

Reviews

Metal Carbonyl Anions: from $[\text{Fe}(\text{CO})_4]^{2-}$ to $[\text{Hf}(\text{CO})_6]^{2-}$ and Beyond[†]

John E. Ellis

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received February 14, 2003

A chronological survey of the syntheses and characterizations of homoleptic mononuclear metal carbonyl anions is presented, from the first isolated example, $[\text{Fe}(\text{CO})_4]^{2-}$, to the most recently reported species, $[\text{Hf}(\text{CO})_6]^{2-}$. These materials are of historical interest, since they are the first compounds to contain transition metals in formal negative oxidation states, but remain important reagents in all areas of chemical synthesis and often closely resemble electron-rich nonmetallic compounds in their ability to function as Lewis and Brønsted bases, nucleophiles, and/or reducing agents. Prospects for the syntheses of new carbonyl anions for the very early and late transition metals and the lanthanides and actinides are also discussed.

I. Introduction

Metal carbonyl anions have a rich history in chemistry and are important precursors to a tremendous variety of organometallic, inorganic, and organic species. They are also of considerable interest as the first compounds to contain transition metals in formally negative oxidation states¹ and exhibit reactivity patterns that bear striking similarities to those of halides, chalcogenides, and pnictides.² For example, metal carbonyl monoanions such as $[\text{Co}(\text{CO})_4]^-$, $[\text{Mn}(\text{CO})_5]^-$, $[\text{V}(\text{CO})_6]^-$, etc. are now often considered to be transition-metal analogues of classic pseudohalides.³ Roald Hoffman utilized these and many other significant parallels in transition-metal and main-group chemistry in his remarkable development of “isobal relationships” that are described in his Nobel lecture of 1981 entitled “Building bridges between inorganic and organic chemistry”.⁴

Since the main objective of this brief account is to highlight the synthesis and characterization of homoleptic mononuclear metal carbonyl anions in a historical context, little emphasis will be given to substituted (or heteroleptic) carbonyl anions, such as $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$, or di- and polynuclear carbonyl anions, both tremendously important topics,⁵ or to the reaction chemistry of carbonyl anions, which has been the focus of several prior reviews.^{1,2,6–11} After a short introduction

to metal carbonyls and a survey of the early and truly challenging period of metal carbonyl anion research, roughly from 1905 to 1950, i.e., before Raman, infrared, and nuclear magnetic resonance spectra were routinely available, the carbonyl anions will be grouped and discussed in order of increasing negative molecular charge to emphasize key differences between carbonyl-metalate mono-, di-, tri-, and tetraanions.

Ludwig Mond's discovery of volatile and highly refractive liquid carbonyls of nickel¹² and iron^{13a} (reported almost simultaneously by Berthelot^{13b}) in the late 19th century provided the world with an unprecedented class of organometallic compounds, the first to contain zero-valent metals. The physical properties of these substances were so unbelievably different from those of most previously known transition-metal compounds,¹⁴

(5) Superb accounts of both subjects, organized according to individual metals, appear in: Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, U.K., 1982; Vols. 3–6.

(6) Hieber, W.; Beck, W.; Braun, G. *Angew. Chem.* **1960**, *72*, 795.

(7) (a) King, R. B. *Adv. Organomet. Chem.* **1964**, *2*, 157. (b) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417.

(8) Abel, E. W.; Stone, F. G. A. *Q. Rev. Chem. Soc.* **1970**, *24*, 498.

(9) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342. This account summarizes Collman's detailed studies of the physical and chemical properties of $[\text{Fe}(\text{CO})_4]^{2-}$.

(10) Behrens, H. *Adv. Organomet. Chem.* **1980**, *18*, 1.

(11) Ellis, J. E. *Adv. Organomet. Chem.* **1990**, *31*, 1.

(12) Mond, L.; Langer, C.; Quincke, F. *J. Chem. Soc. (London)* **1890**, 57, 749. A reprint of this article appears in the Journal of Organometallic Chemistry (*J. Organomet. Chem.* **1990**, *383*, 1), a special issue devoted to metal carbonyls on the 100th anniversary of the discovery of $\text{Ni}(\text{CO})_4$.

(13) (a) Mond, L.; Langer, C. *J. Chem. Soc. (London)* **1891**, *59*, 604. (b) Berthelot, M. *C. R. Acad. Sci. Paris* **1891**, *112*, 1343.

(14) The vast majority of transition-metal compounds known in the 19th century were poorly volatile or nonvolatile solids. Important exceptions reported before $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ include the high-valent species CrO_2Cl_2 , Mn_2O_7 , RuO_4 , and OsO_4 . Original literature citations to these molecular oxides appear in: Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds. *Comprehensive Coordination Chemistry*; Pergamon: New York, 1987; Vols. 3–5.

[†] Dedicated to Professor Dr. Wolfgang Beck for his wonderful friendship, collaboration, and support and in recognition of his many outstanding contributions to metal carbonyl anion chemistry over the past 40+ years.

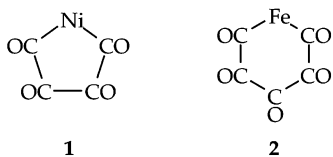
(1) Beck, W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 168.

(2) Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1.

(3) (a) Ellis, J. E. *J. Chem. Educ.* **1976**, *53*, 2. (b) Golub, A. M.; Köhler, H.; Skopenko, V. V. *Chemistry of Pseudohalides*; Elsevier: Amsterdam, 1986; Chapter 1.

(4) Hoffman, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

but similar to nonmetallic substances, that in 1892 Mond proposed distinctly organic-like cyclic structures for $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ (**1** and **2**).¹⁵ However, in 1909



Alfred Werner suggested that these species should be regarded as normal coordination compounds with the metals bound to discrete CO ligands.¹⁶ With Werner's model for metal carbonyls, Irving Langmuir was able to rationalize the stoichiometry of the known mono-nuclear complexes, i.e., $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and $\text{Mo}(\text{CO})_6$, on the basis that the metals would formally achieve the electron count of the next inert gas by binding to the appropriate number of CO ligands.¹⁷ Later, Neville Sidgwick and William Manhot elaborated on this electron-counting scheme¹⁸ and established what is now commonly referred to as the "18-electron"¹⁹ or "noble gas rule",²⁰ a logical extension of the octet rule of G. N. Lewis²¹ to accommodate the valence d subshell of transition metals. Undoubtedly, the most well-known early proponent of Werner's views on the constitution of metal carbonyls was Walter Hieber.²² His extensive and systematic pioneering studies on these compounds were of critical importance in transforming what were originally regarded as laboratory curiosities into materials of key importance throughout science, engineering, and commerce.²³ The strong influence and significance of Werner's ideas on Hieber's early research program (1928–1950) may be gained from the following passage by Helmut Behrens,¹⁰ who was a close associate of Hieber for many years:

One must bear in mind that at this time none of the spectroscopic methods, which are taken for granted nowadays, were available, so that resort had to be made to extremely careful analytical work. However, the so-called 'noble gas rule' was an aid to research at that time, a concept which should not be underestimated since it played a determining role in planning new experiments and contributed to many successes.

In 1932 a Raman study of $\text{Ni}(\text{CO})_4$ provided the first independent evidence for the presence of individual CO

ligands in metal carbonyls.^{24a} Shortly thereafter, the molecular structures of $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ were established (by electron diffraction).^{24b,c} Interestingly, quite precise single-crystal X-ray structural characterizations of these "archetypical metal carbonyls" were reported rather recently in this journal.²⁵

II. Discovery and Isolation of the First Homoleptic Metal Carbonyl Anions and Derivatives Thereof: $[\text{Fe}(\text{CO})_4]^{2-}$ and $[\text{Co}(\text{CO})_4]^-$, 1905–1950

Early investigations of the chemical properties of $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ by Mond and others indicated that iron carbonyl was far more interesting (and substantially less toxic) than nickel carbonyl.²⁶ Although cobalt carbonyls and the group 6 carbonyls were known before 1930, they were more difficult to prepare in quantity than $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$.²⁷ For this reason, most early (≤ 1930) research on the reactions of metal carbonyls involved iron.

In 1905 Sir James Dewar published the first detailed study of the physical and chemical properties of $\text{Fe}(\text{CO})_5$.²⁸ In the context of this review, the following passage is of particular interest:

When a bulb containing iron carbonyl was broken in alcoholic potash solution [i.e., $\text{C}_2\text{H}_5\text{OH-KOH}$], beautiful colourless tabular crystals having a pearly luster were at once produced; at the surface of the liquid these were at once oxidized by the air with the formation of a reddish brown precipitate.

Therein Dewar described nearly 100 years ago the first reaction of a zerovalent metal carbonyl with hydroxide or alkoxide, reactions that are now known to almost invariably result in the formation of either homoleptic or substituted metal carbonyl anions.²⁹ On the basis of studies carried out later on by several groups, it is possible that Dewar's colorless, but apparently quite air sensitive, crystals were $\text{K}_2[\text{Fe}(\text{CO})_4]$ (vide infra).^{30,31} Thus, the man who brought us the Dewar flask also was undoubtedly the first one to prepare metal carbonyl anions! However, the nature of the

(24) (a) Anderson, J. S. *Nature* **1932**, *130*, 1002. (b) $\text{Ni}(\text{CO})_4$: Brockway, L. O.; Cross, P. C. *J. Chem. Phys.* **1935**, *3*, 328. (c) $\text{Fe}(\text{CO})_5$: Ewens, R. V. G.; Lister, M. W. *Trans. Faraday Soc.* **1939**, *35*, 681.

(25) Braga, D.; Grepioni, F.; Orpen, A. G. *Organometallics* **1993**, *12*, 1481.

(26) Mond, R. L. *J. Soc. Chem. Ind.* **1930**, *49*, 271. Details of the particularly toxic properties of $\text{Ni}(\text{CO})_4$ are discussed in this review by R. L. Mond, the son of Ludwig Mond, whose health was seriously affected by repeated exposures to this substance. Insightful comments on the treacherous and insidious nature of $\text{Ni}(\text{CO})_4$ are also presented in a more recent synthesis of this compound: Gilliland, W. L.; Blanchard, A. A. *Inorg. Synth.* **1946**, *2*, 234.

(27) Calderazzo, F.; Ercoli, R.; Natta, G. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P. Eds.; Interscience: New York, 1968; Vol. 1. This is undoubtedly the single most comprehensive review available on the preparation, structure, and properties of metal carbonyls and derivatives thereof. It represents a "gold mine of information" on all aspects of metal carbonyl chemistry and contains a particularly strong historical development of the subject.

(28) Dewar, J.; Jones, H. O. *Proc. R. Soc. (London)* **1905**, *76A*, 558.

(29) A well-referenced account of early research on the reactions of metal carbonyls with hydroxide ion and related Lewis bases appears in: Emeleus, H. J.; Anderson, J. S. *Modern Aspects of Inorganic Chemistry*, 3rd ed.; Van Nostrand: Princeton, NJ, 1960; pp 267–283.

(30) Since precipitation of alkali-metal carbonates has been reported to occur in related reactions of $\text{Fe}(\text{CO})_5$ with hydroxides/alkoxides in alcohols,³¹ it is also possible that the colorless crystals described by Dewar were K_2CO_3 covered by an alcoholic solution of air-sensitive carbonylferrates. However, also see ref 39a (vide infra).

(31) Feigl, F.; Krumholz, P. *Monatsh. Chem.* **1932**, *59*, 314.

(15) Mond, L. *Proc. R. Inst. G. B.* **1892**, *13*, 668. For an especially lucid and detailed account of the early history of metal carbonyls see: Trout, W. E. *J. Chem. Educ.* **1937**, *14*, 453, 575; **1938**, *15*, 77, 113.

(16) Werner, A. *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, 2nd ed.; F. Vieweg und Sohn: Braunschweig, Germany, 1909.

(17) Langmuir, I. *Science* **1921**, *54*, 59.

(18) (a) Sidgwick, N. V. *The Electronic Theory of Valency*; Oxford University Press: London, 1927. (b) Manhot, W. *Ann.* **1929**, *470*, 261. (c) Sidgwick, N. V.; Bailey, R. W. *Proc. R. Soc. (London)* **1934**, *144*, 521.

(19) (a) Mitchell, P. R.; Parish, R. V. *J. Chem. Educ.* **1969**, *46*, 811. (b) Elschenbroich, Ch.; Salzer, A. *Organometallics, A Concise Introduction*, 2nd Ed.; VCH: Weinheim, Germany, 1992; pp 186–191.

(20) Holleman, A. F.; Wiberg, E. *Inorganic Chemistry*, 34th ed.; Academic Press: San Diego, CA, 2001; pp 1174–1177, 1201–1203.

(21) Lewis, G. N. *J. Am. Chem. Soc.* **1916**, *38*, 762.

(22) Hieber, W. *Adv. Organomet. Chem.* **1970**, *8*, 1.

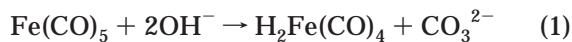
(23) In addition to ref 22, two outstanding accounts of Walter Hieber's scientific career appear in the following articles: (a) Behrens, H. The Chemistry of Metal Carbonyls: The Life Work of Walter Hieber. *J. Organomet. Chem.* **1975**, *94*, 139. (b) Herrmann, W. A. 100 Years of Metal Carbonyls: A Serendipitous Chemical Discovery of Major Scientific and Industrial Impact. *J. Organomet. Chem.* **1990**, *383*, 21.

generally brown to red brown reaction mixtures obtained from the dissolution of $\text{Fe}(\text{CO})_5$ in aqueous or alcoholic alkali remained obscure for many years, due in part to their highly air-sensitive character.

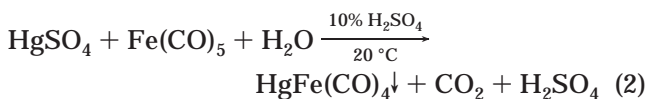
In the early 1920s Freundlich and co-workers investigated these and related solutions³² and discovered that they changed to a bright red upon acidification, accompanied by the formation of an unknown substance having a "characteristic putrid odor" (vide infra). By extracting the acidified reaction mixture with ether, they obtained a red ether-soluble component, much later shown to be $[\text{HFe}_3(\text{CO})_{11}]^-$.³³ Oxidation of the ether fraction with dry CuSO_4 and subsequent removal of ether afforded deep green crystals of the previously known " $\text{Fe}(\text{CO})_4$ ",³⁴ established by Hieber in 1930 to be $\text{Fe}_3(\text{CO})_{12}$.³⁵ In this fashion Freundlich obtained the first qualitative evidence that the $\text{Fe}(\text{CO})_5$ -alkali reactions gave products containing iron tetracarbonyl units.

In the late 1920s Hieber's group discovered that acidification of products obtained from the reaction of $\text{Fe}(\text{CO})_5$ and ethylenediamine generated a substance having an "extraordinarily intense repugnant smell",²² akin to that previously noted by Freundlich (vide supra). Through superb and extremely difficult experimental work, Hieber and Leutert identified the volatile substance derived from both the $\text{Fe}(\text{CO})_5$ -alkali³⁶ and ethylenediamine³⁷ reactions as $\text{H}_2\text{Fe}(\text{CO})_4$, the first carbonyl hydride.³⁸ Because the Brønsted acid character of $\text{H}_2\text{Fe}(\text{CO})_4$ was not established until later,³⁹ for several years Hieber represented the reaction of $\text{Fe}(\text{CO})_5$

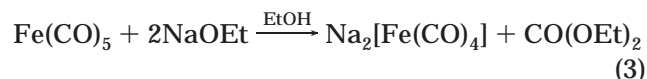
and excess hydroxide ion by eq 1.^{40,41} However, in the



same period of time, Feigl and Krumholz isolated several compounds from $\text{Fe}(\text{CO})_5$ -alkali reactions that were formulated as "salts of iron carbonyl hydride," including $[\text{Ni}(\text{NH}_3)_6][\text{HFe}(\text{CO})_4]_2$ and $\text{Na}[\text{HFe}(\text{CO})_4] \cdot \text{CH}_3\text{OH}$.^{31,42} They also showed that treatment of these products with acetic or sulfuric acids produced $\text{H}_2\text{Fe}(\text{CO})_4$.⁴² Most interesting was a suggestion in 1933 by Feigl and Krumholz that a compound previously reported by Hieber and Leutert as the nonionic $\text{Fe}_2(\text{CO})_4 \cdot (\text{en})_3$ (en = ethylenediamine), obtained from the reaction of $\text{Fe}(\text{CO})_5$ with en ,³⁷ could be reformulated as the ionic species, i.e., $[\text{Fe}(\text{en})_3][\text{Fe}(\text{CO})_4]$.⁴² In 1957 Hieber established that this was indeed the correct formulation!⁴³ Thus, this substance, reported in 1931,³⁷ appears to be the first isolated compound to contain discrete $[\text{Fe}(\text{CO})_4]^{2-}$ units. Significant early studies on iron carbonyl chemistry were also carried out by Hock and Stuhlman, who obtained the first mixed metal carbonyls, e.g. $(\text{ClHg})_2\text{Fe}(\text{CO})_4$ and oligomeric $\text{HgFe}(\text{CO})_4$, by the direct reaction of $\text{Fe}(\text{CO})_5$ with acidic aqueous solutions of HgCl_2 and HgSO_4 , respectively (eq 2).⁴⁴ They also postulated that

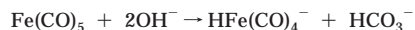


the interaction of $\text{Fe}(\text{CO})_5$ with sodium ethoxide afforded a "sodium analog" of $\text{HgFe}(\text{CO})_4$, i.e., $\text{Na}_2\text{Fe}(\text{CO})_4$, by eq 3.⁴⁵ Although no compelling evidence for the existence



of $[\text{Fe}(\text{CO})_4]^{2-}$ in this or related strongly alkaline solutions was obtained until many years later,³⁹ these early studies, particularly the ones by Feigl and Krumholz,⁴² were the first to point to the likely existence of homoleptic metal carbonyl anions.

(40) For example, see: Hieber, W. *Angew. Chem.* **1936**, *49*, 463. On the basis of the acid dissociation constants of $\text{H}_2\text{Fe}(\text{CO})_4$, $K_1 = 3.6 \times 10^{-5}$ and $K_2 = 1 \times 10^{-14}$, later determined by Hieber,^{39b} and of H_2CO_3 , $K_1 = 1.3 \times 10^{-4}$, and $K_2 = 4.7 \times 10^{-11}$,⁴¹ a more accurate representation of the reaction shown in eq 1 would be



Sternberg et al. have also discussed this issue: Sternberg, H. W.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1957**, *79*, 6116.

(41) See ref 20, p 808.

(42) Feigl, F.; Krumholz, P. *Z. Anorg. Allg. Chem.* **1933**, *215*, 242 and references therein. Hieber and other groups later showed that several of the substances reported by Feigl and Krumholz were genuine salts; however, others were not. For example, " $[\text{Cd}(\text{NH}_3)_2][\text{Fe}(\text{CO})_4]$ " and " $[\text{Cd}[\text{Fe}(\text{CO})_4]]$ ", proposed to be ionic species by Feigl and Krumholz, were later established to be nonelectrolytes containing $\text{Fe}-\text{Cd}$ bonds: Ernst, R. D.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2090, 2098.

(43) Hieber, W.; Sedlmeier, J.; Werner, R. *Chem. Ber.* **1957**, *90*, 278.

(44) (a) Hock, H.; Stuhlmann, H. *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 2097. (b) Hock, H.; Stuhlmann, H. *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 431, 2690. Octahedral $\text{cis}-(\text{ClHg})_2\text{Fe}(\text{CO})_4$ and linear $\text{Fe}-\text{Hg}-\text{Cl}$ units have been shown to be present in the chloromercury complex: Baird, H. W.; Dahl, L. F. *J. Organomet. Chem.* **1967**, *7*, 503. Meanwhile, $\text{HgFe}(\text{CO})_4$ was found to be isomorphous with tetrameric $\text{CdFe}(\text{CO})_4$: Neustadt, R. J.; Cymbaluk, T. H.; Ernst, R. D.; Cagle, F. W., Jr. *Inorg. Chem.* **1980**, *19*, 2375.

(45) Hock, H.; Stuhlmann, H. *Chem. Ztg.* **1931**, *55*, 874; *Chem. Abstr.* **1932**, *25*, 935.

(32) (a) Freundlich, H.; Cuy, E. J. *Ber. Dtsch. Chem. Ges.* **1923**, *56*, 2264. (b) Freundlich, H.; Malchow, W. *Z. Anorg. Allg. Chem.* **1924**, *141*, 317.

(33) (a) Hieber, W.; Brendel, G. *Z. Anorg. Allg. Chem.* **1957**, *289*, 324. (b) Hodali, H. A.; Arcus, C.; Shriver, D. F. *Inorg. Synth.* **1980**, *20*, 218.

(34) Earlier, Dewar and Jones showed that this substance could be obtained by thermolysis of $\text{Fe}_2(\text{CO})_9$: Dewar, J.; Jones, H. O. *Proc. R. Soc. (London)* **1906**, *79A*, 66. Due to the poor solubility and/or stability of " $\text{Fe}(\text{CO})_4$ " in a variety of organic solvents used in cryoscopy, attempts by Dewar and Freundlich to determine its molecular mass were unsuccessful.

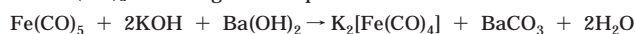
(35) Hieber, W.; Becker, E. *Ber. Dtsch. Chem. Ges.* **1930**, *63*, 1405. Hieber successfully employed $\text{Fe}(\text{CO})_5$ as a solvent (!) in determining the molecular mass of $\text{Fe}_3(\text{CO})_{12}$ by cryoscopic methods.

(36) Hieber, W.; Leutert, F. *Naturwissenschaften* **1931**, *19*, 360.

(37) Hieber, W.; Leutert, F. *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2832.

(38) The isolation and characterization of this highly air sensitive ("explodes in air"), thermally unstable (decomposes above -10°C as a pure liquid), and volatile (extrapolated vapor pressure of 11 Torr at -10°C) colorless liquid (mp -70°C) represented a major early triumph in Hieber's research program. The structure of $\text{H}_2\text{Fe}(\text{CO})_4$ remained controversial for years. Hieber maintained from the beginning that both hydrogens were attached to iron, but an early electron-diffraction study on this substance^{24b} seemed to show that $\text{H}_2\text{Fe}(\text{CO})_4$ had the same basic tetrahedral structure as $\text{Ni}(\text{CO})_4$. Thus, a tautomeric formulation, $\text{Fe}(\text{CO})_2(\text{COH})_2$, was popular in the 1940s (see: Sidgwick, N. V. *Chemical Elements and Their Compounds*; Oxford University Press: London, 1950; pp 547-549). However, later spectroscopic studies unambiguously showed that the dihydride is correctly formulated in the gas and condensed phases as $\text{cis-H}_2\text{Fe}(\text{CO})_4$, containing distorted octahedral iron and two discrete $\text{Fe}-\text{H}$ units. For leading references on and an excellent discussion of $\text{H}_2\text{Fe}(\text{CO})_4$, see: Shriver, D. F.; Whitmire, K. H. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 4, Chapter 31.1, Section 31.1.7.

(39) (a) Krumholz, P.; Stettiner, H. M. A. *J. Am. Chem. Soc.* **1949**, *71*, 3035. In this article is described the first published synthesis of relatively pure $\text{K}_2[\text{Fe}(\text{CO})_4]$, isolated as highly air-sensitive colorless crystals, from the reaction of $\text{Fe}(\text{CO})_5$ with a mixture of aqueous KOH and $\text{Ba}(\text{OH})_2$ according to the equation



Hieber also reported in a 1948 review that $\text{K}_2[\text{Fe}(\text{CO})_4]$ had been obtained earlier by the neutralization of $\text{H}_2\text{Fe}(\text{CO})_4$ by KNH_2 in liquid ammonia.⁶⁴ (b) Hieber, W.; Hübel, W. *Z. Naturforsch.* **1952**, *7B*, 322.

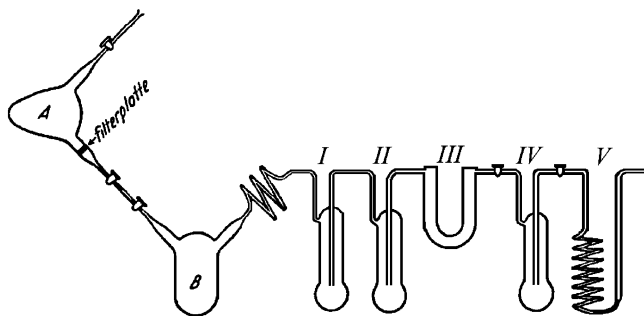


Figure 1. Apparatus used in the original isolation of pure $\text{HCo}(\text{CO})_4$ (from ref 49; reproduced by permission of Wiley/VCH).

Shortly after the discovery of $\text{H}_2\text{Fe}(\text{CO})_4$,^{36–38} Hieber and co-workers began to examine the action of oxygen and nitrogen bases on $\text{Co}_2(\text{CO})_8$.^{46,47} Acidification of products from these reactions often led to the formation of an extremely sensitive material with a highly repulsive odor, reminiscent of $\text{H}_2\text{Fe}(\text{CO})_4$.⁴⁷ Soon thereafter, Hieber isolated the malodorous substance and characterized it as $\text{HCo}(\text{CO})_4$.⁴⁸ Figure 1 depicts the rather elaborate apparatus Hieber and Schulten employed in isolating pure $\text{HCo}(\text{CO})_4$,⁴⁹ which proved to be even less thermally stable as a pure substance than $\text{H}_2\text{Fe}(\text{CO})_4$.^{49–51}

Before Hieber had proven the existence of $\text{HCo}(\text{CO})_4$, an important alternative route to cobalt carbonyl chemistry was reported by Schubert. By employing a distinctly bioinorganic approach (in 1933!), Schubert discovered that strongly alkaline aqueous solutions of a cobalt(II)–cysteine complex efficiently absorbed carbon monoxide at atmospheric pressure and room temperature.⁵² He noted that upon acidification of the resulting solutions with aqueous HCl “some gas is liberated and an extremely choking odor is produced strongly suggestive of impure acetylene”. The unstable substance with “an evil odor” was suggested to be $\text{HCo}(\text{CO})_4$,⁵² on the basis of the isolation of related previously unknown $\text{Hg}(\text{II})$ and $\text{Ag}(\text{I})$ derivatives, $\text{Hg}(\text{Co}(\text{CO})_4)_2$ and $\text{AgCo}(\text{CO})_4$, respectively, and Hieber’s initial report of 1932.⁴⁷ Schubert also found that cysteine or, more accurately, cysteine dianion was not consumed in the carbonylation reaction.⁵² On this basis, Blanchard later represented

(46) Although not initially recognized by Hieber,⁴⁷ many of these reactions provided the first example of complex salts containing $[\text{Co}(\text{CO})_4]^-$ (vide infra). Hieber’s group obtained $\text{Co}_2(\text{CO})_8$ from I.G.-Farbenindustrie Ludwigshafen, which had developed a particularly effective high-pressure synthesis involving direct carbonylation of activated cobalt metal. Mond’s original 1910 synthesis of cobalt carbonyl involved a similar procedure carried out at 150 °C and 30–40 atm of carbon monoxide. For more details, see ref 27, pp 14–15.

(47) Hieber, W.; Mühlbauer, F.; Ehmman, E. A. *Ber. Dtsch. Chem. Ges.* **1932**, *65*, 1090.

(48) Hieber, W. Z. *Elektrochem.* **1934**, *40*, 158; *Chem. Abstr.* **1935**, *28*, 3328.²

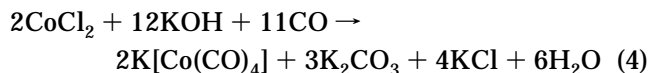
(49) Hieber, W.; Schulten, H. Z. *Anorg. Allg. Chem.* **1937**, *232*, 29. Colorless crystalline $\text{HCo}(\text{CO})_4$, mp -26.2 °C, immediately turns to a yellow hue on melting, due to its facile decomposition to $\text{Co}_2(\text{CO})_8$ and H_2 . Interestingly, the (extrapolated) nbp of $\text{HCo}(\text{CO})_4$ is 47 ± 3 °C,⁵⁰ close to that reported for $\text{Ni}(\text{CO})_4$ (43 °C).²⁷

(50) Orchin, M.; Roth, C. A. J. *Organomet. Chem.* **1980**, *187*, 103.

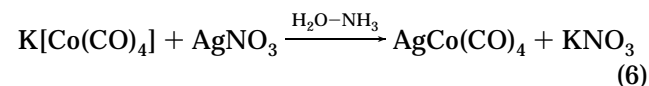
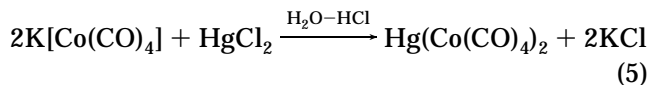
(51) In a later synthesis of $\text{HCo}(\text{CO})_4$, via $\text{K}[\text{Co}(\text{CO})_4]$, it was noted that the vapor of this hydride under a stream of carbon monoxide was quite thermally stable at room temperature. Its odor was described as “so intolerable that the danger from inhaling it is much less than from nickel tetracarbonyl”. See: Gilmont, P.; Blanchard, A. A. *Inorg. Synth.* **1946**, *2*, 238.

(52) Schubert, M. P. J. *Am. Chem. Soc.* **1933**, *55*, 4563.

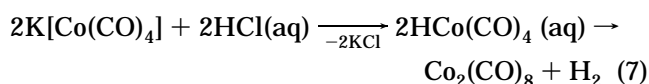
Schubert’s reaction by eq 4.⁵³ Thus, the formation of the



mercury and silver derivatives are now understood in terms of simple “salt displacement” reactions, i.e., eqs 5 and 6. Also, acidification of the original solution led



to the precipitation of $\text{Co}_2(\text{CO})_8$, the latter arising from decomposition of $\text{HCo}(\text{CO})_4$ (eq 7).^{67a}



Schubert’s discoveries were important because $\text{Co}_2(\text{CO})_8$ and derivatives thereof were not previously available by atmospheric-pressure carbonylations of cobalt metal or cobalt salts. Reductions of transition-metal halides, oxides, or related precursors in the presence, or followed by the addition, of carbon monoxide are now the most important general routes to homoleptic metal carbonyls or related anions (vide infra). Although other groups had previously prepared $\text{Ni}(\text{CO})_4$,⁵⁴ $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ ⁵⁵ by the *reductive carbonylation*⁵⁶ of appropriate metal halides or sulfides, Schubert⁵² was the first to directly generate a homoleptic metal carbonyl anion by this method.

The reality of metal carbonyl anions was a contentious issue in the early 1930s. Hieber was particularly critical of Blanchard’s views on $[\text{Fe}(\text{CO})_4]^{2-}$ and $[\text{Co}(\text{CO})_4]^-$,^{57,58} since there was no firm evidence that any compounds containing these metal tetracarbonyl units were ionic in nature. However, the situation dramatically changed in 1938, when Hieber and Fack announced that several classic Werner coordination compounds containing metal carbonyl units, such as $[\text{Ni}(\text{o-phen})_3][\text{HFe}(\text{CO})_4]_2$ and $[\text{Ni}(\text{o-phen})_3][\text{Co}(\text{CO})_4]_2$ (o-phen = *o*-phenanthroline) were strong electrolytes in polar solvents such as acetone and methanol and therefore should be regarded as true salts.⁵⁹ Thus, they established for the first time

(53) Coleman, G. W.; Blanchard, A. A. *J. Am. Chem. Soc.* **1936**, *58*, 2160.

(54) Manchot, W.; Gall, H. *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 678.

(55) (a) Job, A.; Cassal, A. *Bull. Chem. Soc. Fr.* **1927**, *41*, 1041. (b) Job, A.; Rouvillois, J. C. R. *Hebd. Seances Acad. Sci.* **1928**, *187*, 564 and references therein.

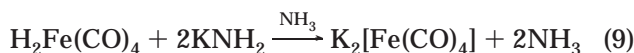
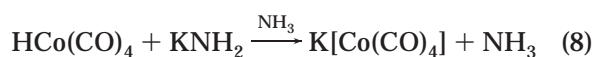
(56) This useful term was first introduced by Harold Podall, who made many important contributions to the syntheses of metal carbonyls in the 1950s and 1960s. See: Podall, H. E. *J. Chem. Educ.* **1961**, *38*, 187.

(57) Blanchard, A. A.; Windsor, M. M. J. *Am. Chem. Soc.* **1934**, *56*, 826. In this article entitled “The Significance of the Hydrides of the Carbonyls of Iron and Cobalt”, Blanchard and Windsor were the first to use the noble-gas rule to propose the existence of metal carbonyl anions, i.e., $[\text{Co}(\text{CO})_4]^-$ and $[\text{Fe}(\text{CO})_4]^{2-}$. They also correctly predicted that the anions would be isostructural with the known isoelectronic $\text{Ni}(\text{CO})_4$.

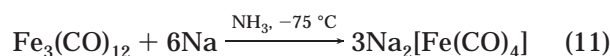
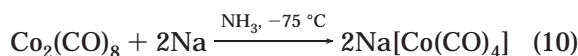
(58) Blanchard, A. A. *Chem. Rev.* **1937**, *21*, 3. Blanchard was an important early participant in metal carbonyl chemistry, and this review is indicative of his creative and original approach to the subject.

(59) Hieber, W.; Fack, E. Z. *Anorg. Allg. Chem.* **1938**, *236*, 83.

that metal carbonyl anions could exist as discrete species in solution.⁶⁰ Shortly thereafter, Blanchard described metal carbonyl anions as compounds containing transition metals in *negative oxidation states* (or valences),⁶¹ a fundamentally new concept in chemistry!⁶² Even a well-known textbook in 1940 included such a revolutionary species as $[\text{Fe}(\text{CO})_4]^{2-}$.⁶³ Although alkali-metal derivatives of metal carbonyls such as $\text{K}[\text{Co}(\text{CO})_4]$ and $\text{Na}_2[\text{Fe}(\text{CO})_4]$ were considered to be entirely plausible species after 1938, none had been isolated or properly characterized. In the early 1940s Hieber's group rectified this situation by isolating colorless, microcrystalline, and *pyrophoric* $\text{Na}[\text{Co}(\text{CO})_4]$ and $\text{Na}_2[\text{Fe}(\text{CO})_4]$ from the reactions of $\text{HCo}(\text{CO})_4$ and $\text{H}_2\text{Fe}(\text{CO})_4$, respectively, with sodium metal in liquid ammonia. Analogous unsolvated potassium salts were also obtained from corresponding reactions with potassium amide in liquid ammonia (eqs 8 and 9).⁶⁴ Behrens then



independently prepared identical and analytically pure unsolvated sodium salts by direct sodium metal reductions of zerovalent metal carbonyls in liquid ammonia (eqs 10 and 11).⁶⁵ In this fashion, Behrens initiated his



important and extensive studies on the syntheses and reactions of metal carbonyl anions in liquid ammonia.¹⁰

III. Beyond $[\text{Fe}(\text{CO})_4]^{2-}$ and $[\text{Co}(\text{CO})_4]^-$: Homoleptic Mononuclear Metal Carbonyl Anions Discovered after 1950

Significant advances since 1950 have greatly facilitated research on metal carbonyls and their anionic derivatives. These include the development of improved routes to previously known neutral carbonyls, particularly $\text{Cr}(\text{CO})_6$ and those of the 4d and 5d elements,^{27,66} the discovery of $\text{Mn}_2(\text{CO})_{10}$,^{67b} $\text{Tc}_2(\text{CO})_{10}$,⁶⁸ and $\text{V}(\text{CO})_6$,⁶⁹

(60) Later on, but before routine single-crystal X-ray structural analyses were available, Hieber and co-workers used magnetic susceptibility measurements to corroborate the ionic nature of similar species in the solid state. For example, see: Hieber, W.; Werner, R. *Chem. Ber.* **1957**, *90*, 286 and references therein.

(61) Blanchard, A. A. *Chem. Rev.* **1940**, *26*, 409.

(62) In contrast, compounds containing main-group metals or metalloids in negative oxidation states had been known previously, particularly Zintl compounds such as Na_4Sn_9 , Na_3Sb_7 , and so forth, many of which have been subsequently isolated as bona fide salts with discrete anions. See: Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; pp 40–42.

(63) Latimer, W. M.; Hildebrand, J. H. *Reference Book of Inorganic Chemistry*, revised ed.; Macmillan: New York, 1940; p 397.

(64) Unpublished results of Behrens ($\text{HCo}(\text{CO})_4$) and H. Lagally ($\text{H}_2\text{Fe}(\text{CO})_4$) reported in: Hieber, W. *FIAT Review of German Science 1939–1946. Inorganic Chemistry Part II*; Office of Military Government for Germany Field Information Agencies Technical: Wiesbaden, Germany, 1948; pp 120–123.

(65) (a) Behrens, H. *Angew. Chem.* **1949**, *61*, 444. (b) Behrens, H. *Z. Naturforsch.* **1952**, *7b*, 78. (c) Behrens, H.; Weber, R. *Z. Anorg. Allg. Chem.* **1955**, *281*, 190.

the use of spectroscopic methods, especially infrared and NMR spectroscopy,⁷⁰ for the characterization of carbonyls, and the development of new methods, techniques, and apparatus for the handling of air- and heat-sensitive organometallics.⁷¹ Also in recent years, the advent of area detector (CCD) technology and greatly improved methods for handling disorder and twinning problems in single crystals has revolutionized the use of X-ray methods⁷² for the structural characterization of metal carbonyl anions and their derivatives. Indeed, it is now often routine practice for research groups involved in metal carbonyl chemistry to carry out single-crystal X-ray analyses of products before more traditional methods have been employed, with one important exception, namely IR spectral analysis.

Infrared spectroscopy remains the single most powerful technique available for monitoring the reactions of metal carbonyls and for the provisional assignment of structures to new products, because the number, relative intensities, shapes, and energies of the IR-active carbonyl stretching modes, i.e., $\nu(\text{CO})$ absorptions, are extremely sensitive functions of the molecular structure and charge, Z , of a carbonyl complex.⁷⁰ Carbonyl stretching frequencies for mononuclear metal carbonyls generally range from 2200 to 1500 cm^{-1} . Ion pairing between cations and metal carbonyl anions can cause dramatic changes in the $\nu(\text{CO})$ region, due to strong perturbation of the geometry of the anion. Edgell was the first to examine this phenomenon in detail for alkali-metal salts of $[\text{Co}(\text{CO})_4]^-$, $[\text{Mn}(\text{CO})_5]^-$, and $[\text{Fe}(\text{CO})_4]^{2-}$ in a variety of solvents.⁷³ Ion-pairing effects may also greatly influence the chemical reactivities and thermal stabilities of metal carbonyl anions. Collman,⁹ Darensbourg and Darensbourg,⁷⁴ and Shriver⁷⁵ have made key contributions to this important area of metal carbonyl anion

(66) The present commercial availability of homoleptic metal carbonyls for 12 of the 27 d-block elements, i.e., $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), $\text{M}_2(\text{CO})_{10}$ ($\text{M} = \text{Mn}, \text{Re}$), $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$), $\text{Co}_2(\text{CO})_8$, $\text{M}_4(\text{CO})_{12}$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$), $\text{Rh}_6(\text{CO})_{16}$, and $\text{Ni}(\text{CO})_4$, also emphasizes the ease with which one can now study metal carbonyl chemistry and the importance of these materials throughout science and engineering.

(67) (a) Oxidation of $\text{HCo}(\text{CO})_4$ by dioxygen rather than hydronium ion, i.e., the cobalt "hydride" is a strong acid in water, may be responsible for the formation of dicobalt octacarbonyl: Calderazzo, F. Personal communication. (b) Brimm, E. O.; Lynch, M. A.; Sesny, W. J. *J. Am. Chem. Soc.* **1954**, *76*, 3831.

(68) (a) Hileman, J. C.; Higgins, D. K.; Kaesz, H. J. *J. Am. Chem. Soc.* **1961**, *83*, 2953. (b) Hieber, W.; Herget, C. *Angew. Chem.* **1961**, *73*, 579.

(69) (a) Natta, G.; Ercoli, R.; Calderazzo, F.; Alberola, A.; Corradini, P.; Allegra, G. *Att. Acad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat.* **1959**, *27*(8), 107. (b) Ercoli, R.; Calderazzo, F.; Alberola, A. *J. Am. Chem. Soc.* **1960**, *82*, 2966. (c) Calderazzo, F.; Ercoli, R. *Chim. Ind. (Milano)* **1962**, *44*, 990. In fact, a magnesium–zinc mixture was employed in the reducing–carbonylating reaction in eq 15. The actual reducing agent was established to be magnesium metal, where zinc is required for a faster reaction: Calderazzo, F. Personal communication.

(70) See ref 19b, pp 222–231, 295–308.

(71) (a) Shriver, D. F.; Drezdson, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986. (b) Wayda, A. L.; Darensbourg, M. Y. *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; American Chemical Society: Washington, DC, 1987.

(72) Clegg, W.; Blake, A. J.; Gould, R. O.; Main, P. *Crystal Structure Analysis: Principles and Practice*, 1st ed.; Oxford University Press: New York, 2001.

(73) (a) Edgell, W. F.; Yang, M. T.; Koizumi, N. *J. Am. Chem. Soc.* **1965**, *87*, 2563. (b) Edgell, W. F.; Watts, A. T.; Lyford, J.; Risen, W. M. *J. Am. Chem. Soc.* **1966**, *88*, 1815. (c) Edgell, W. F.; Barbetta, A. J. *Am. Chem. Soc.* **1974**, *96*, 415 and references therein.

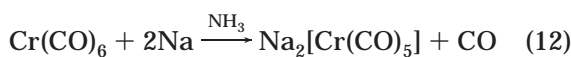
(74) Darensbourg, M. Y.; Darensbourg, D. J.; Burns, D.; Drew, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 3127.

(75) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219 and references therein.

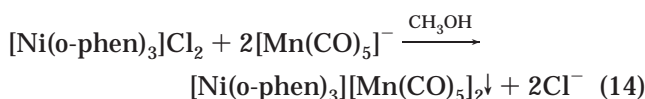
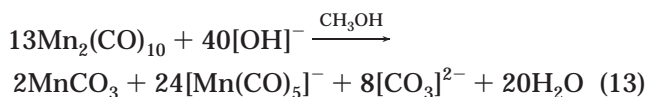
chemistry, which has been superbly reviewed by Marcetta Darensbourg.⁷⁶

In recent years ¹³C NMR spectral analysis has become an increasingly important method for the detection and identification of metal carbonyls, due to substantial improvements in NMR instrumentation.⁷⁷ Indeed, when IR cell materials are incompatible with solvents, as for reactions conducted in liquid ammonia, ¹³C NMR spectroscopy can be the method of choice for the characterization of metal carbonyls in solution.⁷⁸

In the 1950s and thereafter, most metal carbonyl anions were prepared by methods previously introduced by Behrens or Hieber: i.e., either alkali-metal/alkaline-earth-metal reductions¹⁰ or base attack⁶ of zerovalent metal carbonyls. For example, Behrens announced in 1955 that Na₂[Cr(CO)₅] was obtained as a yellow pyrophoric solid from the sodium metal reduction of Cr(CO)₆ in liquid ammonia (eq 12).^{79,80} This discovery



not only provided the first new example of a homoleptic carbonyl anion since [Fe(CO)₄]²⁻ and [Co(CO)₄]⁻ but also established that even the very electropositive early transition metals could possess formal negative oxidation states in compounds. About 2 years later, Hieber employed his classic base attack method to prepare the first isolable compound containing [Mn(CO)₅]⁻; i.e., Mn₂(CO)₁₀ was reacted with methanolic sodium hydroxide to generate a solution of Na[Mn(CO)₅], which was then converted to the slightly soluble and easily handled tris-(*o*-phenanthroline)nickel(II) salt (eqs 13 and 14).⁸¹



Subsequently, many metal carbonyl anions have been produced directly by the reductive carbonylation⁵⁶ of transition-metal halides and related precursors. As mentioned previously, Schubert originally employed this method in the synthesis of [Co(CO)₄]⁻, from the reaction of CO with strongly alkaline aqueous solutions of Co(II) cysteine salts, where the CO functioned as both an incoming ligand and a reducing agent.⁵² However, Schubert's aqueous route is quite unusual,⁸² in that reductive carbonylations generally require reducing agents much stronger than carbon monoxide to produce

(76) Darensbourg, M. Y. *Prog. Inorg. Chem.* **1984**, *33*, 221.

(77) (a) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135. (b) Mann, B. E.; Taylor, B. F. *¹³C NMR Data for Organometallic Compounds*; Academic Press: London, 1981.

(78) See for example: Warnock, G. F. P.; Philson, S. B.; Ellis, J. E. *J. Chem. Soc., Chem. Commun.* **1984**, 893.

(79) Behrens, H. *Angew. Chem.* **1955**, *67*, 521.

(80) Later on it was established that very little carbon monoxide was liberated in this reaction: Weber, R.; Behrens, H. *Z. Anorg. Allg. Chem.* **1957**, *291*, 122.

(81) Hieber, W.; Wagner, G. *Z. Naturforsch.* **1957**, *12B*, 478.

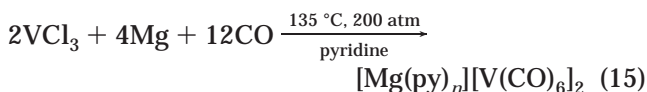
(82) Blanchard has reported on an analogous synthesis of [Co(CO)₄]⁻ by atmospheric-pressure carbonylations of aqueous Co(II) cyanide solutions at high pH,⁵¹ but to the best of my knowledge, no other homoleptic metal carbonyl anion has been produced by a similar procedure in aqueous solution. See ref 27, pp 8–34.

Table 1. Historic and Solution IR Spectral Data for the Carbonylmetalate Monoanions

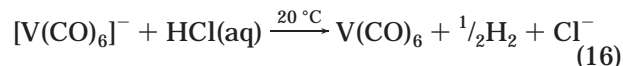
CO anion	date of discovery ⁸³	soln IR, $\nu(\text{CO})$, cm ⁻¹ ^a
[Co(CO) ₄] ⁻	1932 (refs 46, 47, 59)	1888 vs in diglyme ^b (ref 90) ^c
[Rh(CO) ₄] ⁻	1969 (ref 84)	1895 vs in THF (ref 91) ^d
[Ir(CO) ₄] ⁻	1970 (ref 85)	1895 vs in THF (ref 91) ^d
[Mn(CO) ₅] ⁻	1957 (ref 81)	1895s, 1861s in THF (ref 92) ^e
[Tc(CO) ₅] ⁻	1962 (ref 86)	1911s, 1865s in THF (ref 86) ^c
[Re(CO) ₅] ⁻	1959 (ref 87)	1910s, 1864s in THF (ref 86) ^c
[V(CO) ₆] ⁻	1960 (ref 69b)	1859 vs in THF (ref 90) ^f
[Nb(CO) ₆] ⁻	1964 (ref 88)	1854 vs in CH ₂ Cl ₂ (ref 93) ^d
[Ta(CO) ₆] ⁻	1961 (ref 89)	1852 vs in CH ₂ Cl ₂ (ref 93) ^d

^a Only the most intense absorptions are shown. ^b Diglyme = diethylene glycol dimethyl ether. ^c Na⁺ salt. ^d (Ph₃P)₂N⁺ salt. ^e Ph₄As⁺ salt. ^f K⁺ salt.

carbonyl anions, e.g., alkali metals, and are thereby usually incompatible with water. Also, the metal precursors, e.g., transition-metal halides, and the carbonyl anion products often undergo facile and irreversible hydrolysis. For these reasons, most reductive carbonylations are carried out under strictly anoxic conditions in anhydrous polar solvents such as ethers and amines. This synthetic method has been of particular importance when metal carbonyl precursors are unstable or unknown, as was originally the case for the group 4 and 5 metals. Undoubtedly the most significant relatively recent application of the reductive carbonylation method involved Ercoli, Calderazzo, and Alberola's synthesis of the first group 5 metal carbonyl anion, [V(CO)₆]⁻ (eq 15) reported in 1960.^{69b} Treatment of the [V(CO)₆]⁻ with



aqueous HCl provided neutral V(CO)₆, which remains the only known isolable 17-electron homoleptic metal carbonyl (eq 16).⁶⁹



A. Carbonylmetalates(1-). Known mononuclear metal carbonyl monoanions are shown in Table 1, along with their dates of discovery⁸³ and solution infrared spectral data in the $\nu(\text{CO})$ region. Most of these species have been characterized by single-crystal X-ray analysis and shown to have unexceptional structures.⁹⁴ However, recently [Ph₄P][Mn(CO)₅] was found to contain square-pyramidal [Mn(CO)₅]⁻ units, rather than the expected trigonal-bipyramidal structure that has been observed for all other homoleptic metal pentacarbonyl complexes, including [Mn(CO)₅]⁻ with other counterions.⁹⁵

Since the syntheses of carbonyl monoanions known before 1970 have been reviewed in detail by Bruce

(83) The "date of discovery" coincides with the first reported isolation and characterization of a salt containing the respective anion, except for [Co(CO)₄]⁻, which was first isolated in 1932^{46,47} but only established to exist as discrete anions in 1938,⁵⁹ and [Tc(CO)₅]⁻, which is only known in solution and was characterized by its IR spectrum and derivatives thereof.⁸⁶ Excluded from Table 1 are paramagnetic carbonyl anions such as the 19-electron [Cr(CO)₆]⁻ and [Fe(CO)₅]⁻ or the 17-electron [Cr(CO)₅]⁻ and [Fe(CO)₄]⁻, which have been proposed to be intermediates in the reductions of Cr(CO)₆ and Fe(CO)₅, respectively, but are too unstable to directly observe or isolate at normal temperatures. See: Amatore, C.; Krusic, P. J.; Pederson, S. U.; Verpeaux, J.-N. *Organometallics* **1995**, *14*, 640 and references therein.

(84) Chini, P.; Martinengo, S. *Inorg. Chim. Acta* **1969**, *3*, 21.

King,⁷ only those of $[\text{Rh}(\text{CO})_4]^-$ and $[\text{Ir}(\text{CO})_4]^-$ and new mild routes to the group 5 carbonyl anions will be considered herein. Although the tetracarbonylmetalates(1-) of rhodium and iridium were originally prepared by sodium metal reductions of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ ⁸⁴ and $\text{Ir}_4(\text{CO})_{12}$,⁸⁵ respectively, in THF at room temperature under an atmosphere of carbon monoxide, yields were only moderate (50–60%), procedures were difficult, and approximately 3 days was required for maximum conversion. For these reasons alternative routes were sought,⁹⁶ the most successful of which were atmospheric-pressure reductive carbonylations of the respective MCl_3 ($\text{M} = \text{Rh}, \text{Ir}$) carried out in slurries of KOH in DMSO (eq 17).⁹¹ Treatment of the resulting DMSO reaction



mixture with $[\text{PPN}]\text{Cl}$ ($\text{PPN}^+ = (\text{Ph}_3\text{P})_2\text{N}^+$) in aqueous 2-propanol gave precipitates of colorless, thermally stable $[\text{PPN}][\text{M}(\text{CO})_4]$ in 70–75% yields. Large weakly oxidizing cations, such as PPN^+ , had to be used to isolate these strongly reducing anions, since the unsolvated sodium or potassium salts of $[\text{Rh}(\text{CO})_4]^-$ and $[\text{Ir}(\text{CO})_4]^-$ are thermally unstable solids at 20 °C,⁹⁶ unlike analogous salts of $[\text{Co}(\text{CO})_4]^-$; e.g., $\text{K}[\text{Co}(\text{CO})_4]$ melts with decomposition at about 203 °C.¹⁷⁶

Original syntheses of the group 5 hexacarbonylmetalates(1-) involved high-pressure reductive carbonylations of VCl_3 or MCl_5 ($\text{M} = \text{Nb}, \text{Ta}$), typically carried out at 200–400 atm pressure in stainless steel autoclaves at elevated temperatures in pyridine ($\text{M} = \text{V}$)⁶⁹ or diglyme ($\text{M} = \text{V}, \text{Nb}, \text{Ta}$).^{88,89} The vanadium reaction worked well, typically provided $[\text{V}(\text{CO})_6]^-$ in 50–60% yields, and was employed for many years as the commercial source of the vanadate.⁹⁷ In contrast, the niobium and tantalum preparations were notoriously unreliable and dangerous.⁹⁸ Although a later modification was more reproducible, it still required high pressures of CO and afforded only 10–20% yields of

(85) Malatesta, L.; Caglio, G.; Angoletta, M. *J. Chem. Soc., Chem. Commun.* **1970**, 532.

(86) Hileman, J. C.; Juggins, D. K.; Kaesz, H. D. *Inorg. Chem.* **1962**, *1*, 933.

(87) Hieber, W.; Braun, G. *Z. Naturforsch.* **1959**, *14B*, 132.

(88) Werner, R. P. M.; Filbey, A. H.; Manastyrskij, S. A. *Inorg. Chem.* **1964**, *3*, 298.

(89) Werner, R. P. M.; Podall, H. E. *Chem. Ind. (London)* **1961**, 144. IR spectral evidence for $[\text{Nb}(\text{CO})_6]^-$ was also presented in this article, but the latter was not reported as an isolated species until 1964.⁸⁸

(90) Beck, W.; Nitzschmann, R. E. *Z. Naturforsch.* **1962**, *17B*, 577.

(91) Garlaschelli, L.; Della Pergola, R.; Martinengo, S. *Inorg. Synth.* **1990**, *28*, 211.

(92) Ellis, J. E. *J. Organomet. Chem.* **1976**, *111*, 331.

(93) Calderazzo, F.; Englert, U.; Pampaloni, G.; Pelizzi, G.; Zamboni, R. *Inorg. Chem.* **1983**, *22*, 1865.

(94) See: Bruce, M. I. *Index of Structures Determined by Diffraction Methods*. In ref 5, Vol. 9, pp 1209–1520.

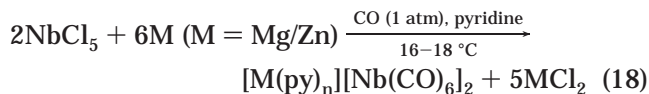
(95) Seidel, R.; Schnautz, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1710.

(96) Garlaschelli, L.; Chini, P.; Martinengo, S. *Gazz. Chim. Ital.* **1982**, *112*, 285.

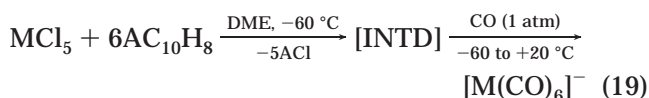
(97) King, R. B. *Organometallic Syntheses*; Academic Press: New York, 1965; Vol. 1 (Transition Metal Compounds), pp 82–84. This invaluable source contains details on the synthesis and characterization of classic metal carbonyls and related organometallics that are difficult to find elsewhere.

(98) I personally experienced more than one explosion while conducting these high-pressure syntheses in the late 1960s. The most “memorable” one involved a rupture disc failure accompanied by a large report and a blue flash of burning CO over 10 m long. Fortunately, I was about 20 m distant or I might not have lived to tell the tale!

$[\text{Nb}(\text{CO})_6]^-$ and $[\text{Ta}(\text{CO})_6]^-$.⁹⁹ Dramatic improvements in the synthesis of these anions were independently reported by the groups of Calderazzo^{93,100} and Ellis¹⁰¹ in 1983. For example, Fausto Calderazzo, Guido Pampaloni, and co-workers obtained nearly 50% yields of $[\text{Nb}(\text{CO})_6]^-$ salts by atmospheric pressure reductive carbonylations of NbCl_5 with excess Mg/Zn in pyridine (eq 18). Corresponding tantalum reactions gave a 6%



yield of $[\text{Ta}(\text{CO})_6]^-$, but preparations carried out at 80–85 °C and 110 atm pressure of CO increased the yield to about 35%.⁹³ An alternative synthesis of these anions involved an initial reduction of the respective MCl_5 by 6 equiv of alkali-metal naphthalene in 1,2-dimethoxyethane (DME) at –60 °C, under an atmosphere of dinitrogen or argon, followed by addition of CO at atmospheric pressure (eq 19), where $\text{A} =$ alkali metal.



Generally 30–50% yields of $[\text{Nb}(\text{CO})_6]^-$ and $[\text{Ta}(\text{CO})_6]^-$ were obtained by the original procedure,¹⁰¹ but a more reliable synthesis of $[\text{Ta}(\text{CO})_6]^-$ ¹⁰² and a substantially higher yield route, 60–70%, to $[\text{Nb}(\text{CO})_6]^-$ ¹⁰³ are now available. Both of these improved methods involve the same basic reaction sequence shown in eq 19, except the niobium synthesis employs $\text{NbCl}_4(\text{THF})_2$, which is more stable in ethers than NbCl_5 , and sodium anthracene was introduced as an alternative reducing agent.¹⁰³ Unlike Calderazzo's syntheses, which were carried out entirely under an atmosphere of CO ,^{93,100} the naphthalene-mediated reactions had to be done in two steps, in part because naphthalene radical anion reacts with CO .¹⁰⁴ Since homoleptic naphthalene complexes of chromium and molybdenum, $\text{M}(\text{C}_{10}\text{H}_8)_2$, had been shown by Kündig and Timms,¹⁰⁵ and independently by Elschenbroich,¹⁰⁶ to function as “naked” metal atom reagents in their extraordinarily facile reactions with CO to give high yields of the respective $\text{M}(\text{CO})_6$, one of the original objectives in examining the niobium and tantalum reactions was to obtain anionic group 5 versions of the neutral group 6 naphthalene complexes. There was hope that these species might function as synthons for atomic Nb^- and Ta^- , i.e., early-transition-metal analogues of Klaus Jonas's remarkable homoleptic ethylenemetalates, $[\text{Co}(\text{C}_2\text{H}_4)_4]^-$ and $[\text{Fe}(\text{C}_2\text{H}_4)_4]^{2-}$.¹⁰⁷ Very recently, the labile intermediates in the sodium

(99) Ellis, J. E.; Davison, A. *Inorg. Synth.* **1976**, *16*, 68.

(100) Calderazzo, F.; Pampaloni, G. *Inorg. Synth.* **1985**, *23*, 34.

(101) Dewey, C. G.; Ellis, J. E.; Fjare, K. L.; Pfahl, K. M.; Warnock, G. F. P. *Organometallics* **1983**, *2*, 388.

(102) Ellis, J. E.; Warnock, G. F. P.; Barybin, M. V.; Pomije, M. K. *Chem. Eur. J.* **1995**, *1*, 521.

(103) Barybin, M. V.; Ellis, J. E.; Pomije, M. K.; Tinkham, M. L.; Warnock, G. F. P. *Inorg. Chem.* **1998**, *37*, 6518.

(104) Büchner, W. *Chem. Ber.* **1966**, *99*, 1485.

(105) Kündig, E. P.; Timms, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 912.

(106) Elschenbroich, C.; Möckel, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 870.

(107) Jonas, K. *Adv. Organomet. Chem.* **1981**, *19*, 97 and references therein.

Table 2. Historic and Solution IR Spectral Data for the Carbonylmetalate Dianions

CO anion	date of discovery ¹¹²	soln IR, $\nu(\text{CO})$, cm^{-1} ^a
$[\text{Fe}(\text{CO})_4]^{2-}$	1931 (refs 37, 43)	1730 vs in DMF ^b (ref 121) ^c
$[\text{Ru}(\text{CO})_4]^{2-}$	1968 (ref 113)	1736 vs in HMPA ^d (ref 122) ^e
$[\text{Os}(\text{CO})_4]^{2-}$	1970 (ref 114)	1738 vs in HMPA (ref 122) ^e
$[\text{Cr}(\text{CO})_5]^{2-}$	1955 (refs 79, 80)	1760s, 1722s in HMPA (ref 123) ^e
$[\text{Mo}(\text{CO})_5]^{2-}$	1959 (refs 115, 116)	1769s, 1723s in HMPA (ref 123) ^e
$[\text{W}(\text{CO})_5]^{2-}$	1963 (refs 115, 117)	1775s, 1731s in HMPA (ref 123) ^e
$[\text{Ti}(\text{CO})_6]^{2-}$	1988 (ref 118)	1748 vs in CH_3CN (ref 120) ^f
$[\text{Zr}(\text{CO})_6]^{2-}$	1987 (ref 119)	1757 vs in CH_3CN (ref 120) ^f
$[\text{Hf}(\text{CO})_6]^{2-}$	1990 (ref 120)	1757 vs in CH_3CN (ref 120) ^f

^a Only the most intense absorptions are shown. ^b DMF = *N,N*-dimethylformamide. ^c K^+ salt. ^d HMPA = hexamethylphosphoramide. ^e Na^+ salt. ^f $[\text{K}(\text{cryptand-2.2.2})]^+$ salt; cryptand-2.2.2 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

naphthalene and sodium anthracene reductions of TaCl_5 and $\text{NbCl}_4(\text{THF})_2$ were isolated and found to be novel tris(arene)metal complexes, $[\text{Ta}(\eta^4\text{-C}_{10}\text{H}_8)_3]^-$ ¹⁰⁸ and $[\text{Nb}((1-4-\eta^4)\text{-C}_{14}\text{H}_{10})_3]^-$,¹⁰⁹ respectively. Solutions of these anions in THF rapidly absorb CO at -60°C to provide essentially quantitative yields of the respective $[\text{M}(\text{CO})_6]^-$. Effective atmospheric-pressure syntheses of $[\text{V}(\text{CO})_6]^-$, which is no longer commercially available, starting from VCl_3 , have been developed by Calderazzo and Pampaloni¹¹⁰ and by Liu and Ellis.¹¹¹

Extensions of these or related procedures for atmospheric-pressure syntheses of homoleptic manganese carbonyls would be a very useful development, since $[\text{Mn}(\text{CO})_5]^-$ and $\text{Mn}_2(\text{CO})_{10}$ are presently only available by high-pressure routes from non-carbonyl precursors.²⁷ Low-pressure syntheses are particularly important for the facile preparation of 99% ^{13}C -labeled metal carbonyls. Often only stoichiometric amounts of the relatively expensive ^{13}C are required in these syntheses; e.g., $[\text{V}(^{13}\text{CO})_6]^-$ ¹¹⁰ and $[\text{Ta}(^{13}\text{CO})_6]^-$ ¹⁰² have been obtained in this fashion from VCl_3 and TaCl_5 , respectively.

B. Carbonylmetalates(2-). Table 2 lists the known mononuclear metal carbonyl dianions, dates of discovery,¹¹² and solution infrared $\nu(\text{CO})$ data. Species that

(108) Brennessel, W. W.; Ellis, J. E.; Pomije, M. K.; Sussman, V. J.; Urnezius, E.; Young, V. G. *J. Am. Chem. Soc.* **2002**, *124*, 10258.

(109) Brennessel, W. W.; Ellis, J. E.; Roush, S. N.; Strandberg, B. R.; Woisetschlager, O. E.; Young, V. G. *Chem. Commun.* **2002**, 2356.

(110) Calderazzo, F.; Pampaloni, G. *Organomet. Synth.* **1988**, *4*, 46.

(111) Liu, X.; Ellis, J. E. Submitted for publication in *Inorg. Synth.*

(112) Dates of discovery represent the first reported isolation of the respective anion. However, as noted in the text, certain of these substances were not properly characterized until later on. For example, as mentioned earlier, $[\text{Fe}(\text{en})_3][\text{Fe}(\text{CO})_4]$ was the first isolated salt containing $[\text{Fe}(\text{CO})_4]^{2-}$, although its ionic nature was not established until 1957.⁴³ Another source²⁷ has credited Hock and Stuhlmann⁴⁵ with the discovery of $[\text{Fe}(\text{CO})_4]^{2-}$; however, to the best of my knowledge they never substantiated their claim for the existence of $\text{Na}_2[\text{Fe}(\text{CO})_4]$. Indeed, alkali-metal salts of $[\text{Fe}(\text{CO})_4]^{2-}$ were not isolated and analyzed until the early 1940s, as described in Hieber's FIAT review in 1948.⁶⁴

(113) Cotton, J. D.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2162.

(114) L'Eplattenier, F.; Pelichet, C. *Helv. Chim. Acta* **1970**, *53*, 1091.

(115) Earlier reference was made to $\text{Na}_2[\text{Mo}(\text{CO})_5]$ and $\text{Na}_2[\text{W}(\text{CO})_5]$ in a paper in 1957, but no compelling data for the existence of these species were presented therein.⁸⁰

(116) (a) Behrens, H.; Haag, W. Z. *Naturforsch.* **1959**, *14B*, 600. (b) Behrens, H.; Haag, W. *Chem. Ber.* **1961**, *94*, 312.

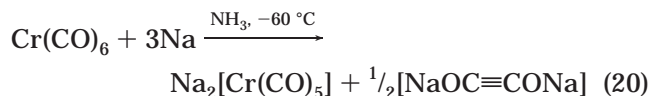
(117) Behrens, H.; Vogl, J. *Chem. Ber.* **1963**, *96*, 2220.

(118) (a) Chi, K.-M.; Frerichs, S. R.; Philson, S. B.; Ellis, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 303. (b) Chi, K.-M.; Frerichs, S. R.; Stein, B. K.; Blackburn, D. W.; Ellis, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 163.

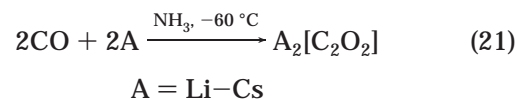
(119) Chi, K.-M.; Frerichs, S. R.; Philson, S. B.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1190.

have been characterized by single-crystal X-ray analyses include $[\text{Fe}(\text{CO})_4]^{2-}$,¹²⁴ $[\text{W}(\text{CO})_5]^{2-}$,¹²⁵ and $[\text{M}(\text{CO})_6]^{2-}$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$),¹²⁰ which showed essentially undistorted tetrahedral, trigonal-bipyramidal, and octahedral structures, respectively, in the presence of large, nearly spherical, and weakly interacting cations, such as $[\text{K}(\text{cryptand-2.2.2})]^+$. In contrast, the geometry of $[\text{Fe}(\text{CO})_4]^{2-}$ was found to be strongly distorted by ion pairing in $\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 3/2(\text{dioxane})$ ^{124a} and $\text{K}_2[\text{Fe}(\text{CO})_4]$.^{124b} Since the pentacarbonylmetalates(2-) of the group 6 elements were the first new carbonyl dianions to be discovered after $[\text{Fe}(\text{CO})_4]^{2-}$, these will be discussed first, followed by those of the group 8 and group 4 elements.

1. $[\text{M}(\text{CO})_5]^{2-}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). Before 1970, $[\text{Fe}(\text{CO})_4]^{2-}$ was the only homoleptic mononuclear metal carbonyl dianion to have been isolated as a satisfactorily pure salt and characterized by IR spectroscopy.¹²¹ Relatively pure samples of $\text{Na}_2[\text{Cr}(\text{CO})_5]$ were available by Behrens' liquid ammonia route⁸⁰ (vide supra), but elemental analyses invariably showed the presence of small but troubling amounts of NaNH_2 , NH_3 , or combinations thereof. In 1973 Behrens reported that recrystallization of these samples from THF afforded pure unsolvated $\text{Na}_2[\text{Cr}(\text{CO})_5]$, which was also characterized by IR spectroscopy for the first time.¹²⁶ Up to 95% yields of bright yellow, powdery, and highly pyrophoric $\text{Na}_2[\text{Cr}(\text{CO})_5]$ have been obtained by Behrens' facile procedure directly from $\text{Cr}(\text{CO})_6$.¹²⁷ Little or no free CO was evolved during the course of Na-NH_3 reduction of $\text{Cr}(\text{CO})_6$.^{10,80} Behrens reported that liberated CO was reduced by sodium to give disodium acetylenediolate, $\text{Na}_2\text{C}_2\text{O}_2$. Thus, at least 3 equiv of sodium was apparently required for the full reduction of $\text{Cr}(\text{CO})_6$ (eq 20).^{10,127} Free CO was previously shown by Buchner to



react with alkali metals in liquid ammonia to generate insoluble acetylenediolate salts (eq 21).¹²⁸ It is believed



that the first step in the reduction of $\text{Cr}(\text{CO})_6$ involves formation of the 19-electron $[\text{Cr}(\text{CO})_6]^-$.⁸³ The latter was

(120) Ellis, J. E.; Chi, K.-M. *J. Am. Chem. Soc.* **1990**, *112*, 6022.

(121) Edgell, W. F.; Yang, M. T.; Bulken, B. J.; Bayer, R.; Koizumi, N. *J. Am. Chem. Soc.* **1965**, *87*, 3080.

(122) Ellis, J. E.; Faltynek, R. A.; Hentges, S. G. Unpublished research, 1975. HMPA = hexamethylphosphoramide. $\text{Na}_2[\text{M}(\text{CO})_4]$ species ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) were formed in essentially quantitative yields by the reduction of the corresponding $\text{M}_3(\text{CO})_{12}$ with stoichiometric amounts of sodium in HMPA for about 1 h at 20°C under an argon atmosphere. Identical spectra in HMPA solutions were obtained from bona fide $\text{Na}_2[\text{M}(\text{CO})_4]$, isolated from the reactions of $\text{M}_3(\text{CO})_{12}$ by sodium in liquid ammonia, as previously described for $\text{M} = \text{Fe}, \text{Ru}$.^{65, 113} Os.¹⁵³

(123) Ellis, J. E.; Hagen, G. P. *J. Am. Chem. Soc.* **1974**, *96*, 7825.

(124) (a) $\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 1.5(\text{dioxane})$: Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 2434. (b) $\text{K}_2[\text{Fe}(\text{CO})_4]$ and $[\text{Na}(\text{crypt-2.2.2})]_2[\text{Fe}(\text{CO})_4]$: Teller, R. G.; Finke, R. G.; Collman, J. P.; Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1104.

(125) $[\text{Na}(\text{crypt-2.2.1})]_2[\text{W}(\text{CO})_5]$: Maher, J. M.; Beatty, R. P.; Cooper, N. J. *Organometallics* **1985**, *4*, 1354.

(126) Lindner, E.; Behrens, H.; Uhlig, D. Z. *Naturforsch.* **1973**, *18B*, 276.

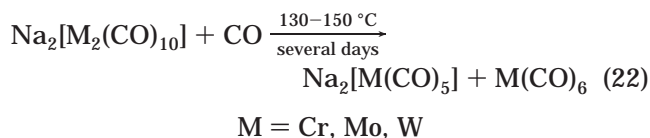
reported to rapidly decompose to afford CO and the 17-electron $[\text{Cr}(\text{CO})_5]^-$,⁸³ both of which can undergo subsequent 1-electron reductions to provide the observed products, $[\text{Cr}(\text{CO})_5]^{2-}$ and $[\text{C}_2\text{O}_2]^{2-}$, the dimer of CO radical anion. However, since Kochi has established that $[\text{Cr}(\text{CO})_6]^-$ can function as a "metalloradical," e.g., it was captured by *n*-Bu₃SnH to afford about 20% yields of the formyl chromium carbonyl, $[\text{Cr}(\text{CO})_5\text{CHO}]^-$,¹²⁹ and Wayland has shown that certain formally 19-electron carbonyl complexes, e.g., (tetramesitylporphyrin)rhodium(II) carbonyl species, (TMP)RhCO, dimerize by C–C bond formation to provide dimetal α,β -diketones, e.g., (TMP)RhC(O)C(O)Rh(TMP),¹³⁰ analogous dimerization of $[\text{Cr}(\text{CO})_6]^-$ is also a possibility. Subsequent reduction of this plausible "dichromate" intermediate, i.e., $[\{\text{Cr}(\text{CO})_5\}_2\{\mu\text{-C}(\text{O})\text{C}(\text{O})\}]^{2-}$, which would be isostructural with the known $[\text{Re}(\text{CO})_5]_2[\mu\text{-C}_2\text{O}_2]$,¹³¹ provides a possible alternative pathway to the observed products and accounts for the fact that little or no CO evolution was observed in Behrens' reaction.

Podall and co-workers proposed in 1961 that reductions of $\text{Cr}(\text{CO})_6$ by sodium amalgam in hot diglyme (105 °C) or refluxing THF gave $\text{Na}_2[\text{Cr}(\text{CO})_5]$, but no data were presented in support of their claim.¹³² A reinvestigation of Podall's reaction in the THF by IR spectroscopy established that the major product was $\text{Na}_2[\text{Cr}(\text{CO})_5]$, but significant amounts of the $\text{Cr}(1-)$ intermediate, $[\text{Cr}_2(\text{CO})_{10}]^{2-}$, were also present.¹²⁷ In contrast, essentially complete reductions of $\text{Cr}(\text{CO})_6$ to $[\text{Cr}(\text{CO})_5]^{2-}$ were obtained with sodium metal in HMPA¹²³ or cesium amalgam in THF.¹²⁷ Cooper and co-workers also showed that the sodium naphthalene reduction of $\text{Cr}(\text{CO})_5(\text{NMe}_3)$ in THF is an effective route to pure $\text{Na}_2[\text{Cr}(\text{CO})_5]$.¹³³ Hegedus and co-workers have employed sodium naphthalene¹³⁴ or potassium graphite (KC_8)¹³⁵ reductions of $\text{Cr}(\text{CO})_6$ in THF to generate $[\text{Cr}(\text{CO})_5]^{2-}$, but no spectroscopic characterizations of these salts were reported. However, they were used to obtain good yields of chromium carbene complexes, such as $\text{Cr}(\text{CO})_5(\text{C}(\text{NMe}_2)\text{H})$,^{134,135} and on this basis, these routes appear to be the best available ones, not involving the use of liquid ammonia, for the direct conversion of $\text{Cr}(\text{CO})_6$ to $[\text{Cr}(\text{CO})_5]^{2-}$.

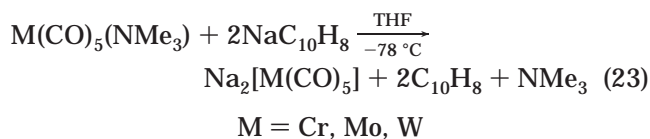
Behrens' success in obtaining high yields of $\text{Na}_2[\text{Cr}(\text{CO})_5]$ by the liquid ammonia route suggested that the procedure would also work for analogous molybdenum and tungsten salts. However, corresponding reductions of $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ provided only small amounts of impure $\text{Na}_2[\text{M}(\text{CO})_5]$.^{115–117} Extraction of the molyb-

denum product by THF, followed by filtration and solvent removal, was reported to give analytically pure yellow $\text{Na}_2[\text{Mo}(\text{CO})_5]$, but no yield or supporting analytical data were presented.¹¹⁶ Although it is not known with certainty why the Behrens route to $\text{Na}_2[\text{Mo}(\text{CO})_5]$ and $\text{Na}_2[\text{W}(\text{CO})_5]$ worked so poorly compared to $\text{Na}_2[\text{Cr}(\text{CO})_5]$, Cooper and co-workers later discovered that the unsolvated molybdenum and tungsten salts were very (Mo) to somewhat (W) thermally unstable at room temperature.¹²⁵ Since Behrens reported that the isolated products were handled at this temperature, they likely suffered significant thermolysis. However, Behrens also stated that $\text{Na}_2[\text{Mo}(\text{CO})_5]$ and $\text{Na}_2[\text{W}(\text{CO})_5]$ underwent further reduction by sodium in liquid ammonia,¹⁰ while $\text{Na}_2[\text{Cr}(\text{CO})_5]$ was inert under these conditions.¹¹ If the soluble disodium salts, $\text{Na}_2[\text{M}(\text{CO})_5]$, of molybdenum and tungsten reacted much faster with Na-NH_3 than the sparingly soluble neutral hexacarbonyls, poor yields of the products would also result. At least two mysteries remain concerning $[\text{Mo}(\text{CO})_5]^{2-}$ and $[\text{W}(\text{CO})_5]^{2-}$; i.e., why are the sodium salts of these anions much less thermally stable and apparently more easily reduced by Na-NH_3 than $\text{Na}_2[\text{Cr}(\text{CO})_5]$ and what are the natures of Behrens' "further reduced" products?¹³⁶

Subsequently, Behrens found that relatively pure samples of $\text{Na}_2[\text{M}(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) were obtained by heating the respective solid $\text{Na}_2[\text{M}_2(\text{CO})_{10}]$ in a sealed tube containing carbon monoxide at 130–150 °C (eq 22),



followed by recrystallization of the reaction mixture from THF–petroleum ether to remove the neutral hexacarbonyls.^{116b,117} By this method, Behrens was able to obtain satisfactorily pure yellow $\text{Na}_2[\text{W}(\text{CO})_5]$ for the first time; however, the synthesis was only carried out on a sub-gram scale and no yield or IR spectral data were reported for the salt.¹¹⁷ The first IR spectral characterizations of $[\text{Mo}(\text{CO})_5]^{2-}$ and $[\text{W}(\text{CO})_5]^{2-}$ were obtained in studies on the reductions of the corresponding $\text{M}(\text{CO})_6$ by sodium in HMPA¹²³ and cesium amalgam in THF.¹²⁷ Although these methods provided complete reduction to the desired anions, the use of toxic and poorly volatile HMPA and mercury had obvious disadvantages. To circumvent these and related problems, John Cooper and co-workers developed significant new alternative syntheses of these dianions involving the reductions of $\text{M}(\text{CO})_5(\text{NMe}_3)$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) by sodium naphthalene in THF (eq 23).¹³³ These are presently the



best routes to $[\text{Mo}(\text{CO})_5]^{2-}$ and $[\text{W}(\text{CO})_5]^{2-}$. Detailed accounts of these and related syntheses, starting from

(127) Ellis, J. E.; Hentges, S. G.; Kalina, D. G.; Hagen, G. P. *J. Organomet. Chem.* **1975**, *97*, 79.

(128) (a) Büchner, W. *Helv. Chim. Acta* **1963**, *46*, 2111. In this article dry $\text{Li}_2\text{C}_2\text{O}_2$ is reported to be a treacherously shock sensitive material. (b) Büchner, W. *Helv. Chim. Acta* **1965**, *48*, 1229.

(129) Narayan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1986**, *5*, 926.

(130) Sherry, A. E.; Wayland, B. B. *J. Am. Chem. Soc.* **1989**, *111*, 5010.

(131) de Boer, E. J. M.; de With, J.; Meijboom, N.; Orpen, A. G. *Organometallics* **1985**, *4*, 259.

(132) Podall, H. E.; Prestridge, H. B.; Shapiro, H. *J. Am. Chem. Soc.* **1961**, *83*, 2057.

(133) Maher, J. M.; Beatty, R. P.; Cooper, N. J. *Organometallics* **1982**, *1*, 215.

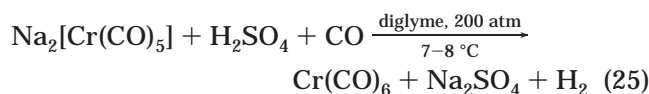
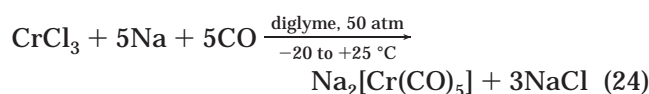
(134) (a) Borel, C.; Hegedus, L. S.; Krebs, J.; Satoh, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1101. (b) Imwinkelreid, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702.

(135) Schwindt, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814.

(136) Behrens has suggested that $\text{Na}_2[\text{M}(\text{CO})_5]$ ($\text{M} = \text{Mo}, \text{W}$) undergo further reduction to provide $\text{Na}_4[\text{M}(\text{CO})_4]^{10}$ (vide infra); however, mull IR spectra of these dark brown, nearly black reduction or decomposition products did not show any absorptions characteristic of bona fide $\text{Na}_4[\text{M}(\text{CO})_4]$ or other metal carbonyl products in the $\nu(\text{CO})$ region.¹¹

neutral hexacarbonyls, have been published.^{125,137} Cooper found that the thermal stabilities of the isolated salts were a sensitive function of both the transition metal and counterion: i.e., Cr > W > Mo and K⁺ > Na⁺ > Li⁺. For example, unsolvated Na₂[Mo(CO)₅] had to be kept at ≤ -30 °C to avoid apparent thermolysis, while the corresponding chromium and tungsten salts remained unchanged at ≤ 0 °C.^{125,138} In an earlier study, the cesium salts Cs₂[M(CO)₅] (M = Cr, Mo, W) were found to be stable indefinitely at room temperature when stored in the dark under an inert atmosphere.¹²⁷ Complexation of the sodium cations in Na₂[M(CO)₅] (M = Mo, W) by cryptand-2.2.1¹³⁹ provided the analytically pure and thermally robust salts [Na(cryptand-2.2.1)]₂[M(CO)₅], thus showing that large and weakly coordinating as well as nonoxidizing counterions are important for the stabilization of [Mo(CO)₅]²⁻ and [W(CO)₅]²⁻ in the solid state.¹²⁵ These and related observations played a crucial role in the later syntheses of the previously unknown hexacarbonyl dianions of Ti, Zr and Hf (vide infra).

Due to the ready availability of the neutral hexacarbonyls of the group 6 metals, much less effort has been made to develop reductive carbonylation procedures for the direct synthesis of group 6 metal carbonyl anions from metal halides or related precursors. In 1961, Podall and co-workers reported on a "novel and simple sodium route" for the synthesis of 65–80% yields of the group 6 neutral hexacarbonyls and proposed, without proof, that the reactions involved the initial formations of the corresponding [M(CO)₅]²⁻.¹³² Except for an acid quench step, the procedure was very similar to the one Podall et al. employed for their high-pressure syntheses of the group 5 hexacarbonylmetalates(1-).^{88,89} For example, reduction of CrCl₃ in diglyme at -20 to +25 °C by an excess (6 equiv) of sodium metal dispersion under 50 atm of CO, followed by aqueous sulfuric acid quench, under 200 atm of CO, afforded an 80% yield of Cr(CO)₆ (eqs 24 and 25). Prior to isolation of the Cr(CO)₆, all of



these "simple" steps were carried out in a sophisticated high-pressure stirring autoclave apparatus. A related high-pressure "sodium-naphthalene complex route" to Cr(CO)₆ was described by Podall in 1962 and involved the initial reaction of CrCl₃ with 6 equiv of NaC₁₀H₈ in diglyme at 25 °C, followed by treatment with CO (ca. 240 atm) for 18 h at room temperature and then with aqueous 6 M HCl.¹⁴⁰ This reaction was also proposed to involve [Cr(CO)₅]²⁻ as a "probable intermediate," but

(137) (a) Maher, J. M.; Beatty, R. P.; Lee, G. R.; Cooper, N. J. *Organomet. Synth.* **1986**, 3, 35. (b) Darensbourg, M. Y.; Slater, S. *Inorg. Synth.* **1983**, 22, 181.

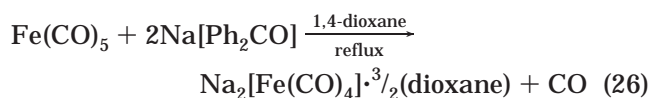
(138) A sample of pure unsolvated Na₂[Cr(CO)₅] stored at room temperature under an inert atmosphere in this laboratory has remained intact after more than 20 years.

(139) cryptand-2.2.1 = 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]-tricosane.

(140) Shapiro, H.; Podall, H. E. *J. Inorg. Nucl. Chem.* **1962**, 24, 925.

the actual nature of the product, prior to the acid quench, remains unknown. The overall reaction gave only a 10% yield of Cr(CO)₆, but the initial step appears to be the first reported example of a *naphthalene-mediated reductive carbonylation of a metal halide* and bears a striking resemblance to the much later developed normal-pressure syntheses of the group 5 carbonyl anions [M(CO)₆]⁻ (M = V, Nb, Ta; vide supra).^{101–103,141} Although Podall's proposal that it is possible to change group 6 metal halides directly to corresponding mononuclear carbonylmetalates, [M(CO)₅]²⁻,^{132,140} has not been verified to date, reactions of CrCl₃, MoCl₅, or WCl₆ in THF with magnesium turnings or sodium amalgam under an atmosphere of CO at room temperature for 10–18 h were reported to give 20–60% yields of [M₂(CO)₁₀]²⁻.¹⁴² This is an interesting and surprising result, since Podall and co-workers previously found that high pressures of CO were apparently necessary in their closely related reductive carbonylation processes.^{132,140}

2. [M(CO)₄]²⁻, M = Fe, Ru, Os. Only an update of significant recent syntheses of [Fe(CO)₄]²⁻ will be included herein. The commercial availability of Na₂[Fe(CO)₄]^{3/2}(dioxane), Collman's reagent, attests to its continuing importance as a metal carbonyl anion precursor,⁹ since no other salts of metal carbonyls are currently marketed. Collman's route to this substance provided 90–100% yields and involves the reaction of Fe(CO)₅ and sodium benzophenone radical anion in boiling 1,4-dioxane (eq 26).¹⁴³ Unsolvated Na₂[Fe(CO)₄]



has been prepared in essentially quantitative yields by the interaction of Fe(CO)₅ with 2 equiv of sodium naphthalene in THF at ≤ -70 °C,¹⁴⁴ a much easier and safer route than Behrens' original synthesis in liquid ammonia.⁶⁵ Reductions of Fe(CO)₅ by K[HB(sec-Bu)₃], i.e., "K-Selectride,"¹⁴⁵ and potassium graphite¹⁴⁶ in THF afforded high yields of colorless K₂[Fe(CO)₄]. Undoubtedly the most interesting recent route to [Fe(CO)₄]²⁻ was Jonas's olefin-mediated reductive carbonylation of ferrocene, which involved the intermediacy of labile and isolable species such as [Fe(C₂H₄)₄]²⁻ and [Fe(1,5-COD)₂]²⁻. The latter rapidly reacted with carbon monoxide at normal pressures to provide essentially quantitative yields of [Fe(CO)₄]²⁻.¹⁰⁷ Reduction of FeCl₃ by 5 equiv of sodium naphthalene in THF, under an atmosphere of CO at ambient temperature, gave solutions containing Na₂[Fe(CO)₄], as shown by their IR

(141) Barybin, M. V.; Pomije, M. K.; Ellis, J. E. *Inorg. Chim. Acta* **1998**, 269, 58.

(142) Sobota, P.; Utko, J.; Janas, Z. *J. Organomet. Chem.* **1982**, 233, C38.

(143) (a) Finke, R. G.; Sorrell, T. N. *Organic Syntheses*, Wiley: New York, 1988; Collect. Vol. VI, p 807. (b) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, 99, 2515.

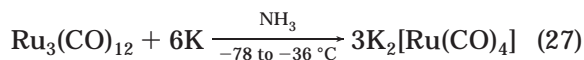
(144) Strong, H.; Krusic, P. J.; San Filippo, J. *Inorg. Synth.* **1990**, 28, 203.

(145) Gladysz, J. A.; Tam, W. *J. Org. Chem.* **1978**, 43, 2279. John Gladysz and co-workers established that the interactions of commercially available trialkylborohydride salts with metal carbonyls provide a useful and fairly general route to a number of homo- and heteroleptic carbonylmetalates; see: Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W. *Inorg. Chem.* **1979**, 18, 553.

(146) Dvorak, D. *Organometallics* **1995**, 14, 570.

spectra, but yields (68–78%) were only reported for organic derivatives, i.e., aldehydes, carboxylic acids, and ketones.¹⁴⁷

Gordon Stone and co-workers reported in 1968 that the reduction of Ru₃(CO)₁₂ by sodium in liquid ammonia provided a very air sensitive “fawn”-colored solid,¹¹³ which was shown by several groups to possess reactivity patterns expected of Na₂[Ru(CO)₄].^{113,148,149} Although the initial IR spectra reported for this substance¹¹³ were more consistent with the presence of [HRu(CO)₄][−], which has a very intense ν(CO) absorption at about 1890 cm^{−1},¹⁵⁰ later spectra of Stone's product, obtained under strictly anaerobic conditions, were shown to be nearly identical with those observed for [Fe(CO)₄]^{2−}; e.g., solutions of Na₂[Ru(CO)₄] in HMPA showed a strong absorption at 1736 cm^{−1}.^{122,151} In 1990, Sheldon Shore and co-workers reported that the analogous reduction of Ru₃(CO)₁₂ by potassium in liquid ammonia afforded an 86% yield of a cream white solid that gave correct analysis for unsolvated K₂[Ru(CO)₄] (eq 27). IR spectra



of K₂[Ru(CO)₄] and Na₂[Ru(CO)₄] were in good agreement with one another and indicated that the latter substance was indeed correctly formulated, despite the fact that no confirming elemental analytical data have been reported to date.

A related reduction of Os₃(CO)₁₂ by 6 equiv of sodium 2,2'-bipyridine in THF gave a colorless, very air-sensitive solid, proposed to be Na₂[Os(CO)₄], on the basis of the close similarity of its IR spectrum in THF, ν(CO) 1787 cm^{−1}, to that previously observed for [Fe(CO)₄]^{2−}, ν(CO) 1786 cm^{−1},¹⁵² and consistent derivative chemistry.¹¹⁴ Stone,¹⁵³ Collman,¹⁵⁴ and Norton¹⁵⁵ later prepared Na₂[Os(CO)₄] by the reduction of Os₃(CO)₁₂ by sodium in liquid ammonia. Although there was initial confusion concerning the nature of this product,¹⁵³ later infrared spectral studies^{122,155} were consistent with its formulation as Na₂[Os(CO)₄]. Also, Shore has obtained analytically pure K₂[Os(CO)₄] by the same route using K–NH₃ and it has nearly identical IR spectral features.¹⁴⁹

3. [M(CO)₆]^{2−} (M = Ti, Zr, Hf). After development of the mild-pressure naphthalene-mediated route to

(147) Devasagayaraj, A.; Periasamy, M. *Transition Met. Chem.* **1991**, *16*, 503.

(148) (a) Cotton, J. D.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2578. (b) Geoffroy, G. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1977**, *99*, 7565. (c) Lindner, E.; Jansen, R.-M.; Mayer, H. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1008. (d) Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956.

(149) Bhattacharyya, N. K.; Coffy, T. J.; Quintana, W.; Salupo, T. A.; Bricker, J. C.; Shay, T. B.; Payne, M.; Shore, S. G. *Organometallics* **1990**, *9*, 2368.

(150) Walker, H. W.; Ford, P. C. *Inorg. Chem.* **1982**, *21*, 2509.

(151) See ref 11, p 6, Figure 2 for the IR spectrum of Na₂[Ru(CO)₄] in HMPA.

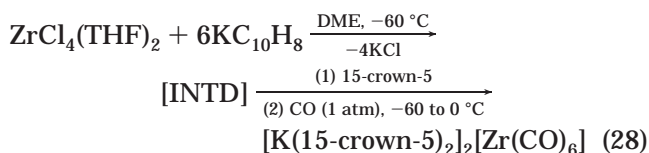
(152) Edgell, W. F.; Huff, J.; Thomas, J.; Lehman, H.; Angell, C.; Asato, G. *J. Am. Chem. Soc.* **1960**, *82*, 1254. This IR spectral value was determined for an aqueous solution of [Fe(CO)₄]^{2−}, no cation specified. In THF, Na₂[Fe(CO)₄] shows an intense broad ν(CO) absorption at 1738 cm^{−1}. See: Curran, D. J.; Graham, P. B.; Rausch, M. D. *Organometallics* **1993**, *12*, 2380.

(153) George, R. D.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 972.

(154) Collman, J. P.; Murphy, D. W.; Fleischer, E. B.; Swift, D. *Inorg. Chem.* **1974**, *13*, 1.

(155) Carter, W. J.; Kelland, J. W.; Okrasinski, S. J.; Warner, K. E.; Norton, J. R. *Inorg. Chem.* **1982**, *21*, 3955.

[Nb(CO)₆][−] and [Ta(CO)₆][−],¹⁰¹ there was considerable interest in extending this procedure to the group 4 elements, since the only prior examples of homoleptic group 4 carbonyls were neutral Ti(CO)₆ and related matrix-isolated “cryomolecules” reported in 1977 by Ozin and co-workers.¹⁵⁶ Synthesis of the first titanium carbonyl anion, [(η⁵-C₅H₅)Ti(CO)₄][−], in 1985, by the sodium naphthalene mediated carbonylation of (C₅H₅)-TiCl₃, established that the naphthalene route had considerable promise in the synthesis of new classes of group 4 carbonyls,¹⁵⁷ but numerous early attempts to access alkali-metal salts of [Ti(CO)₆]^{2−} by similar procedures were total failures. For example, several unsuccessful efforts were made to prepare the unsolvated cesium salt Cs₂[Ti(CO)₆],¹⁵⁸ because of the especially robust nature of the analogous group 6 compounds Cs₂[M(CO)₅] (M = Cr, Mo, W).¹²⁷ Our observations that alkali-metal salts of [(C₅H₅)Ti(CO)₂(dmpe)][−] (dmpe = 1,2-bis(dimethylphosphano)ethane) in THF were very thermally unstable, even at −60 °C, and could not be isolated unless treated with appropriate crown ethers or cryptands¹⁵⁹ and Cooper's report that the cryptand salts [Na(cryptand-2.2.1)]₂[M(CO)₅] (M = Mo, W) were more thermally stable in the solid state than the analogous unsolvated salts (vide supra)¹²⁵ led to the discovery that [Ti(CO)₆]^{2−}^{118a} and [Zr(CO)₆]^{2−}¹¹⁹ could be prepared and isolated as [K(15-crown-5)]₂⁺ or [K(cryptand-2.2.2)]⁺ salts. The same atmospheric-pressure naphthalene-mediated carbonylation procedure previously employed for group 5 hexacarbonylmetalates-(1[−])¹⁰¹ worked satisfactorily for titanium and zirconium, provided effective alkali-metal complexants were added before the carbonylation step (eq 28), where [INTD] =



naphthalenemetalate intermediates.¹⁶⁰ Deep red [Ti(CO)₆]^{2−} and deep red-violet [Zr(CO)₆]^{2−} were thereby obtained in 70–80% and 40–45% isolated yields, respectively, as analytically pure and thermally robust (stable indefinitely at 20 °C) crystalline solids. Although IR and ¹³C NMR spectral data were entirely consistent with the presence of discrete [M(CO)₆]^{2−} units in these products, ⁴⁹Ti (*I* = 7/2, 5.5% abundance)^{118a} and ⁹¹Zr (*I* = 5/2, 11.2% abundance)¹¹⁹ NMR spectra of the 99% ¹³CO-labeled complexes were obtained to unambiguously establish their nature in solution. These spectra consisted of well-resolved binomial septets (Figure 2), as expected for [M(CO)₆]^{2−} species of octahedral sym-

(156) Busby, R.; Klotzbücher, W.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 822. These were prepared by interaction of titanium atoms with excess CO (CO/Ti ≈ 10⁵). Ozin formulated the highest stoichiometry carbonyl as the 16-electron Ti(CO)₆ and concluded that this green substance “is an extremely unstable compound which probably decomposes around 40–45 K to titanium metal and CO”. More recently, corresponding matrix-isolated Zr(CO)_x and Hf(CO)_x have been examined.¹⁶⁷

(157) Kelsey, B. K.; Ellis, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 1344.

(158) Tinkham, M. L.; Seaburg, J. K.; Ellis, J. E. Unpublished research. Also see ref 163.

(159) Frerichs, S. R.; Stein, B. K.; Ellis, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 5558.

(160) Jang, M.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1973.

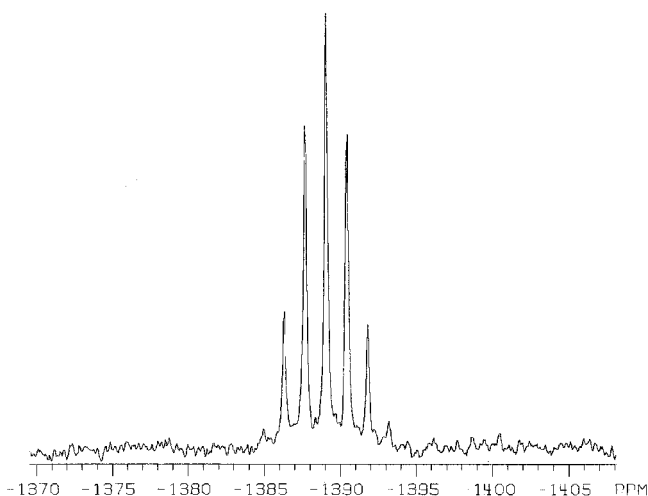
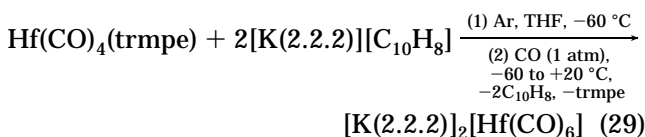


Figure 2. ^{49}Ti NMR spectrum of a 0.05 M solution of 99% ^{13}C -enriched $[\text{Ti}(^{13}\text{CO})_6]^{2-}$ in acetonitrile at 23 °C (from ref 118).

metry.¹⁶¹ Surprisingly, corresponding reductions of $\text{HfCl}_4(\text{THF})_2$ and related salts gave only traces of $[\text{Hf}(\text{CO})_6]^{2-}$. Why the reductive carbonylation failed for hafnium is unknown and is still under investigation. Presently the only effective route to the hafnate(2-) has involved $[\text{K}(\text{cryptand-2.2.2})][\text{C}_{10}\text{H}_8]$ reductions of the zerovalent hafnium complex $\text{Hf}(\text{CO})_4(\text{trmpe})$ ¹⁶² (trmpe = 1,1,1-tris((dimethylphosphino)methyl)ethane) in THF at -60 °C, followed by the addition of CO and slow warming to room temperature (eq 29), where 2.2.2 =



cryptand-2.2.2. Finely divided purple product precipitated in nearly quantitative yield. Recrystallization from THF-pyridine afforded deep red-violet to nearly black single crystals of $[\text{K}(\text{cryptand-2.2.2})]_2[\text{Hf}(\text{CO})_6] \cdot (\text{pyridine})$ suitable for X-ray analysis.¹²⁰ The latter showed essentially undistorted octahedral $[\text{Hf}(\text{CO})_6]^{2-}$ units to be present in the unit cell (Figure 3), thereby confirming the existence of the first compound to contain Hf in a formally negative oxidation state.

Repeated failures to isolate unsolvated alkali-metal salts of $[\text{M}(\text{CO})_6]^{2-}$ strongly suggest that cations as weakly Lewis acidic as Cs^+ can promote facile decomposition of these or related group 4 carbonyl anions.¹⁶³ In this regard the hexacarbonylmetalates(2-) of the group 4 elements resemble the pentacarbonylmetalates(3-) of V, Nb, and Ta, for which unsolvated cesium salts, $\text{Cs}_3[\text{M}(\text{CO})_5]$, can be isolated, but they are definitely "on

(161) Benn, R.; Rufinska, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 851.

(162) Blackburn, D. W.; Chi, K.-M.; Frerichs, S. R.; Tinkham, M. L.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 437.

(163) For example, reduction of $\text{Ti}(\text{CO})_3(\text{dmpe})_2$ ¹¹⁸ by 2 equiv of cesium naphthalene in the presence of 4 equiv of 18-crown-6 in THF at -70 °C, followed by addition of CO (1 atm) and slow warming to 20 °C, afforded a 64% yield of satisfactorily pure $[\text{Cs}(18\text{-crown-6})_2]_2[\text{Ti}(\text{CO})_6]$ as a bright red powder. In contrast, an identical reaction carried out in the absence of 18-crown-6 gave a brown-black solid of unknown nature, which had no IR absorptions from 2000 to 1600 cm^{-1} and was insoluble in pyridine, acetonitrile, HMPA, and other solvents which readily dissolve salts containing $[\text{Ti}(\text{CO})_6]^{2-}$, Tinkham, M. L.; Ellis, J. E. Unpublished research, 1988.

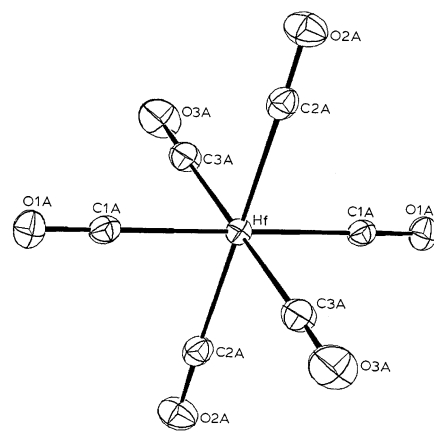


Figure 3. Molecular structure of $[\text{Hf}(\text{CO})_6]^{2-}$, with 50% probability thermal ellipsoids (from ref 120).

the edge of existence" (vide infra). Carbonyl groups attached to electron-rich transition metals have been observed to undergo either Lewis acid promoted reductive coupling¹⁶⁴ or reductive cleavage reactions.¹⁶⁵ In the former reaction, coordinated acetylenediolates, $^-\text{OC}\equiv\text{CO}^-$, or other oxocarbon anions, $\text{C}_n\text{O}_n^{2-}$ ($n = 3-6$),¹⁶⁶ may be produced, while the latter reaction provides metal oxo, L_nMO , and metal ketenylidene, $\text{L}_n\text{-MCCO}$, units.^{165,167} On this basis, it seems most likely that alkali-metal cations facilitate intramolecular reduction of the CO ligands in $[\text{M}(\text{CO})_6]^{2-}$ or intermediate carbonylation products by the strongly reducing group 4 metal centers, followed by facile di- or oligomerization and/or C-O bond cleavage of the reduced CO units. Photolysis or thermolysis of isolable salts of $[\text{M}(\text{CO})_6]^{2-}$ also causes facile decomposition without loss of free CO. However, details of how the hexacarbonylmetalates(2-) readily decompose under a variety of conditions and the natures of their decomposition products remain intriguing unsolved problems in metal carbonyl anion chemistry. It is also noteworthy that the chemical properties of $[\text{Hf}(\text{CO})_6]^{2-}$ have been totally unexplored due to the relative inaccessibility of this unique hafnium complex,¹⁶⁸ which has been the subject of recent theoretical studies.¹⁶⁹

C. Carbonylmetalates(3-, 4-). Table 3 shows the known alkali-metal derivatives of the mononuclear metal carbonyl tri- and tetraanions, the year in which they were first reported,¹⁷⁰ and corresponding infrared

(164) (a) Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712. (b) Bianconi, P. A.; Vrtis, R. N.; Rao, C. P.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *Organometallics* **1987**, *6*, 1968.

(165) (a) Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; Van Duyne, G. D.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1989**, *111*, 9056. (b) Calderazzo, F.; Englert, U.; Guarini, A.; Marchetti, F.; Pampaloni, G.; Segre, A.; Tripepi, G. *Chem. Eur. J.* **1996**, *2*, 412.

(166) West, R., Ed. *Oxocarbons*; Academic Press: New York, 1980.
(167) Interestingly, UV photochemical promoted rearrangements of matrix-isolated $\text{M}(\text{CO})_2$ ($\text{M} = \text{Zr, Hf}$) to OMCCO , i.e., oxo ketenylidene $\text{M}(\text{IV})$ species, have been observed by IR spectroscopy. See: Zhou, M.; Andrews, L. *J. Am. Chem. Soc.* **2000**, *122*, 1531.

(168) To date $[\text{Hf}(\text{CO})_6]^{2-}$ has only been obtained as a $[\text{K}(\text{cryptand-2.2.2})]^+$ salt, by the reductive carbonylation of $\text{Hf}(\text{CO})_4(\text{trmpe})$, which is difficult to prepare in gram quantities.¹⁶² Attempts to use potassium ion complexants far less expensive than cryptand-2.2.2, such as 15-crown-5 and 18-crown-6, have been unsuccessful to date.

(169) (a) Kaupp, M. *Chem. Eur. J.* **1996**, *2*, 348. (b) Szilagy, R. K.; Frenking, G. *Organometallics* **1997**, *16*, 4807. (c) Diefenbach, A.; Bickelhaupt, F. M.; Frenking, G. *J. Am. Chem. Soc.* **2000**, *122*, 6449. (d) Ehlers, A. W.; Ruiz-Morales, Y.; Baerends, E. J.; Ziegler, T. *Inorg. Chem.* **1997**, *36*, 5031.

Table 3. Historic and IR Spectral Data for the Carbonylmetalate Tri- and Tetranions

CO anion	date of discovery ¹⁷⁰	IR, $\nu(\text{CO})$, cm^{-1}
[Co(CO) ₃] ³⁻	1977 (ref 171)	1760 m, 1640 vs, mull (ref 176) ^a
[Rh(CO) ₃] ³⁻	1977 (ref 171)	1664 vs in HMPA (ref 11) ^b
[Ir(CO) ₃] ³⁻	1977 (ref 171)	1666 vs in HMPA (ref 177) ^b
[Mn(CO) ₄] ³⁻	1975 (ref 172)	1805 w, 1670 vs in HMPA (ref 11) ^b
[Re(CO) ₄] ³⁻	1975 (ref 172)	1825 w, 1690 vs in HMPA (ref 11) ^b
[V(CO) ₅] ³⁻	1976 (ref 173)	1800 w, 1590 vs (br), mull (ref 178) ^c
[Nb(CO) ₅] ³⁻	1983 (ref 174)	1810 w, 1580 vs (br), mull (ref 103) ^c
[Ta(CO) ₅] ³⁻	1983 (ref 174)	1813 w, 1560 vs (br), mull (ref 102) ^c
[Cr(CO) ₄] ⁴⁻	1978 (ref 175)	1657 w, 1462 vs, mull (ref 179) ^{b,d}
[Mo(CO) ₄] ⁴⁻	1978 (ref 175)	1680 w, 1471 vs, mull (ref 179) ^{b,d}
[W(CO) ₄] ⁴⁻	1978 (ref 175)	1679 w, 1478 vs, mull (ref 179) ^{b,d}

^a K⁺ salt, mineral oil. ^b Na⁺ salt. ^c Cs⁺ salt, mineral oil; the uncertainty in the positions of the broad low energy peaks is ± 20 cm^{-1} . ^d Silicone fluid mull; low-energy peak for Na₄[W(CO)₄] is bifurcated.

$\nu(\text{CO})$ data. None of these substances has been characterized by a single-crystal X-ray structural analysis to date, but all, except [Rh(CO)₃]³⁻, have been obtained in the form of satisfactorily pure unsolvated alkali-metal salts and exhibit spectral and chemical properties that are entirely consistent with their assigned formulations. Since the syntheses, characterizations, and chemical properties of these substances were reviewed in 1990¹¹ and 1991¹ in some detail, only a few comments, updates, and a brief summary of pertinent results will be included in this section. Full papers on [Nb(CO)₅]³⁻,¹⁰³ [Ta(CO)₅]³⁻,¹⁰² and [Ir(CO)₃]³⁻¹⁷⁷ have recently appeared, as well as the first report on the use of [Re(CO)₄]³⁻ and [Ir(CO)₃]³⁻ in the synthesis of mixed-transition-metal complexes.¹⁸⁰ Although these highly charged compounds are represented in Table 3 and elsewhere in this article as "free anions," it is important to emphasize that these formulations are undoubtedly as unrealistic as ones showing "free" N³⁻, P³⁻, or C⁴⁻ to be present in magnesium nitride, Mg₃N₂, sodium phosphide, Na₃P, or lithium carbide, Li₄C, respectively. Indeed, solution (HMPA) and mull IR spectra of species such as Na₃[Mn(CO)₄] are often extremely similar,¹¹ suggesting that the carbonyl trianions are tightly bound to the sodium cations in a similar way in solution and in the solid state. In a related system Collman and co-workers established by freezing point depression and conductivity studies that Na₂[Fe(CO)₄] in 1-methyl-2-pyrrolidinone, which has about the same dielectric

(170) Dates of discovery represent the first report on these species but not necessarily their first isolation as satisfactorily pure substances.

(171) Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. *J. Chem. Soc., Chem. Commun.* **1977**, 686.

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

(173) Ellis, J. E.; Palazzotto, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 8264.

(174) Warnock, G. F. P.; Sprague, J.; Fjare, K. L.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 672.

(175) Ellis, J. E.; Parnell, C. P.; Hagen, G. P. *J. Am. Chem. Soc.* **1978**, *100*, 3605.

(176) Ellis, J. E.; Barger, P. T.; Winzenburg, M. L.; Warnock, G. F. P. *J. Organomet. Chem.* **1990**, *383*, 521.

(177) Allen, J. M.; Brennessel, W. W.; Buss, C. E.; Ellis, J. E.; Minyaev, M. E.; Pink, M.; Warnock, G. F.; Winzenburg, M. L.; Young, V. G. *Inorg. Chem.* **2001**, *40*, 5279.

(178) Ellis, J. E.; Fjare, K. L.; Hayes, T. G. *J. Am. Chem. Soc.* **1981**, *103*, 6100.

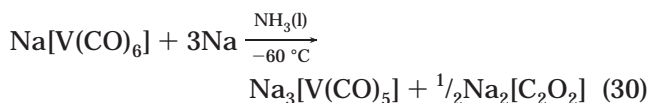
(179) Lin, J. T.; Hagen, G. P.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2296.

(180) Breimar, J.; Rubl, C.; Beck, W. *J. Organomet. Chem.* **1991**, *411*, 395.

constant as HMPA, existed predominantly as a 1:1 electrolyte, i.e., Na⁺[NaFe(CO)₄]⁻; thus, one Na⁺ remained tightly ion paired to [Fe(CO)₄]²⁻ in this highly polar solvent.^{9,143b} No corresponding measurements on solutions of Na₃[M(CO)_x] in HMPA have been carried out.

The first mononuclear carbonyl trianion, [Mn(CO)₄]³⁻, was obtained unexpectedly from the reduction of C₅H₅-Mn(CO)₃ by excess sodium metal in HMPA.¹⁸¹ Infrared spectra of the reaction mixture showed a very intense broad absorption at very low energy, ca. 1670 cm^{-1} , nearly 60 cm^{-1} lower than the band at 1730 cm^{-1} previously observed for [Fe(CO)₄]²⁻ in DMF.¹²¹ Although the possible existence of carbonyl trianions was under active consideration in the early 1970s,¹⁸² only after the identical manganese carbonyl anion and the rhenium analogue had been prepared by reductions of the respective [M(CO)₅]⁻ under the same conditions, and the chemical properties of these species were shown to be entirely consistent with the presence of [M(CO)₄]³⁻ units, were the results of these initial studies communicated in 1975.¹⁷² Since the reductions of Mn₂(CO)₁₀ and Re₂(CO)₁₀ proceeded very smoothly in HMPA to provide high isolated yields (88–98%) of the corresponding unsolvated and exceedingly thermally stable (decomposition ≥ 320 °C) Na₃[M(CO)₄],¹⁸³ it seems very likely that the same procedure should also work to give the unknown Na₃[Tc(CO)₄]. The latter would be of interest as the first compound to contain technetium in a formal oxidation state of -3.

Soon after the carbonyl trianions of manganese and rhenium were announced, related syntheses of Na₃[V(CO)₅]¹⁷³ and Na₃[M(CO)₃] (M = Co, Rh, Ir)¹⁷¹ were reported. However, an efficient route to [Nb(CO)₆]⁻ and [Ta(CO)₆]⁻ had to be developed¹⁰¹ (vide supra) before the niobium and tantalum carbonyl trianions could be accessed.¹⁷⁴ Unlike the carbonyl trianions of the manganese or cobalt triads, which were made from conventional reductions of the carbonyl monoanions at room temperature by sodium metal or sodium naphthalene in HMPA, THF, or DME,^{11,171,172,176,177} analogous reactions of the group 5 [M(CO)₆]⁻ gave only decomposition products, due to the pronounced thermal instabilities of the respective [M(CO)₅]³⁻ in solution and the solid state. Indeed, sodium metal reductions of the hexacarbonylmetalates(1-) had to be carried out at or below -50 °C in liquid ammonia to give high conversion to the trianions. Careful studies showed that a minimum of 3 equiv of sodium metal was required to completely reduce Na[V(CO)₆] to give the characteristic blood red solutions of Na₃[V(CO)₅], along with close to the theoretical amount of "Na₂C₂O₂" (eq 30).^{178,184,185} In this



regard, Behrens' reduction of Cr(CO)₆ by sodium in liquid ammonia provided completely analogous products,¹²⁶ except Na₂[Cr(CO)₅] is thermally stable at room

(181) Ellis, J. E.; Faltynek, R. A.; Hentges, S. G. *J. Organomet. Chem.* **1976**, *120*, 389.

(182) See the section on "Carbonyl trianions" in ref 2.

(183) Warnock, G. F. P.; Moodie, L. C.; Ellis, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 2131.

temperature,¹³⁸ while $\text{Na}_3[\text{V}(\text{CO})_5]$ suffers rapid decomposition at about -5 to 0 °C.¹⁷⁸ Also, as proposed for the reduction of $\text{Cr}(\text{CO})_6$ by sodium in liquid ammonia reaction (vide supra), the corresponding reduction of $[\text{V}(\text{CO})_6]^-$ may proceed via the intermediacy of a presently unknown analogous dimeric complex, $[(\text{OC})_5\text{V}(\mu\text{-C}_2\text{O}_2)\text{V}(\text{CO})_5]^{4-}$, or possibly the monomeric metalloradical $[\text{V}(\text{CO})_6]^{2-}$, since no free CO appears to form in this reaction. Treatment of ammoniacal solutions of $\text{Na}_3[\text{M}(\text{CO})_5]$ with cesium iodide resulted in almost immediate precipitation of beautiful bright orange crystals, likely to be ammonia solvates. When these crystals were dried in vacuo, they crumbled to orange-brown ($M = \text{V}$) to deep brown-red, nearly black ($M = \text{Nb}, \text{Ta}$) powders that gave satisfactory analysis as unsolvated $\text{Cs}_3[\text{M}(\text{CO})_5]$.^{11,102,103,178} Unlike the solid cesium vanadate, which could be handled without incident, *provided* it was not scratched with a metal spatula on a fritted glass surface (**caution! explosion hazard**), the isolated cesium salts of $[\text{Nb}(\text{CO})_5]^{3-}$ and $[\text{Ta}(\text{CO})_5]^{3-}$ were treacherous solids that often exploded with little or no provocation.¹¹ The highly unstable nature of these group 5 cesium salts and our inability to prepare unsolvated $\text{Cs}_2[\text{Ti}(\text{CO})_6]$ (vide supra) are likely to be related issues, but more data are required to establish a definite link.

Since IR spectra could not be conveniently obtained for metal carbonyls in liquid ammonia, the course of the reductions of $[\text{M}(\text{CO})_6]^-$ ($M = \text{V}, \text{Nb}, \text{Ta}$) and identification of the products in solution had to be determined by multinuclear NMR spectroscopy.^{11,102,102,186} For example, by using 99% ^{13}C -labeled $[\text{V}(\text{CO})_6]^-$, ^{13}C , ^{51}V , and ^1H NMR spectra were employed to unambiguously identify $[\text{V}(\text{CO})_5]^{3-}$ and the monoprotonated product, $[\text{HV}(\text{CO})_5]^{2-}$, in liquid ammonia.^{11,78} One particularly interesting feature was the very downfield ^{13}C resonance positions observed for $\text{Na}_3[\text{M}(\text{CO})_5]$ in liquid ammonia at δ_{C} 290, 296, and 293 ppm for V,⁷⁸ Nb,¹⁰³ and Ta,¹⁰² respectively, the most downfield values known for homoleptic mononuclear carbonyls. By comparison, the corresponding values for $[\text{K}(\text{cryptand-2.2.2})][\text{M}(\text{CO})_6]$ in CD_3CN at δ_{C} 245.8, 245.3, and 244.4 ppm for Ti, Zr, and Hf,¹²⁰ respectively, are unexceptional. Martin Kaupp has recently discussed the origin of these and related unusually downfield ^{13}C chemical shifts of early-transition-metal carbonyls.^{169a}

After several metal carbonyl trianions had been prepared, there was interest in determining whether related tetraanions could exist. Since $\text{Cr}(\text{NO})_4$ ^{187,188} was the only known compound to contain a transition metal in a formal oxidation state of -4 ,¹⁸⁹ the isoelectronic $[\text{Cr}(\text{CO})_4]^{4-}$ was chosen as the first "target" molecule.

(184) Freshly prepared disodium acetylenediolate, $\text{Na}_2\text{C}_2\text{O}_2$, from the reaction of CO with sodium in liquid ammonia, is a white to straw-colored solid, like $\text{K}_2\text{C}_2\text{O}_2$, for which the structure is known.¹⁸⁵ However, unlike $\text{K}_2\text{C}_2\text{O}_2$, the sodium salt changes to a dark gray-black (and highly pyrophoric) solid on removal of ammonia. Whether this " $\text{Na}_2\text{C}_2\text{O}_2$ " still contains intact acetylenediolate units or oligomers thereof is apparently unknown.

(185) Weiss, E.; Büchner, W. *Helv. Chim. Acta* **1963**, *46*, 1121.

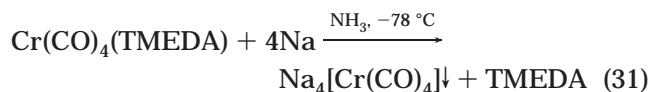
(186) Warnock, G. F. P.; Ellis, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5016.

(187) Heberhold, M.; Razavi, A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1092.

(188) Satija, S. K.; Swanson, B. I. *Inorg. Synth.* **1976**, *16*, 1.

(189) (a) However, the formalism of linear nitrosyls as coordinated NO^+ units in defining metal oxidation states has been criticized in that it leads to "uncomfortably low oxidation states for many metals, e.g., Cr(-IV) in $\text{Cr}(\text{NO})_4$ ": Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth-Heinemann: London, 1997; p

However, unlike $\text{Na}[\text{Mn}(\text{CO})_5]$ (vide supra), $\text{Na}_2[\text{Cr}(\text{CO})_5]$ was found to be stable toward sodium metal in liquid ammonia or HMPA;¹⁹⁰ therefore, clearly a different approach to the tetraanion was necessary. It was known that reductions of heteroleptic transition-metal compounds often resulted in the preferential loss of the weaker or nonacceptor ligands, a reasonable reactivity pattern, since the latter are expected to bind more weakly to the metal as it becomes more electron rich.¹⁹¹ For example, reduction of $[\text{Cr}(\text{CO})_5\text{Cl}]^-$ by sodium in HMPA gave essentially quantitative yields of $[\text{Cr}(\text{CO})_5]^{2-}$, where the nonacceptor or "pure donor" chloride ligand may be viewed as a much better leaving group than CO in this reaction.^{123,192a} On this basis, it was felt that the best possible precursor to $[\text{Cr}(\text{CO})_4]^{4-}$ would be a chromium tetracarbonyl complex containing two "pure-donor" ligated atoms. Since complexes of the type $[\text{Cr}(\text{CO})_4\text{Cl}_2]^{2-}$ were unknown, the readily available $\text{Cr}(\text{CO})_4(\text{TMEDA})$ (TMEDA = $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$) was chosen because coordinated or free TMEDA is quite resistant toward reduction. Soon it was discovered that reduction of $\text{Cr}(\text{CO})_4(\text{TMEDA})$ by sodium in liquid ammonia afforded high isolated yields, 93% based on $\text{Cr}(\text{CO})_4(\text{TMEDA})$, of an insoluble bright yellow powder, which gave satisfactory analyses for unsolvated $\text{Na}_4[\text{Cr}(\text{CO})_4]$ (eq 31).¹⁷⁵ Also, the reaction was surprisingly



clean for a sodium metal reduction of a metal carbonyl in liquid ammonia, since no detectable amounts of the usual contaminants, NaNH_2 and $\text{Na}_2\text{C}_2\text{O}_2$,^{128,185} were present in the product. Analogous orange-yellow $\text{Na}_4[\text{Mo}(\text{CO})_4]$ and orange $\text{Na}_4[\text{W}(\text{CO})_4]$ were isolated in 95 and 97% yields, respectively, by identical procedures. Silicone fluid mull IR spectra of these exceedingly pyrophoric solids showed intense and broad, but well-resolved, bands, a doublet for tungsten, from 1460 cm^{-1} ($M = \text{Cr}$) to about 1500 cm^{-1} ($M = \text{W}$).^{175,179,192b} These values were about $100\text{--}120\text{ cm}^{-1}$ lower than corresponding bands observed in mull spectra of $\text{Na}_3[\text{Mn}(\text{CO})_4]$ and $\text{Na}_3[\text{Re}(\text{CO})_4]$, as expected in terms of previously established trends.^{193,194b} Since IR spectra and the chemical properties of these substances are entirely consistent with the presence of normal metal

450. (b) Malcolm Green has proposed an alternative approach to the organization of transition-metal complexes that avoids the use of often misleading formal oxidation state assignments: Green, M. H. L. *J. Organomet. Chem.* **1995**, *500*, 127.

(190) A solution of sodium metal in HMPA has been found to contain significant concentrations of sodium anion, Na^- , and consequently Na-HMPA is a much stronger reducing medium than Na-NH_3 . See: Edwards, P. P.; Guy, S. H.; Holton, D. M.; McFarlane, W. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1185.

(191) This is now called the "reductive labilization method" and represents an important general route to unusual classes of highly reduced organometallics.^{175,179} See also the synthesis of $[\text{Mn}(\text{CO})_3(\text{NO})]^{2-}$: Chen, Y.-S.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1689.

(192) (a) Cooper and co-workers have prepared several quite remarkable heteroleptic metal carbonyl anions employing related reductive labilization syntheses. $[\text{W}(\text{CO})_4\{\text{P}(\text{i-Pr})_3\}]^{2-}$: Reference 133. $[\text{Cr}(\eta\text{-benzene})(\text{CO})_2]^{2-}$: Leong, V. S.; Cooper, N. J. *Organometallics* **1987**, *6*, 2000. $[\text{Mn}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]^{2-}$: Leong, V. S.; Cooper, N. J. *Organometallics* **1988**, *7*, 2080. $[\text{Cr}(\text{CO})_4\{\text{C}(\text{OMe})\text{Ph}\}]^{2-}$: Lee, S.; Cooper, N. J. *J. Am. Chem. Soc.* **1990**, *112*, 9419 and references therein. (b) Silicone fluid, i.e., dimethylsilicone polymer (Dow Corning 704), was used, since it was far more transparent from 1400 to 1500 cm^{-1} than mineral oil and, unlike Fluorolube, was inert toward the tetrasodium salts.

carbonyl anions containing discrete CO ligands,¹⁹⁵ there is little doubt that they are all best formulated to contain $[M(CO)_4]^{4-}$ units, albeit tightly ion paired to the Na^+ counterions. Their insolubility in a range of non-oxidizing aprotic polar solvents, including THF, DME, DMF, and HMPA, makes them unlikely candidates for single-crystal X-ray structural analyses; however, their solid-state MAS ^{13}C NMR spectra should be obtained to confirm that the ^{13}C chemical shifts of these unique species are in the appropriate range for highly reduced metal carbonyls. Finally, although there have been no reported preparations of “carbonyl pentaanions”, $[M(CO)_x]^{5-}$, unsuccessful attempts to access “ $K_6[M(CO)_3]$ ”, i.e., “carbonyl hexaanions”, by the reductions of $M(CO)_3$ - (PMTA) ($M = Cr, Mo, W$; PMTA = 1,1,4,7,7-pentamethyldiethylenetriamine) with potassium metal in liquid ammonia have been noted.^{11,196}

IV. Concluding Remarks: Where Do We Go from Here?

Homoleptic mononuclear metal carbonyl anions are now well established for all but the earliest (group 3) and latest (groups 10 and 11) transition metals. Syntheses of low-valent carbonyls of the very early and very late transition metals will be especially challenging, due in part to dramatic differences in the relative energies of the valence d electrons on these metals.¹⁹⁷ For low-valent early transition metals, the valence electrons will be of sufficiently high energy that metal to $\pi^*(CO)$ charge transfer may result in irreversible reduction¹⁹⁸ and subsequent transformation of one or more carbonyl ligands: i.e., reductive coupling and/or cleavage of coordinated carbon monoxide. For example, the tremendous reducing ability of low-valent scandium is probably the main reason scandium carbonyls have not been

(193) For a given type of metal carbonyl, $[M(CO)_xL_y]^{z-}$, where x, y, L , and the overall molecular geometry are the same, the mean IR $\nu(CO)$ value generally decreases by about $120 \pm 20 \text{ cm}^{-1}$ as the molecular charge z is lowered by one unit. However, site-specific ion pairing in salts of metal carbonyl anions can cause observed $\nu(CO)$ values to be dramatically different from expected ones.^{75,76}

(194) (a) Willner, H.; Aubke, F. Submitted for publication in *Organometallics*. (b) Lupinetti, A. J.; Strauss, S. H.; Frenking, G. *Prog. Inorg. Chem.* **2001**, *49*, 1 (see p 44, Figure 22). (c) Willner, H.; Aubke, F. *Angew. Chem., Int. Ed.* **1997**, *36*, 2402. (d) Belli Dell'Amico, D.; Calderazzo, F. *Gazz. Chim. Ital.* **1973**, *103*, 1099. In this article the synthesis and characterization of $Au(CO)Cl$ was presented and it was noted: “Whatever the reason may be, the present high wavenumber value observed for the C–O stretching vibration of (the complex) suggests a very low degree of back-donation from the metal to the carbonyl group.” In this fashion, the authors were the first to suggest that CO could function as essentially a σ -donor-only ligand in transition-metal chemistry.

(195) (a) Lin, J. T.; Hagen, G. P.; Ellis, J. E. *Organometallics* **1983**, *2*, 1145. (b) Lin, J. T.; Hagen, G. P.; Ellis, J. E. *Organometallics* **1984**, *3*, 1288.

(196) Rochfort, G. L.; Ellis, J. E. *J. Organomet. Chem.* **1983**, *250*, 265.

(197) Green, M. L. H. *Organometallic Compounds: The Transition Elements*; Methuen: London, 1968; pp 4, 5.

(198) It has been established that there is a substantial red shift in the metal to $\pi^*(CO)$ charge transfer in MLCT bands in going from colorless $[Cr(CO)_6]$ to yellow $[V(CO)_6]^-$: i.e., as the oxidation state of the metal becomes lower. See: Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979; pp 35–40. The deep red colors of $[Ti(CO)_6]^{2-}$ and $[V(CO)_5]^{3-}$ likely arise, at least in part, from further red shifts in analogous MLCT bands. For even more strongly reducing metal centers, these MLCT bands of carbonyl complexes could be sufficiently red-shifted to move into the near-IR region. In this case, intramolecular reduction of coordinated carbonyl groups by the metal would require so little energy that the resulting compounds would be expected to readily decompose under normal conditions.

obtained under normal conditions in condensed phases.¹⁹⁹ In contrast, for the later transition metals, the valence d electrons are at sufficiently low energies that the metal may be incapable of effectively participating in $d\pi-\pi^*$ back-bonding, due to its poor π -donor ability. This is undoubtedly why homoleptic zerovalent copper carbonyls, i.e., $Cu(CO)_x$ ($x = 1-3$), are only known as matrix-isolated “cryomolecules”:²⁰⁰ i.e., the Cu–CO bonds are simply too weak to prevent facile dissociation of free CO (above $\sim 30 \text{ K}$) and subsequent formation of bulk copper metal. Incredibly (and fortunately for Ludwig Mond), just the opposite situation holds for copper’s neighbor in the periodic table, nickel!

What are the prospects for the synthesis of new and isolable homoleptic mononuclear carbonyl anions? In view of the relatively stable nature of the 17-electron and paramagnetic neutral $V(CO)_6$,⁶⁹ several attempts to prepare the isoelectronic $[Ti(CO)_6]^-$ have been made, all without success.²⁰¹ Another possible monoanion would be the 18-electron 7-coordinate scandium complex $[Sc(CO)_7]^-$, but since there is no evidence for the existence of the analogous $Ti(CO)_7$,²⁰² nor are any compounds known to contain scandium in a negative oxidation state, the synthesis of this scandate(1–) would be quite remarkable! To be sure, the group 4 carbonyl dianions $[M(CO)_6]^{2-}$ and the group 5 carbonyl trianions $[M(CO)_5]^{3-}$ are isolable and well defined, but they are also thermally unstable, especially in solutions exposed to visible radiation, and even explosive as solids, in some cases. This instability has been ascribed to facile, but ill-defined, intramolecular reductions of coordinated CO groups by the strongly reducing early transition metals in formal –2 and –3 oxidation states, respectively.¹⁹⁸ On this basis, the possible existence of more highly reduced group 4 carbonyls such as $[Ti(CO)_5]^{4-}$ seems doubtful, although a formal derivative of this tetraanion, i.e., $[Ti(CO)_5(SnPh_3)_2]^{2-}$, is well established.¹ Much more problematic would be group 3 hexacarbonylmetalates, e.g., $[Sc(CO)_6]^{3-}$ (which would be a truly scandalous compound!), since Sc(–III) is expected to be more strongly reducing and therefore even less compatible with discrete CO ligands than Ti(–II) in $[Ti(CO)_6]^{2-}$ or V(–III) in $[V(CO)_5]^{3-}$. For these reasons, the synthesis of any new early-transition-metal homoleptic carbonyl anion would be a most pleasant surprise! In this regard, $[Ti(CO)_6]^-$ and $[Ti(CO)_5]^{4-}$ may be “dark horse” candi-

(199) (a) A scandium(I) carbonyl complex, $[Sc(CO)]^+$, has been observed in the gas phase: Fischer, K. J. *Prog. Inorg. Chem.* **2001**, *50*, 343 and references therein. (b) Highly electrophilic Sc(III) complexes would appear most likely to provide isolable carbonyls of scandium, in which the CO would function primarily as a pure donor ligand.¹⁹⁴ Thus far, Sc(III) carbonyls are only known as highly unstable “cryomolecules”, e.g., $[Sc(CO)O]^+$ (10 K, Ar matrix): Zhou, M.; Andrews, L. *J. Phys. Chem. A* **1999**, *103*, 2013.

(200) Huber, H.; Kündig, P.; Moscovitz, M.; Ozin, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 2097.

(201) One of the most promising of these attempts involved the carbonylation of the 17-electron bis(biphenyl)titanate(1–), which gave nearly quantitative, i.e., 50% yields, of $[Ti(CO)_6]^{2-}$. This and related experiments indicated that $[Ti(CO)_6]^-$ is even more unstable toward disproportionation, i.e., $2Ti^- \rightarrow Ti^0 + Ti^{2-}$, than $V(CO)_6$ and resembles the 17-electron Ta(CO)₆ in this regard.¹⁰² See: Blackburn, D. W.; Britton, D.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1495.

(202) The apparent great instability of $Ti(CO)_7$ or the isoelectronic $[V(CO)_7]^+$ has been attributed to the inability of a relatively “electron poor” d^4 metal center to effectively back-bond to seven carbonyl groups.^{118b} For example, substitution of only one CO group in $Ti(CO)_7$ by a good donor ligand may provide enough stabilization of the remaining titanium carbonyl bonds to allow isolation of the complex, as in the case of $[Ti(CO)_6\{Au(PET_3)\}]^-$: Fischer, P. J.; Young, V. G.; Ellis, J. E. *Chem. Commun.* **1997**, 1249.

dates, since absolutely amazing molecules can sometimes be stabilized by effective ion pairing and/or strong crystalline lattices.

In contrast, the surprisingly robust character of the group 9 carbonyl trianions $[\text{M}(\text{CO})_3]^{3-}$ would appear to bode well for the existence of at least certain tricarbonylmetalate di- and monoanions of the group 10 and 11 elements, respectively. Undoubtedly, $[\text{Ni}(\text{CO})_3]^{2-}$ is the most promising candidate, since Jonas has isolated the homoleptic ethylene analogue as the dilithium compound $[\text{Li}(\text{TMEDA})_2[\text{Ni}(\text{C}_2\text{H}_4)_3]$, one of several known olefin nickelates(2-).²⁰³ Unlike the related iron ethylene complex $[\text{Fe}(\text{C}_2\text{H}_4)_4]^{2-}$, which readily reacts with CO to give high yields of $[\text{Fe}(\text{CO})_4]^{2-}$,¹⁰⁷ carbonylation of the nickel complex evidently failed to produce the elusive $[\text{Ni}(\text{CO})_3]^{2-}$.²⁰⁴ Nevertheless, because ethylene is generally regarded to be a weaker acceptor ligand than CO, the existence of $[\text{Ni}(\text{C}_2\text{H}_4)_3]^{2-}$ and $[\text{Co}(\text{CO})_3]^{3-}$ strongly suggests that $[\text{Ni}(\text{CO})_3]^{2-}$ should be a viable species. Since reductive carbonylations of nickel or platinum (but not palladium²⁰⁵) halides or reductions of $\text{Ni}(\text{CO})_4$ are well established to provide a number of polynuclear carbonyl anions, including $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ and $[\text{Pt}_6(\text{CO})_{12}]^{2-}$,²⁰⁶ clearly more appropriate precursors will be required for syntheses of salts containing $[\text{M}(\text{CO})_3]^{2-}$.²⁰⁷

Prospects for the syntheses of the group 11 carbonyl anions $[\text{M}(\text{CO})_3]^-$ are much less certain, since the M–C bonds in these species will likely prove to be appreciably weaker than those in analogous group 10 dianions or the group 9 monoanions, $[\text{M}(\text{CO})_4]^-$, owing to the relatively weak π -donor ability of group 11 metals.¹⁹⁷ Undoubtedly, $[\text{Cu}(\text{CO})_3]^-$, or a substituted version thereof, is the most promising candidate for synthesis, since even monovalent copper can effectively back-bond to CO, provided a strong donor group is present.²⁰⁸ For example, the Cu(I) complex $\text{Cu}(\text{CO})(\text{Tp}^*)$ ($\text{Tp}^* = \text{hydrido}(\text{tris-3,5-dimethyl-1-pyrazolyl})\text{borate}$) has an IR $\nu(\text{CO})$ band at 2063 cm^{-1} , well below that of free CO, ca. 2150 cm^{-1} , and is thermally robust as a solid (decomposition at $187\text{--}189\text{ }^\circ\text{C}$).²⁰⁹ Since no well-defined compound containing copper in a negative oxidation state is known, the synthesis of $[\text{Cu}(\text{CO})_3]^-$ or related derivatives would be an exciting development. In contrast, $\text{Au}(\text{I}^-)$ is well established as atomic Au^- , which is stable in the gas as well as in condensed phases,²¹⁰ but is of

special interest in that its coordination chemistry remains totally unexplored. In particular, will Au^- bind or simply reduce CO ?²¹¹ Since silver carbonyls tend to be much less stable than related copper or gold complexes, $[\text{Ag}(\text{CO})_3]^-$ would appear to be the least promising candidate for existence or isolation.²¹²

New and exciting vistas are clearly possible for carbonyl anions of the d-block metals. However, the remarkable isolation and structural characterization by Carmona and co-workers of a neutral uranium(III) monocarbonyl, $\text{U}(\eta^5\text{-C}_5\text{Me}_5\text{H})_3\text{CO}$, which has a very low IR $\nu(\text{CO})$ value of 1900 cm^{-1} ,²¹³ demonstrated that uranium in the proper ligand environment can be as effective a π -donor to coordinated CO as d-block transition metals. Also, Andersen, Brintzinger, and co-workers recently discovered that several examples of neutral heteroleptic carbonyls of divalent lanthanides can exist in solution under relatively mild conditions. The most intriguing of these species is the ytterbium dicarbonyl complex $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{CO})_2$, which absorbs at 2072 cm^{-1} , far below that of free CO.²¹⁴ Although there is controversy concerning the structure of the ytterbium carbonyl,²¹⁵ the viability of this species is extraordinary, since no di- or polycarbonyls of f-block elements were previously known to survive at room temperature.^{216–218} These remarkable results demonstrate that 4f- and 5f-block elements can form relatively stable carbonyls and strongly suggest that f-block metal carbonyl chemistry is an important and exciting new area of research, ripe for exploration! Although the prospects for obtaining stable homoleptic carbonyl anions for any of the lanthanides and most of the actinides appear to be quite unfavorable, due to the very strong reducing character of these metals, uranium appears to be exceptional in this regard. Indeed, of all the f-block elements, the chemical properties of uranium most resemble those of the early transition metals. For example, Cummins and co-workers have recently established that low-valent uranium is remarkable in its ability to function as a strong π -donor to a variety of unsaturated hydrocarbons such as naphthalene.²¹⁹ Also, the U(IV)/U(0) standard reduction potential is slightly less negative than corre-

(210) See the citation in ref 207.

(211) Lagowski has shown Au^- to be a potent reducing agent in liquid ammonia: Peer, W. J.; Lagowski, J. *J. Am. Chem. Soc.* **1978**, *100*, 6260.

(212) For example, the essentially isostructural monovalent group 11 carbonyl complexes of the general formula $\text{M}(\text{CO})\text{Tp}^-$ ($\text{Tp}^- = \text{hydridotris}(3,5\text{-bis}(\text{trifluoromethyl})\text{-1-pyrazolyl})\text{borate}$) show the following IR $\nu(\text{CO})$ values: Cu, 2137 cm^{-1} ; Ag, 2162 cm^{-1} ; Au, 2144 cm^{-1} . This establishes the relative π -donor abilities of the group 11 metals in these complexes to be $\text{Cu} > \text{Au} > \text{Ag}$. See: Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 3687 and references therein.

(213) (a) Parry, J.; Carmona, E.; Coles, S.; Hursthouse, M. *J. Am. Chem. Soc.* **1995**, *117*, 2649. (b) del Maro Conejo, M.; Parry, J. S.; Carmona, E.; Scultz, M.; Brennan, J. B.; Beshouri, S. M.; Andersen, R. A.; Rogers, R. D.; Coles, S.; Hursthouse, M. *Chem. Eur. J.* **1999**, *5*, 3000.

(214) Selg, P.; Brintzinger, H. H.; Schultz, M.; Andersen, R. A. *Organometallics* **2002**, *21*, 3100.

(215) A recent computational study suggested that the ytterbium carbonyls could contain O-bound carbon monoxide: Maron, L.; Perrin, L.; Eisenstein, O.; Andersen, R. A. *J. Am. Chem. Soc.* **2002**, *124*, 5614.

(216) A thermally unstable matrix-isolated uranium carbonyl, proposed to be $\text{U}(\text{CO})_6$ ($\nu(\text{CO})\ 1961\text{ cm}^{-1}$) has been known for many years: Slater, J. L.; Sheline, R. K.; Lin, K. C.; Weltner, W. J. *J. Chem. Phys.* **1971**, *55*, 5129.

(217) (a) Zhou, M.; Andrews, L.; Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **1999**, *121*, 9712. (b) Li, J.; Bursten, B. E.; Zhou, M.; Andrews, L. *Inorg. Chem.* **2001**, *40*, 5449 and references therein.

(218) Ellis, J. E.; Beck, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2489 and references therein.

(203) (a) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 752. (b) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 530 and references therein.

(204) Lewis base induced disproportionations of $\text{Ni}(\text{CO})_4$ were once thought to provide salts of the type $[\text{Ni}^{\text{I}}\text{B}_4][\text{Ni}^{\text{II}}(\text{CO})_3] (\text{B} = \text{Lewis base})$. See: Hieber, W.; Nast, R.; Sedlmeier, J. *Angew. Chem.* **1952**, *64*, 468.

(205) Palladium carbonyls tend to be less stable or accessible than analogous nickel or platinum species. See the citation in ref 62, pp 1065–1068.

(206) Bengtsson-Kloo, L.; Iapalucci, C. M.; Longoni, G.; Ulvenlund, S. *Inorg. Chem.* **1998**, *37*, 4375 and references therein.

(207) The existence of relatively stable gaseous atomic Pt^- , owing to the high electron affinity of platinum, suggests that a series of di- or mononuclear platinum carbonyls or related species containing $\text{Pt}(\text{I}^-)$ or $\text{Pt}(\text{II}^-)$, respectively, may be possible. See: Pyykkö, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 3573.

(208) Coordination of a strong donor group to Cu(I) will effectively increase the energy of the $3d^{10}$ subshell to provide a better energy match with the π^* orbitals of the bound CO. Reducing the formal oxidation state of copper from +1 to -1 will have the same effect. However, $[\text{Cu}(\text{CO})_3]^-$ could still be intrinsically unstable, due to the relative ineffectiveness of Cu(I) serving as a π donor to three carbonyl groups.

(209) Abu Salah, O. M.; Bruce, M. I.; Homeister, C. *Inorg. Synth.* **1982**, *21*, 107.

sponding values for the heavier group 4 elements, Zr and Hf;²²⁰ therefore, zero- or even subvalent uranium may not be redox incompatible with coordinated CO. In view of the existence of $[\text{W}(\text{CO})_5]^{2-}$ and $[\text{Hf}(\text{CO})_6]^{2-}$, and since uranium is not constrained by the 18-electron rule,²¹⁸ the possibility of preparing and isolating salts of $[\text{U}(\text{CO})_5]^{2-}$ or the formally 20-electron U(II-) complex $[\text{U}(\text{CO})_6]^{2-}$ may not be total fantasy!

Acknowledgment. Many thanks go to Professor Dietmar Seyferth for his original inception of the "Cover Reviews" for this journal and for encouragement and support to write the present article. I am very grateful to Professor Fausto Calderazzo, who read the entire manuscript and whose many insightful comments helped immeasurably in improving its clarity and content. Also, I thank Professor Friedhelm Aubke for a copy of his and Professor Willner's superb manuscript on " σ -Bonded Metal Carbonyl Cations and Their Derivatives: Syntheses and Structural, Spectroscopic, and Bonding

(219) Diaconescu, P.; Cummins, C. C. *J. Am. Chem. Soc.* **2002**, *124*, 7660 and references therein.

(220) Emsley, J. *The Elements*, 3rd ed.; Clarendon Press: Oxford, U.K., 1998.

Principles," to be published as a "cationic complement" to this article and to emphasize how truly versatile the carbon monoxide ligand is in both transition-metal and main-group chemistry.^{194a} Sincere appreciation is also due to all of my past and present co-workers, who are shown as coauthors in citations for research carried out in this laboratory. Without their valiant efforts, as well as generous funding from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, none of our results in metal carbonyl anion chemistry described herein would have been possible. I am particularly indebted to Professor Doyle Britton, who carried out the single-crystal X-ray structural characterization of $[\text{Hf}(\text{CO})_6]^{2-}$, the "cover molecule," as well as numerous other X-ray structures of our "chemical children" over the years. Special thanks are due to Ms. Christine Lundby for expert and invaluable assistance in transforming an unbelievably messy first draft into a legible manuscript. Finally, I am in substantial debt to members of my research group for their unusual understanding and initiative, as they went virtually "leaderless" during the 2+ months it took to write this "brief account", which kept getting longer and longer.

OM030105L