

Highly Reduced Organometallic Complexes of the Vanadium and Chromium Triads

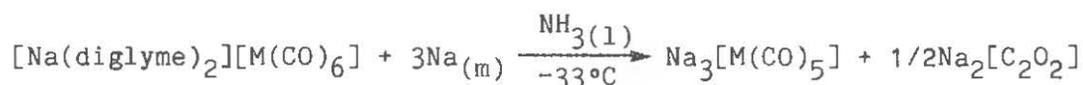
Dave Dempsey

Literature Seminar

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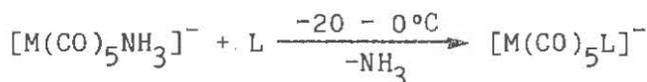
Transition metal carbonyl anions and dianions can be regarded as mimics to the halides and chalcogenides with regard to their reaction chemistry [1]. In 1977 John Ellis reported the synthesis of the first metal carbonyl trianions, $[\text{Mn}(\text{CO})_4]^{3-}$ and $[\text{Co}(\text{CO})_3]^{3-}$ [2]. Existence of these highly reduced trianions suggested that an entire family of super reduced metal carbonyls might exist.

Ellis and coworkers were able to reduce group 5 metals with $\text{Na}_{(m)}$ in liquid NH_3 [3].

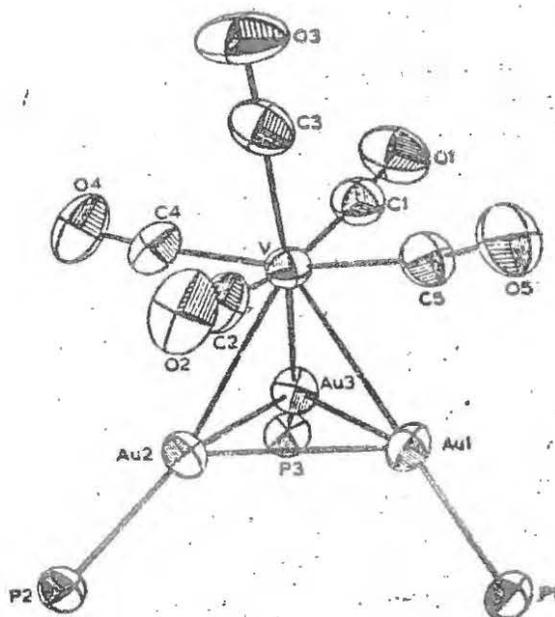


M = V, Nb, Ta

Metathesis of $\text{Na}_3[\text{V}(\text{CO})_5]$ with MCl (M = K, Rb, Cs) yields slightly more stable complexes. The IR spectrum of $\text{Cs}_3[\text{V}(\text{CO})_5]$ shows carbonyl stretches at 1800, 1626, 1563 cm^{-1} , indicating the occurrence of extensive π -backbonding. Attempts to form the hydride anion, $[\text{HM}(\text{CO})_5]^{2-}$, by reacting the trianion with NH_4Cl resulted in the generation of $[\text{M}(\text{CO})_5\text{NH}_3]^-$. This highly unstable complex undergoes facile exchange reactions in the presence of π -acceptor ligands [4].

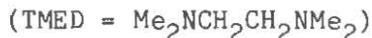
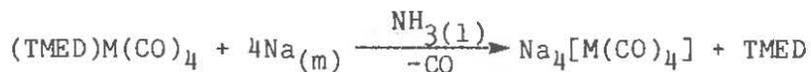


Previous attempts to synthesize the products have resulted in both mono- and disubstituted products [5]. $\text{Na}_3[\text{V}(\text{CO})_5]$ formed $(\text{Ph}_2\text{PAu})_3\text{V}(\text{CO})_5$ when treated with 3 equivalents of Ph_2PAuCl . An X-ray structure analysis revealed the complex to be a tetrahedral Au-V cluster, the first 8-coordinate vanadium complex (see figure below) [6].



Crystal Structure of $(\text{Ph}_2\text{PAu})_3\text{V}(\text{CO})_5$

Unlike the Group 5 metals, direct reduction of $\text{Na}_2[\text{M}(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) gave no isolable products [7]. However reduction was accomplished by Ellis' "labilization reduction" method [7] in which a labile ligand is displaced during the reaction:

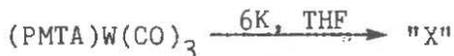


Reaction of the tetraanions with excess NH_4Cl generated the diammine complex $\text{M}(\text{CO})_4(\text{NH}_3)_2$. Curiously, when the tetraanions were treated with 2-3 equivalents of NH_4Cl formation of the dihydride dianion, $[\text{H}_2\text{M}_2(\text{CO})_8]^{2-}$, is observed [7]. The tungsten dihydride when reacted with 2 equivalents of $\text{K}[\text{sec-Bu}_3\text{BH}]$ generated the dihydride dianion monomer:



In contrast, reaction with the molybdenum analog gave $[\text{HMo}(\text{CO})_3]_4^{4-}$ cluster [8].

Reduction of $(\text{PMTA})\text{W}(\text{CO})_3$ ($\text{PMTA} = 1,1,4,7,7$ -pentamethyldiethylenetriamine) with 6 equivalents of $\text{K}_{(m)}$ gave an uncharacterized product "X" in low yields [9].



When "X" reacted with 6 equivalents of Ph_3SnCl followed by metathesis with Et_4NCl in ethanol (EtOH) gave $[(\text{Ph}_3\text{Sn})_2\{(\text{Ph}_2\text{Sn})_2\text{OEt}\}\text{W}(\text{CO})_3]^-$ [9]. An x-ray structure analysis of the isopropanol analog shows a bidentate $[(\text{Ph}_2\text{Sn})_2\text{O-i-Pr}]$ ligand formed from the cleavage of Sn-C bond [10]. Solution IR studies indicate the Sn-C bond is cleaved before the metathesis [9].

Highly reduced transition metal carbonyl anions possess interesting bonding characteristics and can be used as precursors for the synthesis of new organometallic compounds. The synthesis of other highly reduced complexes, such as the presently unknown $[\text{Ti}(\text{CO})_6]^{2-}$, and further study of the reactivity of such complexes is underway in several laboratories.

References

1. Ellis, J. E., "The Reactivity of Metal Carbonyl Anions and Their Derivatives," J. Organometal. Chem. **1975**, 8, 1.
2. (a) Ellis, J. E.; Faltynek, R. A., "Highly Reduced Organometallic Anions. 1. Syntheses and Properties of Tetracarbonylmetalate (3-) Anions of Manganese and Rhenium," J. Am. Chem. Soc. **1977**, 99, 1801.
(b) Ellis, J. E.; Barger, P. T.; Winzenburg, M. L., "Derivatives of Tricarbonylmetalates (-III) of Cobalt, Rhodium, and Iridium," J. Chem. Soc., Chem. Commun. **1977**, 686.

3. (a) Fjare, K. L.; Hayes, T. G.; Ellis, J. E., "Highly Reduced Organometallics. 4. Synthesis and Chemistry of Pentacarbonylvanadate(3-) Ion, $V(CO)_5^{3-}$," J. Am. Chem. Soc. **1981**, 103, 6100.
 (b) Warnock, G. F.; Sprauge, J.; Fjare, K. L.; Ellis, J. E., "Highly Reduced Organometallics. 10. Synthesis and Chemistry of Pentacarbonylmetallate(3-) Ions of Niobium and Tantalum, $M(CO)_5^{3-}$," J. Am. Chem. Soc. **1983**, 105, 672.
4. (a) Fjare, K. L.; Ellis, J. E., "Highly Reduced Organometallics. 7. The Synthesis of Alkyl and Phenyl Isocyanide and Related Monosubstituted Vanadium Carbonyl Anions, $V(CO)_5L^-$, by Thermal Substitution of (Amine)pentacarbonylvanadate(1-), $V(CO)_5NH_3^-$," Organometallics **1982**, 1, 898.
 (b) Fjare, K. L.; Ellis, J. E., "Highly Reduced Organometallics. 8. The Synthesis of (Phosphine)pentacarbonylvanadate(1-), $V(CO)_5PR_3^-$, by the Thermal Substitution of (Amine)pentacarbonylvanadate(1-), $V(CO)_5NH_3^-$," Organometallics **1982**, 1, 1373.
5. (a) Rehder, D. J., "Photochemistry Substitutions of Hexacarbonylvanadate(1-)," J. Organometal. Chem. **1972**, 37, 303.
 (b) Rehder, D. J., "Substitution Products of $[V(CO)_6]^-$ and $[\eta^5-CpV(CO)]$ with Di- and Tetra-Tertiary Phosphines," J. Organometal. Chem. **1976**, 122, 53.
6. Ellis, J. E.; "Highly Reduced Organometallics. 5. Synthesis, Properties, and the Molecular Structure of $(Ph_3PAu)_3V(CO)_5$, A Gold-Vanadium Cluster," J. Am. Chem. Soc. **1981**, 103, 6106.
7. Lin, J. T.; Hagen, G. P.; Ellis, J. E., "Highly Reduced Organometallics. 9. Synthesis and Characterization of the Tetrasodium Tetracarbonylmetallates (4-) of Chromium, Molybdenum, and Tungsten, $Na_4M(CO)_4$. Their Reactions with Weak Acids to Generate $H_2M_2(CO)_8^{2-}$ (M = Cr, Mo, W)," J. Am. Chem. Soc. **1983**, 105, 2296.
8. Lin, J. T.; Ellis, J. E., "Highly Reduced Organometallics. 15. Coordinatively Unsaturated Tetranuclear Hydrido Carbonyl Clusters of Molybdenum and Tungsten. Structural Characterization of $[(n-C_3H_7)_4N]_4[HMo(CO)_3]_4$," J. Am. Chem. Soc. **1983**, 105, 6252.
9. Rochfort, G. L.; Ellis, J. E., "Highly Reduced Organometallics. 11. Formal Derivatives of the Tricarbonylmetallates (6-) of Chromium, Molybdenum, and Tungsten," J. Organomet. Chem. **1983**, 250, 265.
10. Rochfort, G. L.; Ellis, J. E. "Highly Reduced Organometallics. 12. The Reaction of Carbonyltungstate anion with Triphenyltin Chloride Resulting in a Phenyl-tin Bond Cleavage. X-Ray Structural Characterization of the Novel Salt: $[Me_4N]((Ph_3Sn)_2\{(Ph_3Sn)_2O-i-Pr\}W(CO)_3)$," J. Organomet. Chem. **1983**, 250, 277.