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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References and Notes

(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 $Ph_3SnV(CO)_4dppe$[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.

(14) A recent review on known carbonyl anions and derivatives thereof is: J. E. Ellis, *J. Organomet. Chem.*, **86,** 1 (1975).

(15) J. E. Ellis, S. G. Hentges, R. A. Faltynek, M. C. Palazzotto, T. Hayes, and M. Winzenberg, to be submitted.

(16) A review on 17, 16, and 15 electronically equivalent groups is: J. E. Ellis, *J. Chem. Educ.*, **53,** 2 (1976).

(17) For other work on the use of metal carbonyl fragments see J. E. Ellis, R. Fennell, and E. A. Flom, *Inorg. Chem.*, **15,** 2031 (1976).

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