A, B, and C, plus a nonconcerted route like D are the possible pathways to topomerization of the meso structure mentioned above. An analysis of these based on the meso

configuration reveals that *only pathway C is consistent with the observed spectral changes.* Hence regardless of whether the molecule adopts a helically chiral or meso static conformation the N-(i-C_3H_7)$_2$ groups execute concerted rotations as described by C.

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Chemistry of Metal Carbonyl Anions. 8.[1] Derivatives of Pentacarbonylvanadate(−III), $V(CO)_5{}^{3-}$

Sir:

Our recent discovery, that noncluster binary carbonyl trianions of manganese and rhenium, $M(CO)_4{}^{3-}$, are readily synthesized by the reduction of corresponding $M_2(CO)_{10}$ or $M(CO)_5{}^-$ in hexamethylphosphoramide (HMPA),[2] prompted us to investigate whether other "superreduced" organometallics could be prepared.

We now report that the reaction of hexacarbonylvanadate(−I) with sodium metal in *liquid ammonia*[3,4] yields a pyrophoric, deep red substance (I) which has reactivity patterns consistent with those expected of $V(CO)_5{}^{3-}$. For example, the first known derivatives of pentacarbonylvanadate(−III) are prepared in good yield (50–75%) by reacting I with excess Ph_3MCl (M = Sn, Pb). After metathesis of Na^+ for tetraethylammonium ion, the air stable salts $[Et_4N][(Ph_3M)_2V(CO)_5]$[5] (M = Sn, Pb), containing new seven coordinate carbonylvanadate anions, are isolated. Spectra for these substances in THF are very similar in the carbonyl stretching frequency region (ν(CO) for M = Sn, 1985 s, 1931 sh, 1884 vs, 1862 sh cm^{-1}; M = Pb, 1990 s, 1891 vs, 1864 sh cm^{-1}). Although these spectra are significantly less complicated than those observed for related neutral $Ph_3SnV(CO)_5L$ (L = phosphine),[6] they are not consistent with molecules of D_{5h} symmetry for which only one infrared active band is expected.[7] More spectacularly, triphenylphosphinegold chloride reacts with I to give bright purple and air-stable $(Ph_3PAu)_3V(CO)_5$ (ν(CO) in THF 1958 s, 1889 vs, 1845 s cm^{-1}),[8] the first example of an eight-coordinate vanadium carbonyl.[9]

Attempts to further characterize I by infrared spectra have been thwarted by its extreme thermal instability. I cannot be handled in solution or as a solid above −20 °C. In the absence of added reactant, I decomposes primarily to non-carbonyl containing material in addition to small yields (<5%) of $V(CO)_6{}^-$. Proof that complete reduction of $V(CO)_6{}^-$ occurs in liquid ammonia has been obtained by slowly warming solutions of I to room temperature in the presence of triphenylphosphine or 1,2-bis(diphenylphosphino)ethane (dppe). Extensive decomposition occurs during this process; however, the only detectable metal carbonyl containing products in the resulting mixtures are $V(CO)_5PPh_3{}^-$[10] or $V(CO)_5Ph_2PCH_2CH_2PPh_2{}^-$,[11] respectively. Isolation of the latter species, which contains an uncoordinated phosphine, confirms that a pentacarbonylvanadium unit is present during the decomposition of I[12] and provides further evidence that I is likely to be a highly reduced pentacarbonylvanadate species.[13]

Our work strongly suggests that an entire family of highly reduced metal carbonyl anions[14] should exist. However, certain of these, in addition to the one described above, may prove to be thermally and/or solvolytically unstable and thus elude detection unless preparations are conducted at low temperature. We have strong evidence that other carbonyl species such as $Co(CO)_4{}^-$ and $Ni(CO)_4$ also provide "superreduced" carbonyl anions.[15] These prove to be valuable sources of 15- and 16-electron cobalt and nickel carbonyl fragments, respectively, for organometallic syntheses.[16,17] Ultimately, it is hoped that through these studies we can arrive at some general conclusions on how much negative charge can be added to a transition metal center before reduction and/or loss of coordinated ligands occur.

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(1) Part 7: J. E. Ellis, S. G. Hentges, and R. A. Faltynek, *J. Organomet. Chem.*, in press.

(2) J. E. Ellis and R. A. Faltynek, *J. Chem. Soc., Chem. Commun.*, 966 (1975).

(3) Reduction of $V(CO)_6{}^-$ in HMPA at room temperature results in complete loss of coordinated carbon monoxide.

(4) Treatment of bis(diglyme)sodium hexacarbonylvanadate with a slight excess over the required amount of sodium metal (3.3 equiv) in liquid ammonia (50–75 ml per gram of carbonyl complex) at −78 °C provides a deep red solution free of $V(CO)_6{}^-$ within 30 min. Removal of liquid ammonia at −50 °C under vacuum provides a dark red solid which rapidly decomposes to a brown tar above −20 °C.

(5) M = Sn. Anal. Calcd for $C_{49}H_{50}NO_5Sn_2V$: C, 57.93; H, 4.94; N, 1.37; Sn, 23.62. Found: C, 57.88; H, 4.78; N, 1.18; Sn, 23.15. M = Pb. Anal. Calcd for $C_{49}H_{50}NO_5Pb_2V$: C, 49.11; H, 4.21; N, 1.17; Pb, 34.58. Found: C, 48.71; H, 4.19; N, 1.18; Pb, 34.27. The tin and lead salts are crystalline, yellow and orange substances, respectively, which decompose above 100 °C without melting.

(6) A. Davison and J. E. Ellis, *J. Organomet. Chem.*, **36**, 113 (1972).

(7) Ion pair effects are known to complicate spectra of carbonyl anions but are probably unimportant here since the spectra of these salts in HMPA are virtually identical with those in THF. Several groups have shown that HMPA is an especially useful solvent for recording infrared spectra of carbonyl monoanions since they are largely independent of cation and concentration, and consistent with those expected for an uncoordinated carbonyl anion in an essentially symmetrical "solvent-surrounded" ion environment. E.g., see M. Y. Darensbourg, D. J. Darensbourg, D. Burns, and D. A. Drew, *J. Am. Chem. Soc.*, **98**, 3127 (1976); ref. 1.

(8) Anal. Calcd for $C_{59}H_{45}Au_3O_5P_3V$: C, 45.17; H, 2.89; Au, 37.67; P, 5.92; V, 3.25; mol wt, 1569. Found: C, 44.94; H, 2.92; Au, 37.02; P, 5.60; V, 3.15; mol wt in benzene by osmometry: 1530. Also, the substance shows no conductivity in THF.

(9) If the η-cyclopentadienyl group is assumed to occupy three positions in the coordination sphere, then $(C_5H_5)_2V(CO)_2{}^+$ also contains an eight-coordinate vanadium: F. Calderazzo and B. Baciarelli, *Inorg. Chem.*, **2**, 721 (1963).

(10) Isolated as $[Et_4N][V(CO)_5PPh_3]$ in 10% yield and identical with genuine material reported previously: A. Davison and J. E. Ellis, *J. Organomet. Chem.*, **31**, 239 (1971).

(11) Infrared evidence that this species forms as an intermediate during the photolysis of $V(CO)_6{}^-$ in the presence of dppe has been presented (ref 9); however, the material was otherwise uncharacterized. We have isolated orange red, crystalline $[Et_4N][V(CO)_5Ph_2PCH_2CH_2PPh_2]$ in 9% yield and confirmed its formulation on the basis of elemental analysis: Anal. Calcd for $C_{39}H_{44}NO_5P_2V$: C, 65.09; H, 6.16; N, 1.95. Found: C, 64.95; H, 6.13; N, 1.97; infrared spectra (ν(CO) in THF: 1970 s, 1861 m, 1828 vs cm^{-1}) and chemical evidence (e.g., it reacts with Ph_3SnCl to quantitatively produce the known $Ph_3SnV(CO)_4$dppe[6]).

(12) We suggest that I reduces ammonia or possibly coordinated carbon monoxide to provide coordinatively unsaturated $V(CO)_5{}^-$ and/or $V(CO)_5NH_3{}^-$ (D. Rehder, *J. Organomet. Chem.*, **37**, 303 (1972)) which then reacts with phosphines to yield the observed species. The possibility that coordinated carbon monoxide is reduced in this process is particularly exciting and is under investigation. If this occurs, it will undoubtedly help to define the lowest molecular charge possible for binary metal carbonyl anions.

(13) At this time we cannot exclude the possibility that I is, in fact, $HV(CO)_5{}^{2-}$, $[V(CO)_5]_2{}^{4-}$, or, possibly, a paramagnetic radical anion. All of these species could give rise to derivatives of pentacarbonylvanadate(−III) in the observed yields.

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