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Adventures with Substances Containing Metals in Negative Oxidation States[†]

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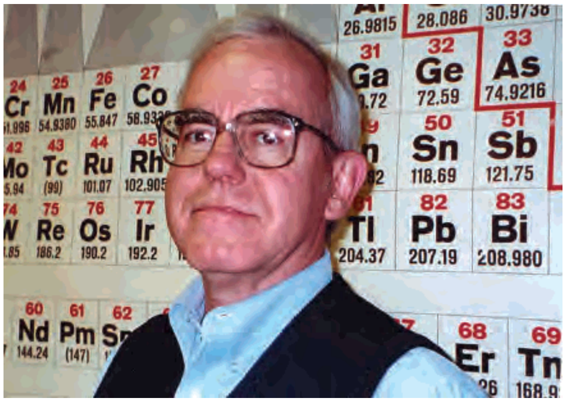
A brief history of substances containing s,p- and d-block metals in negative oxidation states is described. A classification of these species and discussions of formal oxidation state assignments for low-valent transition metals in complexes are included, along with comments on the innocent and noninnocent character of ligands in metalates. Syntheses of highly reduced carbonyl complexes formally containing transition metals in their lowest known oxidation states of III– and IV– are discussed. Atmospheric-pressure syntheses of early-transition-metal carbonyls involving alkali-metal polyarene-mediated reductions of non-carbonyl precursors have been developed. In the absence of carbon monoxide, these reactions afford homoleptic polyarenemetalates, including the initial species containing three aromatic hydrocarbons bound to one metal. In several instances, these metalates function as useful synthons for "naked" spin-paired atomic anions of transition metals.

Introduction

The adventures[1] to be described in this paper involve the synthesis and characterization of anionic carbonyls and related complexes of d-block elements that my students and I have carried out over the past 34+ years at the University of Minnesota. However, to properly set the stage for our efforts, it will be necessary to first consider pertinent aspects of the history of free and ligand-stabilized metal anions, including some recent exciting discoveries in this area. The anionic main-group species are of particular interest because they represent the first compounds to contain metals in negative oxidation states or valencies.[2]

Main-Group Metal Anions

More than 100 years ago, Joannis discovered that Na metal dissolved elemental Pb, Sb, and Bi in liquid ammonia to afford intriguing highly air-sensitive solutions. These new substances were originally called "definite alloys of sodium" because removal of ammonia gave entities of fixed composition with a metallic appearance.[3] However, the liquid-ammonia solutions were often transparent and highly colored, indicating that the soluble components were of much different character than the ammonia-free alloys. For example, Na–Pb reactions in ammonia gave solutions ranging from reddish-brown to dark-green, with excess Pb. In 1907, Kraus reported that the dark-green solutions were electrically



John Ellis was born in 1943 in San Pedro, CA. He received a B.S. degree from the University of Southern California and a Ph.D. from the Massachussetts Institute of Technology under the direction of Professor Alan Davison. He joined the faculty at the University of Minnesota, where he has been professor of chemistry since 1984. Honors include a Humboldt Senior Scientist Award, spent in Professor Wolfgang Beck's group at Ludwig-Maximilians-Universität in Munich, Germany, and the F. Albert Cotton Award in Synthetic Inorganic Chemistry for the synthesis and characterization of compounds containing metals in their lowest known oxidation states. Basic research in inorganic–organometallic chemistry remains an exciting enterprise, and he hopes to continue work in this area for many years to come.

[†] Dedicated to Professor F. Albert Cotton for his support and encouragement throughout the years and for coauthoring with Geoffrey Wilkinson a most remarkable textbook that helped to solidify my interests in inorganic chemistry more than 40 years ago. This paper is based on the address for the inaugural (2004) F. Albert Cotton Award in Synthetic Inorganic Chemistry sponsored by the F. Albert Cotton Endowment Fund and presented at the 227th National Meeting of the American Chemical Society, Anaheim, CA, on March 30, 2004.

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conducting and, on the basis of conductivity data, boldly suggested that they contained the ions “Na$^+$ and $\mathrm{Pb_2}^-$”[4] (eq 1). Later research by Zintl established that the dark-green Pb species had the composition $\mathrm{Na_4Pb_9}$, so Kraus’s proposal was quite close to the correct empirical formula! Zintl’s group also determined the composition of numerous related ammoniacal solutions and showed that they were all best formulated as salts of main-group metal or metalloidal anions.[5,6]

$$\mathrm{Na} + \text{excess Pb} \xrightarrow[-50\ °\mathrm{C}]{\mathrm{NH_3}} \mathrm{Na}^+ + \text{“}\mathrm{Pb_2}^-\text{”} \tag{1}$$

By employing effective alkali-metal cation complexants, such as crown ethers or cryptands, in the 1970s, Corbett and others showed that many of these materials, now called Zintl compounds or phases, were isolable as bona fide salts containing discrete anions,[7] e.g., eq 2. Exciting new discoveries continue to be made in this burgeoning field of homopolyatomic main-group anion chemistry.[8]

$$4\mathrm{NaSn}_{2.25} + 4(\text{cryptand } 222) \xrightarrow[20\ °\mathrm{C}]{\mathrm{en}} [\mathrm{Na}(\text{cryptand } 222)]_4\mathrm{Sn}_9 \tag{2}$$

Monatomic Metal Anions

Detection of monatomic metal anions in the gas phase by mass spectroscopy dates back to the 1930s,[9] when Hg$^-$,[10] now known to be unstable,[11] and possibly Cr$^-$ and Ni$^-$ [12] were noted. However, the observation of ^{6}Li$^-$ and ^{7}Li$^-$, in the correct isotopic ratios, in 1947 appears to be the first unambiguous evidence for the existence of a stable atomic metal anion.[13] This result confirmed an earlier computed electron affinity for atomic Li,[14] which predicted the stability of Li$^-$ in the gas phase, a species that has not yet been found in a condensed phase.

Monatomic metal anions, M^{Z-}, have also been observed in the solid state and/or solution for Au, Ag, Pt, and the heavier alkali metals, i.e., Na−Cs. Undoubtedly, the first synthesis of such a species was unknowingly carried out by Zintl’s group, who discovered that AuI in liquid ammonia reacted with 2 equiv of Na metal to afford a poorly soluble species formulated as the alloy phase NaAu, along with sodium iodide.[5] On the basis of later work by Peer and Lagowski,[15] vide infra, it appears almost certain that Zintl had generated ammoniacal solutions of Au$^-$ long ago, albeit in low concentration.[16]

An early claim for the existence of a monatomic metal anion, Re$^-$ or “rhenide ion”, in an aqueous solution was made in 1937.[17,18] Electrochemical studies seemed to support the existence of Re$^-$,[19] but later studies fully discredited these early reports.[20] Despite the fact that there is no compelling evidence for Re$^-$ in solution, it still appears in some standard reduction potential diagrams.[21] Nearly 30 years after the first erroneous report on Re$^-$, the anion was finally observed in the gas phase and the electron affinity of atomic Re was estimated.[22]

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(1) Adventure: An exciting, risky, and/or dangerous endeavor but one that may have romantic qualities, especially when it yields surprising new results! A seminar of the same title was presented by this writer on Feb 23, 2000, as the annual “Faculty Lecture” to the Faculty of Natural Sciences, Mathematics and Physics at the University of Pisa, Pisa, Italy.

(2) Oxidation states, oxidation numbers, and valencies of metals in compounds are considered to be synonymous in this paper, as they have been in the past in many textbooks. For example, see: (a) Latimer, W. M.; Hildebrand, J. H. *Reference Book of Inorganic Chemistry*; Macmillan: New York, 1940; p 467. (b) Pauling, L. *General Chemistry*; W. H. Freeman: San Francisco, 1947; pp 172−174, 188, 189, 196, 197, etc. Also, see refs 56−58, regarding *formal oxidation state* assignments, vide infra.

(3) Joannis, A. *C. R. Hebd. Seances Acad. Sci.* **1891**, *113*, 795; **1892**, *114*, 585; *J. Chem. Soc., Abstr.* **1892**, *62*, 275, 773.

(4) Kraus, C. A. *J. Am. Chem. Soc.* **1907**, *29*, 1557.

(5) (a) Zintl, E.; Goubeau, J.; Dullenkopf, W. *Z. Phys. Chem.* **1931**, *154A*, 1. (b) Zintl, E.; Harder, A. *Z. Phys. Chem.* **1931**, *154A*, 47; *Chem. Abstr.* **1931**, *25*, 3260.

(6) Compounds containing metalloids or semimetals in negative oxidation states occur in nature, e.g., loellingite ($\mathrm{FeAs_2}$), dyscrasite ($\mathrm{Ag_3Sb}$), berzelianite ($\mathrm{Cu_2Se}$) (and some $\mathrm{Ag_2Se}$), and tetradymite ($\mathrm{Bi_2Te_3}$), which formally contain As(I−), Sb(III−), Se(II−), and Te(II−), respectively. Also zinc telluride, likely in impure form, containing Te(II−), was obtained and acidified by Sir Humphry Davy in 1810 to obtain hydrogen telluride. See: Partington, J. R. *A Textbook of Inorganic Chemistry*, 5th ed.; Macmillan: London, 1937; p 536.

(7) Corbett, J. D. *Chem. Rev.* **1985**, *85*, 383. This outstanding review contains a detailed chronological survey of “polyatomic Zintl anions” and related species.

(8) (a) Corbett, J. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 670. (b) Li, X.; Kuznetsov, A. E.; Zhang, H.-F.; Boldyrev, A. I.; Wang, L.-S. *Science* **2001**, *291*, 859. (c) Goicoechea, J. M.; Sevov, S. *J. Am. Chem. Soc.* **2004**, *126*, 6860 and references cited therein.

(9) The following sources provide detailed information on the early history of gas-phase studies of monatomic metal anions: (a) Massey, H. S. W. *Negative Ions*, 2nd ed.; Cambridge University Press: London, 1950. (b) Pritchard, H. O. *Chem. Rev.* **1953**, *52*, 529.

(10) Arnot, F. L.; Milligan, J. C. *Proc. R. Soc. London, Ser. A* **1936**, *156*, 538.

(11) Zollweg, R. J. *J. Chem. Phys.* **1969**, *50*, 4251.

(12) Sloane, R. H.; Press, R. *Proc. R. Soc. London, Ser. A* **1938**, *168*, 284.

(13) Sloane, R. H.; Love, H. M. *Nature* **1947**, *159*, 302.

(14) You-Wu, T. *Philos. Mag.* **1936**, *22*, 837. This computed electron affinity for atomic Li, 0.54 eV, is not far from the currently accepted value, 0.62 eV; see ref 26a.

(15) Peer, W. J.; Lagowski, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 6260.

(16) Schmidbauer, H.; Dash, K. C. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 239. This review contains an outstanding account of the history of Au$^-$ in condensed phases.

(17) Lundell, G. E. F.; Knowles, H. B. *Bur. Stand. J. Res.* **1937**, *18*, 629. Because Mn (and later Re, discovered in 1925) and the halogens are depicted as members of the group VII family of elements in Mendeleev’s original periodic table,[18] which was commonly used in the United States into the 1960s, it undoubtedly “made sense” in 1937 to propose the existence of Re$^-$. The latter would be formally analogous to Br$^-$ or I$^-$ but is electronically quite different. See: Pauling, L. *Chem. Eng. News* **1947**, *25*, 2970. A well-known textbook of 1940 rather forcefully stated “when perrhenate is reduced in acid solution with zinc, eight equivalents of oxidizing agent are required to oxidize the solution, and this constitutes evidence for the existence of the rhenide ion, Re$^-$”. See: Reference 2a, pp 374 and 375.

(18) Emsley, J. *The Elements*, 3rd ed.; Clarendon Press: Oxford, U.K., 1998; p 270.

(19) (a) Rulfs, C. L.; Elving, P. J. *J. Am. Chem. Soc.* **1951**, *73*, 3287. (b) Maun, E. K.; Davidson, N. *J. Am. Chem. Soc.* **1950**, *72*, 3509 and references cited therein. Electrochemical studies showed that $\mathrm{ReO_4}^-$ underwent an apparent 8-electron reduction in aqueous perchloric or sulfuric acid.

(20) (a) Ginsberg, A. V. *Transition Metal Chemistry*; Carlin, R. L., Ed.; Dekker: New York, 1965; Vol. 1, pp 112−228. In this well-referenced early review on “Hydride Complexes of the Transition Metals”, Ginsberg describes the history of “Re$^-$”. His attempts to prepare this species ultimately resulted in the isolation and characterization of the first thermally robust binary transition-metal hydride, $[\mathrm{ReH_9}]^{2-}$, perhaps a more remarkable substance than “Re$^-$”! Interestingly, he also stated that, “The original ‘rhenide’ solutions, obtained in acid media,[17] also probably contain rhenium hydride ions (but not $\mathrm{ReH_9}^{2-}$) ...” To the best of my knowledge, the nature of this historically significant species still remains unknown. However, because it does not react with CO, it seems unlikely to be a coordinatively unsaturated low-valent species.[19b] (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 2nd ed.; Interscience: New York, 1966; pp 978 and 979.

(21) (a) Jolly, W. L. *Modern Inorganic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1991; p 159. (b) See: Reference 18, p 172.

In 1943, Sommer reported on the production of thin films of alkali metal−Au compounds of composition MAu, for M = Na−Cs, by the direct combination of the elements at elevated temperatures under high vacuum.[23] Apparently, he was unaware of the earlier Zintl work on NaAu[5] but noted that the Na and K products showed metallic luster and were opaque to visible radiation like normal alloys or intermetallics. However, Sommer discovered that the Cs product was a qualitatively different substance and exclaimed "the extremely transparent AuCs layer is particularly striking".[23] Later the CsAu species was shown to be a semiconductor and to have a CsCl-type crystalline lattice.[24] In 1958 and 1959, these and other considerations led to independent proposals that CsAu was substantially ionic in character; i.e., it likely contained cesium auride, Cs^+Au^-,[24,25] the first monatomic metal anion to exist in a condensed phase! And this daring proposal came well before Au^- had been observed in the gas phase or the high electron affinity of atomic Au was established.[26] Despite the unusual character of CsAu, the nature of this substance in the solid state remained uncertain until the late 1970s. Meanwhile, some very exciting studies involving alkali-metal anions, or alkalides, were carried out principally by James Dye and his associates.

Although the heavier alkali metals (M = Na−Cs) had long been known to dissolve in ethers, alkylamines, and similar aprotic polar organic solvents to afford pale- to deep-blue electrically conducting solutions, whose visible−IR spectra were often metal-dependent,[27,28] the nature of these solutions remained poorly understood and controversial for many years. In 1969, Matalon et al. first proposed that they contained the alkali-metal anions, Na^-, K^-, Rb^-, and Cs^-,[29] species that had been observed previously in the gas phase.[30] However, only after truly heroic and masterful efforts of Dye's group in the isolation, structural characterization, metal NMR spectral identification, and confirmation by numerous other physical techniques did the world have unambiguous evidence for the existence of monatomic metal anions in solution and the solid state.[31] Most remarkable was Dye's report in 1974 that cryptand 222 promoted the disproportionation of Na metal in ethylamine to afford golden crystals of diamagnetic [Na(cryptand 222)][Na], the X-ray structure of which showed a true salt containing discrete atomic Na^- units (eq 3).[32,33] Obtaining suitable crystals of this exceedingly sensitive substance was very difficult, as noted in the following passage: "Thus, even though nearly a hundred crystals were isolated [and carefully sealed into capillary tubing], only three crystals satisfied all of the necessary conditions for X-ray structural determination."[32a] Interestingly, elemental I_2 was later shown to react with cryptand 222 in the same fashion as Na (eq 4) only in this case the cation is the interesting component of the salt![34]

$$2\mathrm{Na} + \text{cryptand 222} \xrightarrow{\mathrm{EtNH_2}} [\mathrm{Na}(\text{cryptand 222})]^+\mathrm{Na}^- \qquad (3)$$

$$\mathrm{I_2} + \text{cryptand 222} \xrightarrow{\mathrm{CHCl_3}} [\mathrm{I}(\text{cryptand 222})]^+\mathrm{I}^- \qquad (4)$$

Dye's group really "led the way" in the judicious use of alkali-metal complexants for the isolation of unusual free or ligand-stabilized metal anions that otherwise could not exist in the solid state. Indeed, Corbett has acknowledged that his selection of cryptands for the remarkable isolation of alkali-metal salts of Zintl ions "was guided by the reports of Dye and co-workers."[7] Of course, without the combined genius and efforts of Jean-Marie Lehn[35] and Charles Pedersen,[36] the "Fathers" of cryptands and crown ethers, respectively, our understanding of highly reactive metal anions would be much poorer than it is now. By employing all-nitrogen cryptands or perazacryptands, which are more resistant toward reduction than normal cryptands, recently Dye has obtained crystalline salts of Na^- and K^- that are thermally stable at room temperature.[37] Another amazing, but less thermally stable salt of Na^-, recently reported by Dye, is [AdzH][Na], dec > −25 °C, where $AdzH^+$, or internally protonated 3^6adamanzane, "is so kinetically resistant to deprotonation that it survives in ... alkali metal solutions in ... amines".[38] The use of this unusual cation in the isolation of other highly reactive anions may be anticipated!

Shortly after Dye's report on Na^- appeared,[32a] Hotop and Lineberger published their classic review on "Binding Energies in Atomic Negative Ions".[26a] Chemists became aware of the existence of numerous stable monatomic metal anions in the gas phase, including Pt and Au, whose remarkably high electron affinities for the neutral atoms are exceeded only by those of neutral halogen atoms.[39] Undoubtedly, these reports inspired reexaminations of the mysterious CsAu, as well as searches for other simple metal anions in condensed phases. In 1978, photoelectron spectra, i.e., X-ray photoelectron spectrometry or electron spectroscopy for chemical analysis, were reported for CsAu and RbAu and provided the first quantitative evidence for the existence of

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(27) (a) Cafasso, F.; Sundheim, B. R. *J. Chem. Phys.* **1959**, *31*, 809. (b) Down, J. L.; Lewis, J.; Moore, B.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3767. (c) Dye, J. L.; Dewald, R. R. *J. Phys. Chem.* **1964**, *68*, 135.

(28) In contrast, vis−IR spectra of dilute solutions of alkali metals in liquid ammonia are independent of the metal and are known to contain ammoniated electrons or electrides, $[e(H_3N)_x]^-$, i.e., electrons trapped within approximately spherical boxes and stabilized by H bonding to ammonia molecules. See: Edwards, P. P. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 135.

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(32) (a) Tehan, F. J.; Barnett, B. L.; Dye, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 7203. (b) Dye, J. L. *J. Chem. Educ.* **1977**, *54*, 332. (c) Cryptand 222 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

(33) Dye, J. L. *Sci. Am.* **1977**, *237* (1), 92. This popular article entitled "Anions of the Alkali Metals" includes a colored photograph showing gorgeous crystals of [Na(cryptand 222)][Na].

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(38) Redko, M. Y.; Vlassa, M.; Jackson, J. E.; Misiolek, A. W.; Huang, R. H.; Dye, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 5928. The adamanzane is related to hexamethylenetetramine, where all methylenes have been replaced by propylene groups. Because of the flexibility of the propylene units, all four equivalent N atoms can point inward to form an approximate tetrahedral cage about the effectively trapped proton.

(39) Certain gas-phase molecules such as CN or PtF_6 have electron affinities that are larger than those of neutral atoms. See Reference 21a, pp 577−579.

Au^- in the solid state.[40] Earlier proposals for these species were thereby corroborated.[24,25] Almost simultaneously, Lagowski showed that Cs, Rb, or K metals in liquid ammonia dissolved Au metal (shades of the original studies of Joannis![3]) to afford electrically conducting solutions, whose IR−UV−visible spectra were nearly independent of cations and free of ammoniated electrons. On this basis, he proposed the existence of Au^- in liquid ammonia, the first time a monatomic transition-metal anion had been directly observed in solution[15] (eq 5, where am = NH_3). Soon thereafter,

$$Cs(s) + Au(s) \xrightarrow{NH_3} Cs^+(am) + Au^-(am) \qquad (5)$$

detailed electrochemical studies were reported for the auride ion in liquid ammonia, which indicated that Au^- is about 0.4 V less reducing than the ammoniated electron.[41] Subsequently, Au-197 Mössbauer studies on CsAu and related aurides corroborated the ionic character of these species in the solid state.[42] Evidence for the existence of Au^- in ethylenediamine[43] and Ag^- in liquid ammonia[44] has also been presented. However, undoubtedly, the most definitive characterization of an auride salt was Jansen's recent single-crystal X-ray structural characterization of $[Me_4N][Au]$, the first salt of a monatomic metal anion with a nonmetallic cation! This substance was obtained by the metathesis of CsAu with Me_4NCl in liquid ammonia (eq 6).[45] Whereas

$$CsAu(am) + [Me_4N]Cl(am) \xrightarrow{NH_3(l)} [Me_4N][Au](am) + CsCl(s) \qquad (6)$$

CsAu has been described as a bright-yellow[42] to golden-brown solid, *the tetramethylammonium salt forms* transparent colorless crystals! Interestingly, crystalline $[Me_4N][Au]$ is isomorphous with $[Me_4N][Br]$ and slowly decomposes at room temperature. In contrast, the previously reported, but not structurally characterized, potassium cryptand salt, [K(cryptand 222)][Au], also a white solid, is less thermally stable (dec > −10 °C).[42,46] A highly informative (and entertaining) "mini-review" by Pyykkö on the auride anion and related species,[47] including a discussion of Au^- as a pseudohalide, was published following Jansen et al.'s isolation and characterization of dark-blue crystalline $CsAu-NH_3$, obtained from CsAu in liquid ammonia.[48] As noted in a recent review, the coordination chemistry of Au^- remains totally unexplored.[49]

Doubtlessly, the most remarkable (and surprising) recent development in monatomic metal anion research was Jansen et al.'s preparation and structural characterization of dicesium platinide, Cs_2Pt, containing Pt^{2-}, the first known monatomic metal dianion![50] *Dark-red transparent hexagonal* prisms of the product were obtained by the direct reaction of Cs and Pt metals at 700 °C in a Ta container (eq 7), followed by a nontrivial separation by hand from excess liquid Cs in a drybox. The availability of Pt^{2-} raises many exciting possibilities for future redox and coordination chemistry of this formal transition-metal analogue of a chalcogenide ion. However, some aspects of the chemical properties of this substance may already have been revealed by Bogdanovic et al. because their "Platinum Grignard Reagent", $[Pt(MgCl)_2(THF)_x]$, where THF = tetrahydrofuran, can be formulated as containing Pt(II−), provided that the quite electropositive Mg is present in its normal divalent state.[51] Bogdanovic has also prepared other intriguing Mg−transition metal "intermetallics", which may also contain d-block elements in formally negative oxidation states.[52]

$$2Cs(g) + Pt(s) \xrightarrow{700\ °C} (Cs^+)_2(Pt^{2-})(s) \qquad (7)$$

Classification of Metal Anions and Comments on the Oxidation State Assignments

Metal anions may be classified as "free", as in the case of mono- or polyatomic species of the type described above, or "ligand-stabilized" versions, where the ligands are neutral and good acceptors, e.g., carbon monoxide (CO). To date, only transition metals afford "ligand-stabilized" metal anions. However, it has been proposed that such species may be possible for f-block elements, particularly U.[49] Presently unknown main-group anions, such as RSn^{3-} and RBi^{2-}, where R = H, hydrocarbyl, or related substituents, would also be in this category. Tables 1 and 2 show this classification scheme and depict "free" or unligated metal anions and ligand-stabilized versions, respectively. A chronological survey of homoleptic d-block complexes of the latter type is depicted in Table 2. Because metal carbonyl anions were the first species established to contain transition metals in negative oxidation states,[49] several of these anions are shown for different metals and molecular charges. For other ligands, only the first described example of a given type and molecular charge is shown, except for the two rare 17-electron metalates. Also, certain highly charged species in Table 2 are probably misrepresented, or at least oversimplified, by depicting them as discrete anions because their existence may depend on tight ion pairing or covalent bonding with cations. For example, Klaus Jonas has classified $[Ni(1,5\text{-}COD)_2]^{2-}$, or more accurately, $[Li(THF)_2]_2[Ni(COD)_2]$, and related dilithium alkenenickelates as "non-salt-like" compounds because they do not undergo appreciable ionization in solvents such as THF.[84] Similarly, the highly charged carbonylmetalates $[Mn(CO)_4]^{3-}$ and $[W(CO)_4]^{4-}$ likely interact so tightly with their alkali-metal counterions that referring to these species as "trianions" and "tetraanions" is about as unreasonable as formulating lithium nitride to contain free "N^{3-}". Nevertheless, in terms of conventional

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Table 1. Examples of "Free" or Unligated Metal Anions

atomic metal anions	year	ref
1. Gas Phase		
first stable example, Li^-	1947	13
many exist that have yet to be observed in condensed phases, including Li^-, Pt^-, Ir^-, etc.		26
numerous polyatomic metal anions have also been observed, including exciting new species, such as Al_4^{2-}		8b, 53
2. Condensed Phase		
(a) monatomic anions		
Cs^+Au^-	1943	23
Na(cryptand 222)$^+$Na$^-$	1974	32a
related salts of K^-, Rb^-, and Cs^-	1975	31, 33
$2Cs^+Pt^{2-}$	2003	50
(b) polyatomic anions		
Pb_9^{4-}, Sn_9^{4-}, Hg_4^{6-}, and numerous others, including many of which are best described as "alloy" phases and do not contain discrete anions	1931−present	7, 8, 54, 55

Table 2. Examples of Ligand-Stabilized "Metal Anions", i.e., Coordination Compounds Containing Metals in Formal Negative Oxidation States[a,2,56,58]

complex	year[59]	ref	complex	year[59]	ref
$[Fe(CO)_4]^{2-}$	1931	60	$[W(CO)_4]^{4-}$	1978	72
$[Co(CO)_4]^-$	1932	61	$[Fe(C_2H_4)_4]^{2-}$	1979	73
$[Cr(CO)_5]^{2-}$	1955	62	$[Ti(C_6H_6)_2]^-$	1984[b]	74
$[V(CO)_6]^-$	1960	63	$[Nb(mes)_2]^-$	1988	75
$[Co(PF_3)_4]^-$	1965	64	$[Co(CNXyl)_4]^-$	1989	76
$[Os(PF_3)_4]^{2-}$	1969	65	$[Ru(CNtBu)_4]^{2-}$	1992	77
$[Co(P(OMe)_3)_4]^-$	1973	66	$[Mn(1,5\text{-}COD)_2]^{2-}$	1992[b]	78
$[V(C_6H_6)_2]^-$	1975	67	$[Co(1,4\text{-}tBu_2C_4H_4)_2]^-$	1993	79
$[Ni(1,5\text{-}COD)_2]^{2-}$	1975	68	$[Zr(C_{10}H_8)_3]^{2-}$	1994	80
$[Mn(CO)_4]^{3-}$	1975	69	$[Ir(tropp^{Ph})_2]^-$	1998	81
$[Co(C_2H_4)_4]^-$	1976	70	$[Co(tmbp)_2]^-$	2000	82
$[Co(PMe_3)_4]^-$	1977	71	$[Co(C_{14}H_{10})_2]^-$	2002	83

[a] 1. All contain d-block elements and "acceptor ligands", such as CO, CNR, PR_3, PX_3, alkenes, dienes, aromatic hydrocarbons, and related species.[57] 2. Almost all are electronically saturated; i.e., they satisfy the inert gas formalism. Homoleptic mononuclear examples with different molecular charges and ligands are depicted with their year of "discovery".[59] Homoleptic di-, tri-, and polynuclear metalates are also known, particularly for metal carbonyls. **Identification of ligands**: CO = carbon monoxide; PF_3 = trifluorophosphane; $P(OMe)_3$ = trimethyl phosphite; C_6H_6 = benzene; 1,5-COD = 1,5-cyclooctadiene; C_2H_4 = ethylene; PMe_3 = trimethylphosphane; mes = 1,3,5-trimethylbenzene; CNXyl = 2,6-dimethylphenyl isocyanide; CNtBu = *tert*-butyl isocyanide; 1,4-$tBu_2C_4H_4$ = 1,4-di-*tert*-butyl-1,3-butadiene; $C_{10}H_8$ = naphthalene; $tropp^{Ph}$ = benzocycloheptenyldiphenylphosphane;[81] tmbp = 4,4′,5,5′-tetramethyl-2,2′-biphosphinine; $C_{14}H_{10}$ = anthracene. [b] Rare examples of isolable 17-electron complexes containing metals in negative oxidation states.

rules for assigning oxidation states,[2,56,58] the compounds in Table 2 are best considered to contain metals in formal negative oxidation states.

Certain compounds were excluded from Table 2 because the ligands are so easily reduced that the oxidation states of the metals are poorly defined, at best. 1,4-Diazabuta-1,3-dienes (or α-diimines),[85] alkynes,[86] 2,2′-bipyridines, and similar ligands containing quite low energy lowest unoccupied molecular orbitals of appropriate symmetry for back-bonding are particularly problematic in this regard. For example, Herzog and co-workers prepared a series of anionic homoleptic bipy or 2,2′-bipyridine complexes, which were originally formulated to contain metals in negative oxidation states.[87] Indeed, $[Ti(bipy)_3]^-$, $[V(bipy)_3]^-$, and $[Zr(bipy)_3]^{2-}$ are still often incorrectly identified as formal Ti(I−), V(I−), and Zr(II−) species, respectively.[88,89] However, recently a structural characterization of $[Li_2(THF)_{8.5}]$[Zr-

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(53) Ho, J.; Ervin, K. M.; Lineberger, W. C. *J. Chem. Phys.* **1990**, *93*, 6987 and references cited therein.

(54) Seo, D.-K.; Corbett, J. D. *Science* **2001**, *291*, 841 and references cited therein.

(55) Kuznetsov, A. E.; Corbett, J. D.; Wang, L.-S.; Boldyrev, A. I. *Angew. Chem., Int. Ed.* **2001**, *40*, 3369.

(56) Formal oxidation states are defined as the charge remaining on the metal when all ligands are removed in their most stable forms, which are generally closed-shell and diamagnetic. Small-molecule ligands usually have only one stable closed-shell form, and this is the situation for most of the ligands shown in Table 2, e.g., CO, PF_3, $P(OMe)_3$, PMe_3, benzene, ethylene, 1,5-cyclooctadiene, or isocyanides (CNR).[57] However, when ligands can readily lose or gain electrons, more than one stable closed-shell structure may arise and ambiguous or meaningless oxidation-state assignments will result. For example, 2,2′-bipyridine undergoes facile reduction to give a diamagnetic dianion. Paramagnetic metal complexes can be particularly problematic when ligands form especially stable radical anions, such as the 2,2-bipyridine monoanion. C. K. Jorgensen referred to the former class of ligands as "innocent", i.e., usually unambiguous metal oxidation assignments are possible, while the latter ligands are distinctly "noninnocent". For a scholarly and highly entertaining account of the strengths and virtues, as well as the pitfalls, of metal oxidation-state assignments, Jorgensen's classic monograph on the subject is highly recommended.[58] Other ambiquities can arise with formal oxidation-state assignments, especially when metal−metal bonds involving different metals or identical metals having much different ligand sets are present. Malcolm Green has considered these and other difficulties with oxidation-state assignments in "A New Approach to the Formal Classification of Covalent Compounds of the Elements". See: Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127.

(57) For more examples, see: Elschenbroich, Ch.; Salzer, A. *Organometallics*, 2nd ed.; VCH Publishers: Weinheim, Germany, pp 206−241, 252−279, and 348−369.

(58) Jorgensen, C. K. *Oxidation Numbers and Oxidation States*; Springer-Verlag: New York, 1969.

(59) The year of "discovery" coincides with the first reported isolation of a salt containing the respective anion, except for bis(benzene)vanadate(1−)[67] and tetrakis(*tert*-butyl isocyanide)ruthenate(2−), and an analogous xylyl isocyanide complex,[77] which are only known in solution.

(60) Hieber, W.; Leutert, F. *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2832. $[Fe(en)_3][Fe(CO)_4]$, where en = ethylenediamine, was the first isolated salt containing $[Fe(CO)_4]^{2-}$, although its ionic nature was not established until 1957. See ref 49 for more details.

(61) Hieber, W.; Mühlbauer, F.; Ehmann, E. A. *Ber. Dtsch. Chem. Ges.* **1932**, *65*, 1090. Salts containing this anion were obtained by the action of O and N bases on $Co_2(CO)_8$, but the ionic nature of these species was not established until many years later. See ref 49 for more details.

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

(63) Ercoli, R.; Calderazzo, F.; Alberola, A. *J. Am. Chem. Soc.* **1960**, *82*, 2966.

(64) Kruck, T.; Lang, W.; Engelmann, A. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 148.

(65) Kruck, T.; Prasch, A. *Z. Anorg. Allg. Chem.* **1969**, *371*, 1.

(66) Muetterties, E. L.; Hirsekorn, F. J. *J. Chem. Soc., Chem. Commun.* **1973**, 683.

(67) Elschenbroich, Ch.; Gerson, F. *J. Am. Chem. Soc.* **1975**, *97*, 3556.

(68) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 752.

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

(70) Jonas, K.; Mynott, R.; Krüger, C.; Sekutowski, J. C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 767.

(71) Hammer, R.; Klein, H.-F. *Z. Naturforsch.* **1977**, *32B*, 138.

(bipy)$_3$] was carried out and showed that interatomic distances of the coordinated bipy ligands were "very similar to those of a bipyridine dianion".[90] These data suggest that the actual oxidation state of the Zr in [Zr(bipy)$_3$]$^{2-}$ is much closer to 4+ than 2−!

Anionic complexes containing 1,3,5,7-cyclooctatetraene, COT, which readily forms the planar aromatic 10π electron COT^{2-}, have similar difficulties, particularly when COT binds as a nonplanar ligand to transition metals. For example, a careful examination of the structure and interatomic distances of [Nb(C$_8$H$_8$)$_3$]$^-$ led Guggenberger and Schrock to propose that the complex contained Nb(I) rather than Nb(I−).[91] Also, recently [Co(η^4-C$_8$H$_8$)$_2$]$^-$, a dark-green substance, was shown to contain nonplanar COT rings with a planar array of coordinated diene units about cobalt (Figure 1), consistent with a d^8 Co(I) complex.[83] In contrast, related but dark-red [Co(η^4-1,4-di-*tert*-butyl-1,3-butadiene)$_2$]$^-$ [79] and [Co(η^4-anthracene)$_2$]$^-$ [83] (Figure 2) have similar approximately tetrahedrally coordinated dienes about Co, appropriate for d^{10} Co(I−). In both the Nb and Co complexes, COT functions as a sufficiently better acceptor ligand than the substituted 1,3-butadiene or anthracene that the coordinated COT ligands appear to have appreciable anionic character.

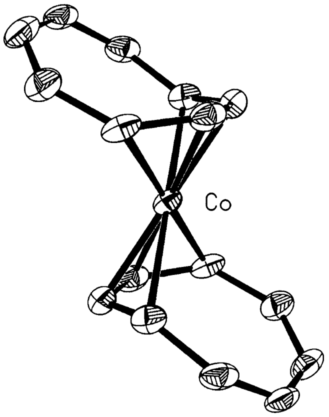

Figure 1. Structure of bis(1−4-η^4-1,3,5,7-cyclooctatetraene)cobaltate(1−), with H atoms omitted for clarity.

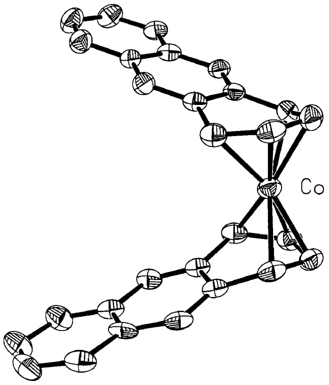

Figure 2. Structure of bis(1−4-η^4-anthracene)cobaltate(1−), with H atoms omitted for clarity.

In this regard, perhaps the most interesting ligand shown in Table 2 is Mathey's 4,4′,5,5′-tetramethyl-2,2′-biphosphinine, tmbp, effectively a tetramethyl-substituted diphospha-2,2′-bipyridine, in the sense that its character clearly changes from "innocent" to "noninnocent"[56,58] as one proceeds from [M(tmbp)$_2$]$^-$, where M = Co and Rh,[82] to the more electron-rich [Ru(tmbp)$_2$]$^{2-}$.[92] The Co and Rh monoanions have nearly tetrahedral ligand environments about the metals, indicative of d^{10} M(I−) species,[93] whereas the Ru dianion is square-planar, consistent with d^8 Ru(0). Thus, d^{10} Ru(II−) seems to be sufficiently strongly reducing in this environment that it effectively transfers two electrons to the biphosphinine ligand set; i.e., Ru(II−) is "redox incompatible" with neutral tmbp.[94] Similarly, X-ray structural evidence indicates that highly reduced group IV complexes, [M(tmbp)$_3$]$^{2-}$, where M = Ti, Zr, and Hf, contain significantly reduced ligands, so the authors conclude the following: "From these data, it is clear that the −2 oxidation state of Zr is only formal."[90,95] We have made quite similar comments concerning tris(η^4-naphthalene)zirconate(2−),[80] but this species is included in Table 2 because it does react with CO to afford a "bona fide" d^6 Zr(II−) complex, [Zr(CO)$_6$]$^{2-}$.[80]

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

(73) Jonas, K.; Schieferstein, L.; Krüger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 550.

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(75) Bandy, J. A.; Prout, K.; Cloke, F. G. N.; de Lemos, H. C.; Wallis, J. M. *J. Chem. Soc., Dalton Trans.* **1988**, 1475.

(76) Warnock, G. F.; Cooper, N. J. *Organometallics* **1989**, *8*, 1826.

(77) Corella, J. A., II; Thompson, R. L.; Cooper, N, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 83.

(78) Jonas, K.; Häselhoff, C.-C.; Goddard, R.; Krüger, C. *Inorg. Chim. Acta* **1992**, *198−200*, 533.

(79) Cloke, F. G. N.; Hitchcock, P. B.; McCamley, A. *J. Chem. Soc., Chem. Commun.* **1993**, 248.

(80) Jang, M.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1965.

(81) (a) Boulmaaz, S.; Mlakar, M.; Loss, S.; Schönberg, H.; Deblon, S.; Wöhrle, M.; Nespar, R.; Grützmacher, H. *Chem. Commun.* **1998**, 2623. (b) Related [Ir(dppf)$_2$]$^-$, where dppf = 1,1′-bis(diphenylphosphano)-ferrocene, has been reported: Longato, R.; Riello, L.; Bandoli, G.; Pilloni, G. *Inorg. Chem.* **1999**, *38*, 2818.

(82) Mezailles, N.; Rosa, P.; Ricard, L.; Mathey, F.; LeFloch, P. *Organometallics* **2000**, *19*, 2941.

(83) Brennessel, W. W.; Young, V. G., Jr.; Ellis, J. E. *Angew. Chem., Int. Ed.* **2002**, *41*, 1211.

(84) Jonas, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 520. To the best of my knowledge, these olefinnickelates(2−) have only been obtained as Li$_2$ complexes.

(85) (a) Daff, B. J.; Etienne, M.; Donnadieu, B.; Knottenbelt, S. Z.; McGrady, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 3818 and references cited therein. (b) Cloke, F. G. N.; deLemos, H. C.; Sameh, A. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1344.

(86) Maher, J. M.; Fox, J. R.; Foxman, B. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 2347.

(87) (a) Herzog, S.; Zühlke, H. *Z. Chem.* **1966**, *6*, 382. (b) McWhinnie, W. R.; Miller, J. D. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 135.

(88) (a) Holleman, A. F.; Wiberg, E. *Inorganic Chemistry*, 34th ed.; Academic Press: San Diego, CA, 2001; p 1336 and 1355. (b) See: Reference 18, p 216. (c) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth-Heinemann: Oxford, U.K., 1997; p 960. (d) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley: New York, 1999; p 715. However, also see p 351 concerning such anionic complexes.

(89) (a) Jørgensen was one of the first to question the presence of "negative-valent or subvalent" transition metals in these anionic bipyridyl complexes. See: Reference 58, pp 163−165. (b) Later König and Herzog reported that electronic spectra of [M(bipyl)$_3$]$^-$, where M = Cr, V, and Ti, were consistent with the presence of coordinated bipy$^-$ and/or bipy^{2-}. See: König, E.; Herzog, S. *J. Inorg. Nucl. Chem.* **1970**, *32*, 585, 601, and 613.

(90) Rosa, P.; Mezailles, N.; Ricard, L.; Mathey, F.; LeFloch, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 1823.

(91) Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6693. All COT rings are nonplanar in this complex.

(92) Rosa, P.; Mezailles, N.; Ricard, L.; Mathey, F.; LeFloch, P.; Jean, Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 1251.

(93) As discussed in a recent paper,[83] the geometries of the CoP$_4$ units in [Co(dppe)$_2$]$^-$, where dppe = 1,2-bis(diphenylphosphano)ethane, and [Co(η^2-tmbp)$_2$]$^-$ are nearly identical and close to tetrahedral, indicating both cobaltates are best formulated as d^{10} Co(I−) species.

Indeed, as a metal center becomes more electron-rich or highly reduced, all acceptor ligands are expected to become less innocent in character, *if they survive intact*. A good example is provided by Jonas' $[Ni(\eta^2\text{-norbornene})_2]^{2-}$, isolated with Li(TMEDA), where TMEDA = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine, counterions, which has been described as a "square-planar, centrosymmetric 16 electron complex".[84] X-ray structural analysis of the coordinated norbornene units reveals mean C−C and Ni−C distances of 1.551 and 1.947 Å, which are consistent with two norbornene dianions σ-bonded to d^8 Ni(II); i.e., the complex is effectively a substituted nickelaspiropentane.[96] The mean Li−C distance of 2.41 Å also indicates that the bound norbornene units have appreciable carbanion character.[97]

Prelude to Highly Reduced Organometallics

In the late 1920s and early 1930s, Walter Hieber and associates discovered that the reactions of $Fe(CO)_5$ and $Co_2(CO)_8$ with a variety of O and N bases, followed by acidification, generated quite malodorous, air-sensitive, and thermally unstable substances.[98] Through elegant and difficult experimental work, they were formulated as the first volatile transition-metal hydrides, $H_2Fe(CO)_4$[99] and $HCo(CO)_4$,[100] respectively. Several of the nonvolatile precursors were later established to contain discrete metal carbonyl anions, including $[Fe(CO)_4]^{2-}$ and $[Co(CO)_4]^-$.[98] Arthur Blanchard pointed out in 1940 that if $Ni(CO)_4$ is formulated to contain zerovalent Ni, then the Fe and Co in these isoelectronic anions should be viewed as having "polar valencies" (or formal oxidation states) of 2− and 1−, respectively.[101] It was not until the 1950s and 1960s that several new homoleptic carbonylmetalate mono- and dianions were prepared,[49] collectively, the first organoelement compounds to contain metals in negative oxidation states.

In the late 1960s, inorganic chemists began to appreciate amazing similarities in the molecular structures and reactivity patterns of metal carbonyls and related low-valent transition-metal complexes and those of nonmetal compounds. Jack Halpern wrote a truly "trail-blazing" review on homogeneous catalysis in which he compared the characteristic reactivity patterns of electronically saturated and unsaturated organic species with those of 18-, 17-, and 16-electron transition-metal complexes.[102] For example, he likened the 18-electron $[Mn(CO)_5]^-$, the 17-electron $[Co(CN)_5]^{3-}$, and the 16-electron $IrI(CO)(PPh_3)_2$ to carbanions, $R_3\overset{\bullet}{\underset{\bullet}{C}}{}^{-}$, organic free radicals, $R_3C^{\bullet}$, and carbenes, $R_2\overset{\bullet}{\underset{\bullet}{C}}$, respectively. Lawrence Dahl then introduced the very useful term "electronically equivalent groups" to describe main-group and transition-metal moieties, which required the same number of electrons to satisfy their valence requirements. For example, he showed that the 15-electron $Co(CO)_3$ group had the same bonding capabilities as, and was electronically equivalent to, 5-electron atomic As[103] and Sb[104] and therefore behaved as a pseudopnicogen.[105] In this sense, the tetrahedral cluster $[Ir(CO)_3]_4$ can be considered to be a transition-metal analogue of P_4 or As_4. At about the same time, Jorgensen wrote "the $Mn(CO)_5$ moiety is a kind of pseudohalogen"[106] and "$Mn(CO)_5^-$ ... as a kind of pseudohalide like CN^-, NCS^- and most RS^-, forming its oxidized dimer after loss of two electrons".[107]

As a graduate student struggling to make sense of the myriad of chemical properties of metal carbonyls and related species, I found the above ideas of Halpern, Dahl, and Jorgensen to be tremendously exciting, and they forced me to think of metal carbonyls, in particular, as "nonmetallic compounds in disguise". These deliberations later prompted the writing of two articles in which the reaction chemistries of carbonylmetalate mono- and dianions were compared with those of halides and chalcogenides, respectively. Also, qualitative relationships between 17-, 16-, and 15-electron metal carbonyl units and those of nonmetal 7-, 6-, and 5-electron groups, respectively, were explored.[108] Soon thereafter, Roald Hoffmann elegantly showed that all of these and many other remarkable parallels in d- and s,p-block element chemistry could be understood, or at least rationalized, on the basis of a remarkable construct, "the isolobal analogy", which is described in his Nobel lecture of 1981.[109]

In my formative years as an inorganic chemist, the "good book", Cotton and Wilkinson's *Advanced Inorganic Chemistry*, taught me the considerable utility of formal oxidation state assignments, notwithstanding occasional issues,[56,58,111] in helping to organize and systematize the chemistry of the elements. Thus, the position of a given atom in the periodic table imposes definite limits on its maximum (positive) oxidation state. For example, Ti cannot achieve oxidation states higher than IV (or 4+) in chemical combination. In contrast, at least for the group 3−9 transition metals, there appear to be no a priori limits on minimum values, other than those imposed by the nature of the ligands and the noble gas or 18-electron rule. The existence of $Mn(CO)(NO)_3$,[110] formally containing Mn(III−),[111] and isoelectronic with the

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(94) Cation−anion interactions may also play a critical role in the stabilization of the square-planar geometry of $[Ru(tmbp)_2]^{2-}$, wherein both axial positions of the square plane are occupied by $[Li(THF)_3]^+$ counterions. Although the alkali-metal cation−metal anion interactions have been described as being "very weak",[92] they are undoubtedly significantly stronger and more polarizing than the corresponding ones with the nearly tetrahedral $[M(tmbp)_2]^-$, where M = Co and Rh, which have essentially spherical and weakly perturbing $[Na(cryptand\ 222)]^+$ counterions. In this regard, structural characterization of $[Ru(tmbp)_2]^{2-}$ as an alkali-metal cryptand salt would be of substantial interest to see whether the dianion's structure will be effectively independent of the cation.

(95) For an outstanding review on tmbp and related ligands and their coordination chemistry, see: Mezailles, N.; Mathey, F.; LeFloch, P. *Prog. Inorg. Chem.* **2001**, *49*, 455.

(96) It should be emphasized that norbornene is a strained alkene and is thereby expected to be a stronger acceptor and a "less-innocent" ligand than ethylene, 1,5-cyclooctadiene, or other similar unstrained alkenes or nonconjugated dienes.

(97) Similar Li−C distances are observed in bona fide organolithium compounds. See: Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

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

(99) (a) Hieber, W.; Leutert, F. *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2832. (b) Hieber, W.; Leutert, F. *Naturwissenschaften* **1931**, *19*, 360.

(100) Hieber, W. *Z. Elektrochem.* **1934**, *40*, 158; *Chem. Abstr.* **1935**, *28*, 3328.[2]

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

(102) Halpern, J. *Adv. Chem. Ser.* **1968**, *70*, 1.

(103) Foust, A. S.; Foster, M. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 5631.

(104) Foust, A. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7337.

(105) Pnicogen or pnictide is often used as the family name for the group 15 elements, N, P, As, Sb, and Bi.

(106) See: Reference 58, pp 237 and 238.

(107) Jørgensen, C. K. *Modern Aspects of Ligand Field Theory*; North-Holland: Amsterdam, The Netherlands, 1971; pp 437−439.

(108) (a) Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1. (b) Ellis, J. E. *J. Chem. Educ.* **1976**, *53*, 2.

(109) Hoffmann, R. *Angew. Chem., Int. Ed.* **1982**, *21*, 711.

(110) Barraclough, C. G.; Lewis, J. *J. Chem. Soc.* **1960**, 4842.

known $Ni(CO)_4$, $[Co(CO)_4]^-$, and $[Fe(CO)_4]^{2-}$, suggested that the metal tetracarbonyl series might be extendable to the isoelectronic $[Mn(CO)_4]^{3-}$. Nothing like this had been reported in the literature, so the chances of obtaining this species and possibly other homoleptic metal carbonyl trianions were really exciting when I began research at the University of Minnesota in 1971 as an assistant professor. However, it required considerable effort, frustration, and futility before these "raw ideas" were transformed into publishable results.

Highly Reduced Organometallics

Since these early days, a continuing theme in my research program has been to establish how much negative charge can be added to a metal complex before irreversible reduction, transformation, and/or loss of coordinated ligands occur. Answers to questions of this sort will most certainly depend on the metal, ligand set, and counterions but will be important in defining the lower limits possible for negative oxidation states of transition metals. Also, studies in this area will provide insight on the relative susceptibility of coordinated ligands to reduction, an area that still remains very poorly explored but one that promises exciting new discoveries of a fundamental nature. My initial studies involved highly reduced metal carbonyls, but within the past 15 years, thanks to some very talented graduate students and postdocs, we have moved into transition-metal polyarene, trifluorophosphane, isocyanide, alkene, and related areas, with several objectives, one of which is to determine whether salts of homoleptic transition-metal trianions or more highly reduced species are possible for any of these ligands. A roughly chronological survey of "highly reduced organometallics" and related topics from my research program will now be presented, following a brief review of prior routes to carbonylmetalates.

Metal Carbonyl Mono- and Dianions

As mentioned previously, carbonylmetalates were first obtained by the action of O and N donors on neutral metal carbonyls. Although Walter Hieber was largely responsible for the development of this useful procedure,[98] the original report on such a reaction recently has been traced back to an article by Sir James Dewar,[49] who described the interaction of $Fe(CO)_5$ with ethanolic KOH. Quite air-sensitive colorless crystals of an unknown substance were quickly produced in Dewar's reaction.[112] The product might have been $K_2[Fe(CO)_4]$, which was isolated in the 1940s from a similar aqueous KOH reaction (eq 8).[113] In this process, coordinated CO served as the reducing agent in the conversion of Fe(0) to Fe(II−).

$$Fe(CO)_5 + 2KOH + Ba(OH)_2 \xrightarrow{H_2O} K_2[Fe(CO)_4] + BaCO_3 + 2H_2O \quad (8)$$

Notably, corresponding reactions of $Cr(CO)_6$ with hydroxide or alkoxides do not afford $[Cr(CO)_5]^{2-}$ [114] because of the more reactive nature of this dianion compared to $[Fe(CO)_4]^{2-}$. Thus, pentacarbonylchromate(2−) appears to be too basic and easily oxidized to coexist with water or alcohols. However, Helmut Behrens, who first examined the reactions of metal carbonyls with alkali metals in liquid ammonia,[115] discovered that $Cr(CO)_6$ was reduced by $Na-NH_3$ to give high yields of $Na_2[Cr(CO)_5]$ and the explosive byproduct disodium acetylenediolate, $Na_2[C_2O_2]$ (eq 9).[49,62] Dilute solutions of alkali metals in Hg,

$$Cr(CO)_6 + 3Na \xrightarrow{NH_3(l)} Na_2[Cr(CO)_5] + {}^1/_2Na_2[C_2O_2] \quad (9)$$

i.e., amalgams, were also first employed in the 1950s to obtain carbonylates from neutral metal carbonyls.[116] Sometimes the alkali-metal amalgams provided Hg derivatives, instead of the desired anions;[117] however, unexpected and exciting mixed Hg−transition metal complexes may be accessed from amalgam reductions.[118]

One of my first research projects at the University of Minnesota was to examine the chemistry of $[M(CO)_5]^{2-}$, where M = Cr, Mo, and W, because little was known about these interesting species, despite the fact that they were first reported in the 1950s.[62,119] Unfortunately, the $Na-NH_3$ route developed by Behrens for the successful conversion of $Cr(CO)_6$ to $Na_2[Cr(CO)_5]$ worked very poorly for Mo and W.[49,115] Sodium amalgam reductions of $M(CO)_6$, where M = Cr−W, in refluxing THF were claimed to give the respective $[M(CO)_5]^{2-}$,[120] but we later showed that these reactions were also largely unsuccessful for the heavier group 6 metals.[121]

A report on the reaction of $Cr(CO)_6$ with Na in hexamethylphosphoramide, Na−HMPA, really sparked our interest[122] because no one had previously examined the reductions of transition-metal complexes in this unusual medium. Except for its high toxicity,[123] which was not established when we began this research, HMPA is a nearly ideal solvent for the generation and study of metal carbonyl anions. Unlike most

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(111) Diamagnetic metal nitrosyls containing linear MNO units have been traditionally assumed or defined to contain coordinated NO^+ because this molecule is isoelectronic with CO. This convention also provides a useful explanation for the fact that linear nitrosyls are much better acceptors than terminal carbonyl groups. However, for polynitrosylmetal complexes, containing only linear nitrosyls, such as $Mn(CO)(NO)_3$ or $Cr(NO)_4$, this leads to the assignment of unreasonably low formal oxidation states for the metals; i.e., because free NO^+ is intrinsically a strong oxidant, it is totally incompatible with strongly reduced metal centers. Considerations of this type led to the Enemark−Feltham notation for transition-metal nitrosyls, which ignores the issue of meaningless oxidation-state assignments for compounds of this class. See: Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *23*, 339.

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

(113) Krumholz, P.; Stettinger, H. M. A. *J. Am. Chem. Soc.* **1949**, *71*, 3035.

(114) King, R. B. *Adv. Organomet. Chem.* **1964**, *2*, 157. This review entitled "Alkali Metal Derivatives of Metal Carbonyls" is an outstanding account of early syntheses of metal carbonyl anions.

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

(116) Wender, I.; Sternberg, H. W.; Orchin, M. *J. Am. Chem. Soc.* **1952**, *74*, 1216. To the best of my knowledge, this paper is the first to report on the use of alkali-metal amalgams to prepare metal carbonyl anions.

(117) (a) Dighe, S. V.; Orchin, M. *Inorg. Chem.* **1962**, *1*, 956. (b) King, R. B. *J. Inorg. Nucl. Chem.* **1963**, *22*, 1296.

(118) For example, see: Rosenfeld, D. C.; Wolczanski, P. T.; Barakat, K. A.; Buda, C.; Cundari, T. R. *J. Am. Chem. Soc.* **2005**, *127*, 8262 and references cited therein.

(119) Weber, R.; Behrens, H. *Z. Anorg. Allg. Chem.* **1957**, *291*, 122.

(120) (a) Podall, H. E.; Prestridge, H. M.; Shapiro, H. *J. Am. Chem. Soc.* **1961**, *83*, 2057. (b) Amiet, R. G.; Reeves, R. G.; Pettit, R. *Chem. Commun.* **1967**, 1208. (c) Ward, J. S.; Pettit, R. *Chem. Commun.* **1970**, 1419.

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

(122) Kaska, W. C. *J. Am. Chem. Soc.* **1968**, *90*, 6340.

(123) HMPA has been shown to be a potent carcinogen to laboratory rats and must be handled with extreme care. See: Zapp, J. A. *Science* **1976**, *190*, 422.

highly polar aprotic solvents, HMPA is unusually resistant to attack by strong reducing agents or bases and is nearly transparent to IR radiation in the usual metal carbonyl stretching frequency region, 2200−1600 cm^{-1}. Also, because of its relatively high dielectric constant of about 30 at 20 °C, its ability to strongly bind to alkali-metal cations, especially Li^+, Na^+, and K^+, and quite weak interactions with most anions, IR spectra of relatively dilute solutions ($\leq$0.01M) of alkali-metal salts of carbonylmetalate mono- or dianions are essentially those of the unperturbed anions.[124] In addition, HMPA dissolves alkali metals to afford metastable and deep-blue solutions,[125] similar to those of liquid ammonia but undoubtedly more strongly reducing, at least in the case of Na.[28,126] Subsequently, Gary Hagen in our group showed that the group 6 hexacarbonyls underwent smooth reductions by Na−HMPA to afford solutions of $Na_2[M(CO)_5]$, where M = Cr, Mo, and W, and for the first time we were able to confirm the existence of $[Mo(CO)_5]^{2-}$ and $[W(CO)_5]^{2-}$ by IR spectroscopy (eq 10).[127] In contrast to the

$$M(CO)_6 + 3Na \xrightarrow{\text{HMPA, 20 °C}} Na_2[M(CO)_5] + {}^1/_x[NaCO]_x \quad (10)$$

$$M = Cr, Mo, and W$$

analogous reduction of $Cr(CO)_6$ by Na in liquid ammonia (eq 9), the nature of the sodium carbonyl byproduct(s) obtained in HMPA remains unknown.

After this result, we were intrigued by the prospects of accessing new carbonylmetalates in HMPA, particularly compounds containing transition metals in rare or unknown oxidation states—something that always excites an inorganic chemist! One of our first targets was the then unknown $[CpMn(CO)_2]^{2-}$, where Cp = C_5H_5 = cyclopentadienyl, isoelectronic with the well-established $[CpFe(CO)_2]^-$.[128] Because a related dianion, $[CpV(CO)_3]^{2-}$, had been obtained by alkali-metal reductions of $CpV(CO)_4$[129] (eq 11), it was felt that the reduction of $CpMn(CO)_3$ by Na−HMPA might afford the desired product. On the basis of the IR spectrum

$$CpV(CO)_4 + 2Na \xrightarrow[\text{or } NH_3]{\text{Na−Hg/THF}} Na_2[CpV(CO)_3] + CO \quad (11)$$

of $[CpFe(CO)_2]^-$, which exhibited IR ν(CO) bonds at 1865 and 1788 cm^{-1} (for the $^nBu_4N^+$ salt) in THF,[130] we expected the corresponding spectrum for the unknown $[CpMn(CO)_2]^{2-}$, unperturbed by ion pairing, to have respective bands at about 120 ± 20 cm^{-1} lower in energy than those of the iron monoanion, i.e., ca. 1740 and 1660 cm^{-1}.[131] In fact, treatment of $CpMn(CO)_3$ with an excess (6 equiv) of Na metal in HMPA produced a species that had only one intense and quite broad IR absorption at about 1670 cm^{-1}. Clearly, its IR spectrum was not consistent with the presence of $[CpMn(CO)_2]^{2-}$, which John Cooper's group later obtained from a different precursor.[132] Much to Robert Faltynek's and my surprise, the addition of excess chlorotriphenylstannane, a reagent long known to be effective in the derivatization of metal carbonyl anions,[133] afforded a new substance in 64% isolated yield, based on $CpMn(CO)_3$, that was totally devoid of a cyclopentadienyl group: *cis*-$[Mn(CO)_4(SnPh_3)_2]^-$![134]

In retrospect, loss of the cyclopentadienyl group from $CpMn(CO)_3$ might have been anticipated from its reaction with Na in HMPA. Thus, Podall and Giraitis[135] had previously shown that treatment of the methylcyclopentadienyl analogue, $MeCpMn(CO)_3$, with Na metal in hot (125 °C) diglyme [bis(2-methoxyethyl) ether] under about 50 atm of pressure of CO, followed by hydrolysis and steam distillation, afforded about a 50% yield of $Mn_2(CO)_{10}$. They proposed that the first step in the reaction involved a reductive cleavage of the methylcyclopentadienylmanganese unit, as depicted by eq 12.[135] Although ferrocene was earlier shown to be

$$MeCpMn(CO)_3 + 2Na + 2CO \xrightarrow[\text{50 atm of CO}]{\text{diglyme, 125 °C}} Na[Mn(CO)_5] + Na[MeCp] \quad (12)$$

completely reduced by Li metal in ethylamine or liquid ammonia to Fe metal and LiCp,[136] Podall's reduction seems to be the first reaction of this type to afford a reduced transition-metal complex. Many years later, Klaus Jonas began his pioneering studies on the reductive cleavage reactions of metallocenes in the presence of alkenes, which resulted in the formation of incredible homoleptic alkenemetalates, such as $[Co(C_2H_4)_4]^-$ [70] and $[Fe(C_2H_4)_4]^{2-}$,[73] shown in Table 2, and numerous other unique low-valent metal complexes.[137]

Metal Carbonyl Tri- and Tetranions

1. Tetracarbonylmetalates(3−) of Mn and Re. During the reduction of $CpMn(CO)_3$ by Na−HMPA, the first product observed was $[Mn(CO)_5]^-$. However, IR absorptions due to this species rapidly decayed when additional Na was added, and this resulted in the appearance and growth of the unknown substance absorbing at 1670 cm^{-1}. Excess Na had

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

(125) Normant, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1046.

(126) In contrast to liquid ammonia,[28] Na dissolves in HMPA to afford significant concentrations of Na^-. See: Edwards, P. P.; Guy, S. E.; Holton, D. M.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* **1981**, 1185.

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

(128) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

(129) (a) Fischer, E. O.; Vigoureux, S. *Chem. Ber.* **1958**, *91*, 2205. (b) Fischer, E. O.; Schneider, R. J. J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 569.

(130) (a) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263. (b) Shortly after the above paper appeared, which described the first isolation of a tetraalkylammonium salt of $[C_5H_5Fe(CO)_2]^-$, Keith Pannell published an outstanding IR spectral study on the solution structure of $Na[C_5H_5Fe(CO)_2]$ in THF: Pannell, K. H.; Jackson, D. *J. Am. Chem. Soc.* **1976**, *98*, 4433. These two papers contained the first IR spectral characterizations of alkali-metal salts of $[C_5H_5Fe(CO)_2]^-$.

(131) See footnote 193 of ref 49. However, for very highly reduced metal carbonyls, IR ν(CO) values at lower energies than expected are often observed for asymmetric stretching modes.[132]

(132) Leong, V. S.; Cooper, N. J. *Organometallics* **1988**, *7*, 2080. IR ν(CO) values of $Na_2[C_5H_5Mn(CO)_2]$, to which cryptand 222 was added in THF, showed major peaks at 1735 and 1600 cm^{-1}, which are in agreement with expected values for a largely unperturbed dianion of this type.[131]

(133) (a) Hein, F.; Kleinert, P.; Jehn, W. *Naturwissenschaften* **1952**, *44*, 34. (b) Gorsich, R. D. *J. Am. Chem. Soc.* **1962**, *84*, 2486. Hein was the pioneer in the synthesis of mixed main group−transition metal carbonyl compounds, the first being reported in 1941. See: Hein, F.; Pobloth, H. *Z. Anorg. Allg. Chem.* **1941**, *248*, 84.

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

(135) Podall, H. E.; Giraitis, A. P. *J. Org. Chem.* **1961**, *26*, 2587.

(136) Trifan, D. S.; Nicholas, L. *J. Am. Chem. Soc.* **1957**, *79*, 2746.

(137) (a) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295. (b) Jonas, K. *Pure Appl. Chem.* **1990**, *62*, 1169. (c) Jonas, K.; Häselhoff, C.-C.; Goddard, R.; Krüger, C. *Inorg. Chim. Acta* **1992**, *198−200*, 533 and references cited therein.

Scheme 1. Syntheses of Tetracarbonylmetalates(3−) of Mn and Re

$$M_2(CO)_{10} + 2\ Na \xrightarrow[Hg]{THF} 2\ Na^+[M(CO)_5]^-;\ M = Mn, Re$$

$$Na^+[M(CO)_5]^- + 3\ Na \xrightarrow[20\ °C]{HMPA} 3\ Na(HMPA)_x{}^+[M(CO)_4]^{3-} + ...$$

$$3[Na(HMPA)_x]^+[M(CO)_4]^{3-} \xrightarrow[-33\ °C]{NH_3(l)} Na_3[M(CO)_4]\downarrow + 3xHMPA$$

HMPA = hexamethylphosphoramide = $(Me_2N)_3PO$

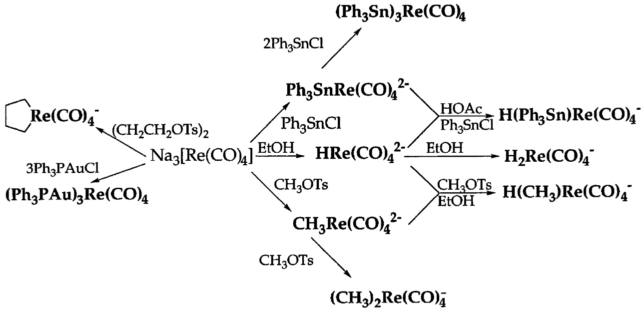
$Na_3[Mn(CO)_4]$, dec. ~ 320 °C, beige solid

Anal. Calcd. for $C_4O_4MnNa_3$: C, 20.36; H, 0.00, Na, 29.23
Found C. 20.10; H, 0.005; Na, 29.15

$Na_3[Re(CO)_4]$, dec. ~ 340 °C, Ocher solid

Anal. Calcd. for $C_4O_4Na_3Re$: C, 13.08; H, 0.00; Na, 18.78
Found C, 12.91; H, 0.12; Na, 18.75

Scheme 2. Some Reactions of $Na_3[Re(CO)_4]$



$$[M(CO)_4]^{3-} + 2H_2O \xrightarrow[0\ °C]{HMPA} \xrightarrow[Ph_4AsCl,\ 0\ °C]{aqueous} [Ph_4As][H_2M(CO)_4]\downarrow$$

(70-80%; M = Mn, Re)

no effect on the latter species, so it was remarkably inert toward further reduction! Shortly thereafter, Faltynek demonstrated that reduction of bona fide $Na[Mn(CO)_5]$ under the same conditions provided the same highly reduced carbonylmetalate. Reduction of $Na[Re(CO)_5]$ or $Re_2(CO)_{10}$ by Na−HMPA also gave the analogous carbonylrhenate in high conversion (as judged from yields of derivatives). Attempts to isolate satisfactorily pure samples of these substances were unsuccessful in the early 1970s. However, after several months, we had enough spectroscopic and chemical evidence to propose with some confidence that the precursors were the metal carbonyl trianion salts, $Na_3[M(CO)_4]$,[138] i.e., Mn and Re analogues of $[Fe(CO)_4]^{2-}$ and $[Os(CO)_4]^{2-}$, respectively.[49] IR spectral data also effectively ruled out the presence of other plausible tetracarbonylmetalates, such as the monohydrides, $[HM(CO)_4]^{2-}$, which were later identified, vide infra, as paramagnetic dianions, $[M(CO)_4]^{2-}$, or diamagnetic dimers, $[M_2(CO)_8]^{4-}$, all of which should have IR carbonyl stretching frequencies at higher energies.[139] About 10 years later, Garry Warnock made the important discovery that the treatment of HMPA solutions of $Na_3[M(CO)_4]$ with liquid ammonia caused rapid precipitation of these trisodium salts as satisfactorily pure unsolvated products (Scheme 1).[140] The high thermal stabilities of these species, with decomposition points well above 300 °C, appear to be unprecedented for metal carbonyls. Warnock also carefully examined protonations of these species, which resulted in the spectral characterizations of $[HM(CO)_4]^{2-}$ and the isolation of the dihydrides, $[H_2M(CO)_4]^-$.[140] The previously unknown $[H_2Mn(CO)_4]^-$ was of particular interest because it was the Mn analogue of the first carbonyl hydride, $H_2Fe(CO)_4$.[98,99] Several reactions of $Na_3[Re(CO)_4]$ are shown in Scheme 2. Additional information on the synthesis and the still poorly explored chemistry of these species has appeared in reviews.[49,141] In due course, single-crystal X-ray studies will be important for their structural authentication. Also, the Tc analogue, $Na_3[Tc(CO)_4]$, remains unknown but should be readily accessible via appropriate reductions of $Tc_2(CO)_{10}$.[141]

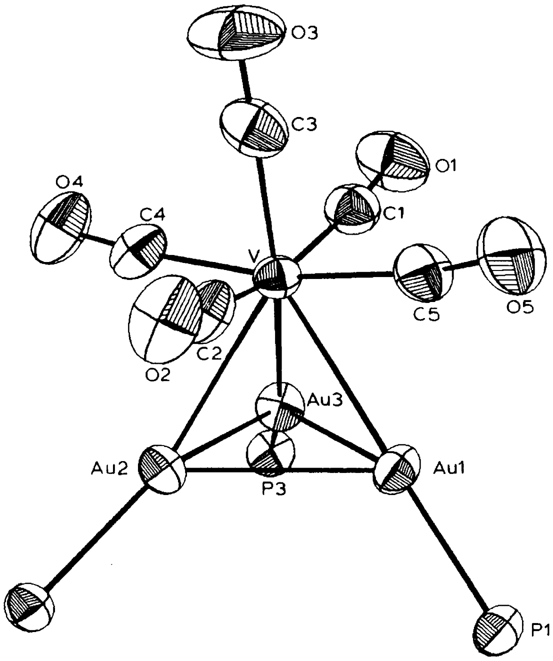


Figure 3. Structure of $V(CO)_5(AuPPh_3)_3$, with phenyl groups omitted for clarity (from ref 144).

2. Pentacarbonylvanadate(3−). These were exciting times for us in research, and the race was on to determine whether carbonyl trianions of other transition metals could be obtained. Although attempts to reduce $[Na(diglyme)_2][V(CO)_6]$ by Na in HMPA gave only yellow-brown decomposition products of unknown nature, Michael Palazzotto soon discovered that analogous reductions in liquid ammonia at −60 °C provided beautiful blood-red solutions, from which formal derivatives of $[V(CO)_5]^{3-}$ were obtained.[142] These included the seven-coordinate $[V(CO)_5(SnPh_3)_2]^-$ [143] and the eight-coordinate $[V(CO)_5(AuPPh_3)_3]$, later shown to be a unique tetrahedral cluster containing three Au atoms and one V atom (Figure 3).[144] The close similarity between Behren's synthesis of $Na_2[Cr(CO)_5]$ (eq 9) and our route to $Na_3[V(CO)_5]$ is quite striking. However, unlike $Na_2[Cr(CO)_5]$, which is stable indefinitely at room temperature under an inert atmosphere,[49] the dark-red V product, obtained after evaporation of liquid ammonia, rapidly decomposes at about 0 °C to a black uncharacterized solid.[145] Treatment of ammoniacal solutions of $Na_3[V(CO)_5]$ with 3 equiv of RbI or CsI resulted in the precipitation of very slightly soluble orange (Cs) to bright-red (Rb) microcrystals. After these were

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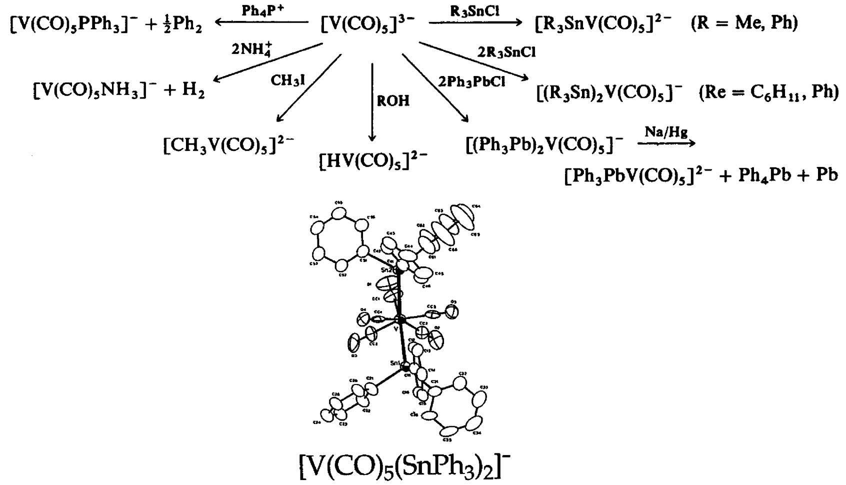
(138) Ellis, J. E.; Faltynek, R. A. *J. Chem. Soc., Chem. Commun.* **1975**, 966.
(139) Ellis, J. E.; Faltynek, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 1801.
(140) Warnock, G. W.; Moodie, L. C.; Ellis, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 2131.
(141) Ellis, J. E. *Adv. Organomet. Chem.* **1990**, *31*, 1.
(142) Ellis, J. E.; Palazzotto, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 8264.
(143) Ellis, J. E.; Hayes, T. E.; Stevens, R. E. *J. Organomet. Chem.* **1981**, *216*, 191.
(144) Ellis, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 6106.
(145) Ellis, J. E.; Fjare, K. L.; Hayes, T. G. *J. Am. Chem. Soc.* **1981**, *103*, 6100.

Scheme 3. Reactions of $[V(CO)_5]^{3-}$ with Main-Group Electrophiles



dried in vacuo, high yields (88−90%) of satisfactorily pure unsolvated deep-red-brown $Rb_3[V(CO)_5]$, dec ~ 130 °C, and yellow-brown $Cs_3[V(CO)_5]$, dec ~ 200 °C, were isolated.[145]

There remained a nagging concern that the original ammoniacal solutions might contain the monohydride, $[HV(CO)_5]^{2-}$, or some species other than the proposed $[V(CO)_5]^{3-}$. Again, Warnock came to the rescue by examining the reduction of 99% ^{13}C-enriched $[V(CO)_6]^-$ in liquid ammonia at −50 °C with ^{1}H, ^{13}C, and ^{51}V NMR spectroscopy, a technically very demanding study! He unambiguously established that the dark-red product was the fluxional nonhydridic $[V(CO)_5]^{3-}$, which had a very downfield average terminal carbonyl ^{13}C NMR resonance of +290 ppm, a world's record value when reported in 1984![146] The addition of 1 equiv of ammonium chloride or ethanol to $Na_3[V(CO)_5]$ in liquid ammonia caused the solution to rapidly change from a dark-red to a yellow-orange hue. NMR spectra showed that all $[V(CO)_5]^{3-}$ had been consumed and replaced by the fluxional monohydride, $[HV(^{13}CO)_5]^{2-}$ ($\delta_H = -4.8$ ppm, sextet of octets, $J_{V-H} = 27.7$ Hz, $J_{C-H} = 10.8$ Hz),[147] which was subsequently isolated as satisfactorily pure $[Et_4N]_2[HV(CO)_5]$.[148] Attempts to convert $[HV(CO)_5]^{2-}$ to the still unknown dihydride, $[H_2V(CO)_5]^-$, in liquid ammonia at −70 °C resulted instead in the rapid evolution of gas, presumably H_2, and the formation of a striking deep-magenta solution, from which high yields of $[V(CO)_5(NH_3)]^-$ were isolated as the Ph_4As^+ salt (eq 13).[145] Dieter Rehder had previously obtained the identical ammine anion via photolysis of $[V(CO)_6]^-$ in liquid ammonia.[149] Representative reactions of $[V(CO)_5]^{3-}$ are shown in Scheme 3. Other aspects of the chemical and spectroscopic properties of $[V(CO)_5]^{3-}$ have been discussed previously.[49,141]

$$[V(CO)_5]^{3-} \xrightarrow[-NH_3]{NH_4^+} [HV(CO)_5]^{2-} \xrightarrow[-NH_3]{NH_4^+} \underset{??}{[H_2V(CO)_5]^-} \xrightarrow[-H_2]{NH_3} [V(CO)_5(NH_3)]^- \quad (13)$$

3. Tricarbonylmetalates (3−) of Co, Rh, and Ir. Subsequently, reductions of the group 9 tetracarbonylmetalates, $[M(CO)_4]^-$, where M = Co, Rh, and Ir, by Na and K in liquid ammonia or Na in HMPA were shown to provide highly reduced species with very intense and broad IR bands in the same 1600−1700-cm^{-1} region as that observed for $[M(CO)_4]^{3-}$, where M = Mn and Re, and $[V(CO)_5]^{3-}$. Interestingly, $Na[Co(CO)_4]$ was inert toward reduction by Na in HMPA, but colorless $Na[M(CO)_4]$, where M = Rh and Ir, were easily reduced in this medium to produce deep-yellow to yellow-brown solutions containing single intense broad peaks at about 1650 ± 10 cm^{-1}.[141] Treatment of the insoluble and impure products in liquid ammonia or the soluble Rh or Ir species in HMPA with electrophiles provided several derivatives of tricarbonylmetalates(3−). These included [*trans*-$M(CO)_3(SnPh_3)_2]^-$,[150] for which X-ray structures were recently reported of the Co and Ir salts (Figure 4).[151] Satisfactorily pure unsolvated olive-brown $Na_3[Co(CO)_3]$[152] and orange $Na_3[Ir(CO)_3]$[151] were later obtained. However, few definitive data are yet available for the

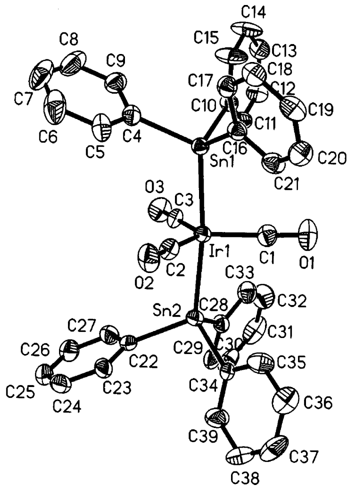


Figure 4. Structure of $[Ir(CO)_3(SnPh_3)_2]^-$, with H atoms omitted for clarity (from ref 151).

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(146) Warnock, G. F.; Philson, S. B.; Ellis, J. E. *J. Chem. Soc., Chem. Commun.* **1984**, 893.

(147) See ref 141, Figure 9.

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

(149) Rehder, D. *J. Organomet. Chem.* **1972**, *37*, 303.

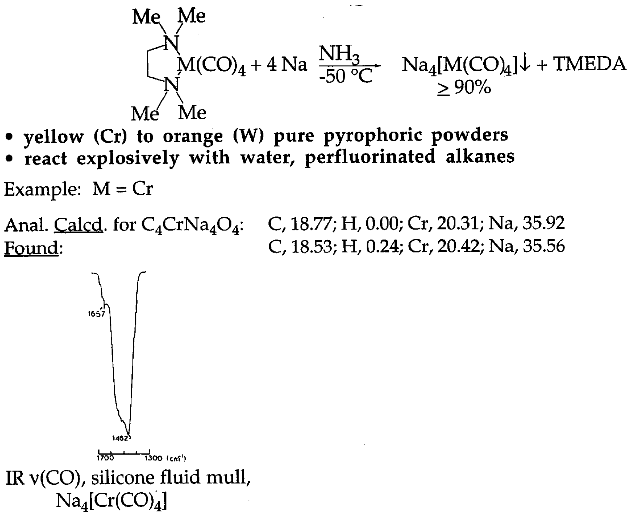
(150) Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. *J. Chem. Soc., Chem. Commun.* **1977**, 686.

(151) 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., Jr. *Inorg. Chem.* **2001**, *40*, 5279.

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

presumably analogous Rh complex, $Na_3[Rh(CO)_3]$, or protonation reactions of these carbonyls.[151,152] The good solubility of $Na_3[Rh(CO)_3]$ and $Na_3[Ir(CO)_3]$ in HMPA suggests that these species may be good candidates for single-crystal X-ray structural studies. IR spectra of these compounds in the carbonyl stretching frequency region show only one strong absorption, appropriate for a trigonal-planar array of carbonyl groups about the metal center. However, because of the highly charged nature of these anions, their “ideal geometry” will likely be perturbed in solution and in the solid state by strong ion pairing to counterions. Recently, the isoelectronic $Zn(CO)_3$, a “cryomolecule”, stable at 7 K, has been identified in an Ar matrix and is believed to possess a trigonal-planar structure.[153]

Scheme 4. Synthesis and Characterization of $Na_4[M(CO)_4]$, Where M = Cr, Mo, and W



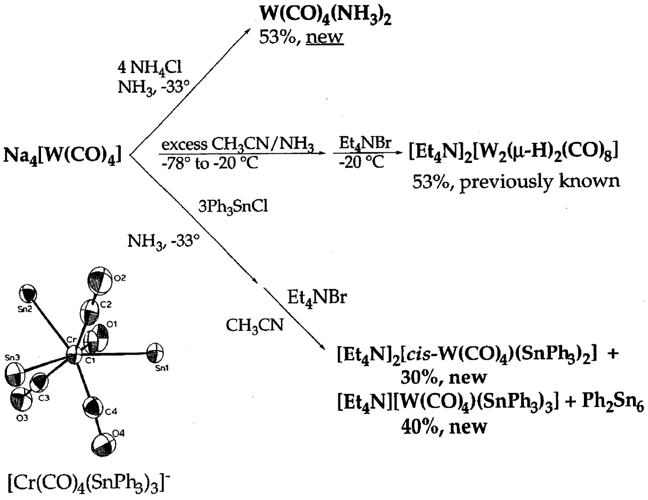
- yellow (Cr) to orange (W) pure pyrophoric powders
- react explosively with water, perfluorinated alkanes

Example: M = Cr

Anal. Calcd. for $C_4CrNa_4O_4$: C, 18.77; H, 0.00; Cr, 20.31; Na, 35.92
Found: C, 18.53; H, 0.24; Cr, 20.42; Na, 35.56

IR ν(CO), silicone fluid mull, $Na_4[Cr(CO)_4]$

Scheme 5. Some Chemical Reactions of $Na_4[W(CO)_4]$ and the Structure of $[Cr(CO)_4(SnPh_3)_3]^-$[a]



[a] Phenyl groups are omitted for clarity.

4. Tetracarbonylmetalates(4−) of Cr, Mo, and W. Our discovery that $[Mn(CO)_5]^-$ was easily reduced to $[Mn(CO)_4]^{3-}$ under a variety of conditions[141] led us to consider whether $[Cr(CO)_5]^{2-}$ might undergo an analogous reduction to $[Cr(CO)_4]^{4-}$, isoelectronic with the known $Cr(NO)_4$.[154] Unfortunately, $Na_2[Cr(CO)_5]$ proved to be totally inert toward reduction by Na−NH_3 or Na−HMPA, so other reactants had to be considered. A prior observation that $[Cr(CO)_5Cl]^-$ was quantitatively converted to $[Cr(CO)_5]^{2-}$ by Na in HMPA[127] suggested that an appropriately substituted chromium tetracarbonyl complex, $Cr(CO)_4L_2$, might be a suitable precursor to the unknown $[Cr(CO)_4]^{4-}$.[155] Hagen discovered that the reaction of the easily accessible $Cr(CO)_4$(TMEDA) by 4 equiv of Na in liquid ammonia provided, within 3 h at −50 °C, a homogeneous pale-yellow and pyrophoric solid. This proved to be satisfactorily pure unsolvated $Na_4[Cr(CO)_4]$ and was obtained in 88−93% yields! Mull IR spectra showed a single intense broad peak at unusually low energy for a carbonyl anion, 1460 ± 20 cm^{-1}, i.e., about 200 cm^{-1} lower than the corresponding absorption of $Na_3[Mn(CO)_4]$ in HMPA. This feature suggests that the Na cations strongly interact with the carbonyl O atoms in the solid;[156] i.e., the compound seems to be best formulated as $[Cr(CONa)_4]_x$.[157] Chemical properties of this substance are consistent with those expected of a highly reduced tetracarbonylchromate. For example, treatment of liquid ammonia suspensions of this species with excess NH_4Cl or acetonitrile resulted in the formation of the known *cis*-$Cr(CO)_4(NH_3)_2$ (65% yield) or the new $[Cr(CO)_4(\mu\text{-}H)]_2^{2-}$ (53% yield as Et_4N^+ salt), respectively,[158] where the latter is a chromium analogue of the previously known and structurally characterized W complex, $[H_2W_2(CO)_8]^{2-}$.[159] Also, the reaction of carbonylchromate(4−) with 2 equiv of Ph_3SnCl gave the new organotin derivative, $[cis\text{-}Cr(CO)_4(SnPh_3)_2]^{2-}$, in 54% isolated yield as a slightly air-sensitive $[Et_4N]^+$ salt. The latter salt combined with additional Ph_3SnCl in THF to afford $[Cr(CO)_4(SnPh_3)_3]^-$, the first seven-coordinate Cr complex to contain only monodentate ligands.[160,161] Reductions of $Mo(CO)_4$(TMEDA) and $W(CO)_4$(TMEDA) under the same conditions were also shown to provide high yields of the analogous tetrasodium salts of these elements (Scheme 4). Chemical properties of $Na_4[W(CO)_4]$ were examined by Jiann Tsuen-Lin and found to be very similar to those of the Cr analogue (Scheme 5). More information on these unique species, as well as prospects for the synthesis of other homoleptic carbonylmetalate tetraanion salts, was discussed previously.[49,141] Whether any compounds containing transi-

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(153) Jiang, L.; Xu, Q. *J. Am. Chem. Soc.* **2005**, *127*, 8906.

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

(155) The “reductive labilization” rule[157] for the synthesis of unusual classes of metal carbonyl anions holds that when 18-electron heteroleptic metal carbonyl complexes undergo reduction, the poorer acceptor/better donor ligands will often be preferentially lost as the metal center is reduced. Thus, reduction of $[Cr(CO)_5Cl]^-$ causes preferential labilization of the Cl^-; effectively, the latter is a better leaving group than CO in this process. This simple concept should also work to good advantage in predicting the outcomes of reductive cleavage reactions of other classes of low-valent transition-metal complexes, provided the ligands do not undergo facile reduction. For example, most neutral or anionic metal carbonyl nitrosyls are not smoothly reduced perhaps because the coordinated nitrosyl groups are first changed to coordinated hyponitrites, which then suffer facile decomposition. See: Ellis, J. E.; Chen, Y.-S. *Inorg. Chim. Acta* **2000**, *300−302*, 675.

(156) Darensbourg, M. Y. *Prog. Inorg. Chem.* **1984**, *33*, 221. This review has an outstanding account of the influence of contact ion pairing on the IR spectra of metal carbonyl anions.

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

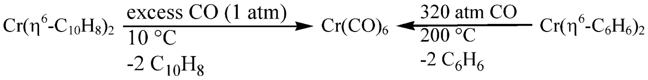
(158) Lin, J.-T.; Hagen, G. P.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2296.

(159) Churchill, M. R.; Chang, S. W. Y. *Inorg. Chem.* **1979**, *25*, 145.

(160) Lin, J.-T.; Hagen, G. P.; Ellis, J. E. *Organometallics* **1983**, *2*, 1145.

(161) Lin, J.-T.; Hagen, G. P.; Ellis, J. E. *Organometallics* 1984, *3*, 1288.

Scheme 6. Comparison of the Carbonylations of Bis(naphthalene)chromium and Bis(benzene)chromium



$$Cr(\eta^6\text{-}C_{10}H_8)_2 \xrightarrow[\substack{10\ °C \\ -2\ C_{10}H_8}]{\text{excess CO (1 atm)}} Cr(CO)_6 \xleftarrow[\substack{200\ °C \\ -2\ C_6H_6}]{\text{320 atm CO}} Cr(\eta^6\text{-}C_6H_6)_2$$

tion metals in formal oxidation states lower than 4− will be possible is unknown.

"Mild Routes" to Early-Transition-Metal Carbonyls

After $[V(CO)_6]^-$ was shown to undergo facile reduction to $[V(CO)_5]^{3-}$ by Na metal in liquid ammonia, we were very keen to determine whether the hexacarbonylmetalates(1−) of Nb and Ta could be reduced to the respective $[M(CO)_5]^{3-}$. However, syntheses of $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ required high-pressure (≥200 atm) reactors,[162] which were not available at the University of Minnesota. In retrospect, this was a "blessing in disguise" because it forced me to consider possible mild, and far safer, routes to these monoanions. There were enticing hints in the literature that these and other early-transition-metal carbonyl anions might be accessible from non-carbonyl precursors with conventional laboratory apparatuses. In particular, Kündig and Timms and Elschenbroich and Möckel independently reported in 1977 on the metal atom vapor synthesis and isolation of bis(naphthalene)chromium(0) and discovered that both naphthalenes were rapidly displaced by CO at 10 °C and normal pressure to give $Cr(CO)_6$.[163,164] In contrast, Fischer and Öfele's bis(benzene)chromium required quite forcing conditions to achieve the same result[165] (Scheme 6). Earlier, Henrici-Olivè and Olivè published electron paramagnetic resonance evidence for the bis(naphthalene)metal complexes of V(0) and Cr(I,I−). They had prepared these materials by conventional routes, i.e., reductions of VCl_3 and $CrCl_3$ by lithium naphthalene in THF.[166] To the best of my knowledge, the Olivès never isolated these products or examined their reactions with CO or other potential acceptor ligands. However, undoubtedly the single most important prior result in our quest for a mild route to $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ was Stanley Wreford's unprecedented atmospheric-pressure synthesis of a tantalum carbonyl from a non-carbonyl precursor. He observed that $TaCl_4(dmpe)_2$, where dmpe = 1,2-bis(dimethylphosphano)ethane, underwent facile reduction by sodium naphthalene in THF, under normal pressures of CO, to afford a 46% isolated yield of $Ta(CO)_2(dmpe)_2Cl$ (eq 14).[167] On the basis of the results of Timms and

$$TaCl_4(dmpe)_2 + 3NaC_{10}H_8 + 2CO \xrightarrow[-3NaCl]{\text{THF, 20 °C}} Ta(CO)_2(dmpe)_2Cl + 3C_{10}H_8 \quad (14)$$

Kündig,[163] Elschenbroich and Möckel[164] and Datta and Wreford,[167] it seemed obvious that alkali-metal naphthalene-mediated reductive carbonylations of $NbCl_5$ and $TaCl_5$ should afford the desired hexacarbonylmetalates. Our first attempts, carried out at −60 °C in THF or 1,2-dimethoxyethane (DME), under an atmosphere of CO, resulted in only 1−3% isolated yields of products. However, by first treatment of the metal pentahalides with 6 equiv of lithium or sodium naphthalene (or 1-methylnaphthalene) under an Ar atmosphere at −60 °C in DME, followed by removal of the Ar in vacuo, addition of normal pressures of CO, and slow warming of the reaction mixture to room temperature over a period of 6−12 h, up to 53% isolated yields of $[Ta(CO)_6]^-$ were realized, as tetraalkylammonium salts. Yields of $[Nb(CO)_6]^-$ were usually lower, 30−40% (eq 15), where A = Li or Na and M = Nb or Ta. Improved routes to

$$MCl_5 + 6AC_{10}H_8 \xrightarrow[\substack{\text{2. CO (1 atm)} \\ -60 \text{ to } +20\ °C \\ -6C_{10}H_8,\ -5ACl}]{\text{1. DME, } -60\ °C} A[M(CO)_6] \quad (15)$$

$[Ta(CO)_6]^{-}$[169] and $[Nb(CO)_6]^{-}$[170] are now available, in addition to related normal-pressure syntheses of $[V(CO)_6]^-$.[171,172] It also must be emphasized that, at about the same time, Fausto Calderazzo and Guido Pampaloni independently developed quite different, but very effective, atmospheric-pressure syntheses for these group 5 hexacarbonylmetalates.[49,173,174] Having secured a facile route to $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$, we then examined their alkali-metal reductions in liquid ammonia. This study resulted in the isolation and characterization of $Cs_3[M(CO)_5]$, where M = Nb and Ta, which are doubtlessly *the most difficult to handle* and surprisingly shock-sensitive solids we have ever dealt with in research[141,175,176] (Scheme 7). Preparation and characterization of the corresponding monohydrides, $[HM(CO)_5]^{2-}$, have also been described in some detail.[148,169,170]

Although development of a "mild route" to hexacarbonylmetalates(1−) represented a key advance in our study of carbonyl and related low-valent chemistry of the group 5 elements, what I found most exciting were the prospects for extending this study to other early transition metals because atmospheric-pressure syntheses of carbonylmetalates from non-carbonyl precursors were mainly available only for the later transition metals, beyond the group 7 triad.[49] In particular, we initially targeted the group 4 elements because

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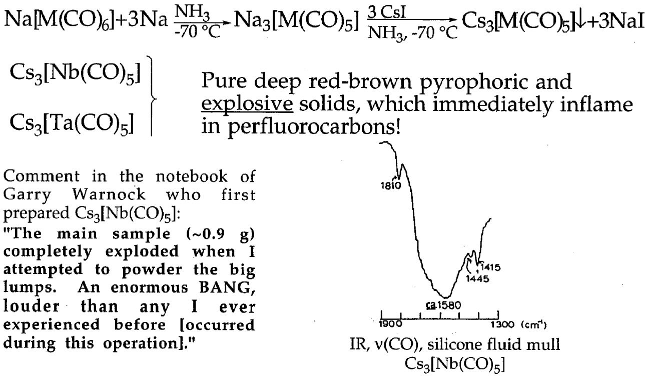
(175) After we had achieved these syntheses and submitted the work for publication, a reviewer pointed out that we had already reported on the preparation of $[V(CO)_5]^{3-}$, so why should the synthesis of the Nb and Ta analogues be viewed as significant? This individual had clearly not read Cotton and Wilkinson's "Advanced Inorganic Chemistry" with sufficient care to appreciate the often profound differences that exist in the chemical properties of a particular 3d-block complex and formally analogous 4d- and 5d-block species from identical triads. Also, Behrens had previously shown that reductions of $Mo(CO)_6$ and $W(CO)_6$ by Na in liquid ammonia worked very poorly as routes to the respective $Na_2[M(CO)_5]$, whereas the corresponding reduction of $Cr(CO)_6$ gave high yields of $Na_2[Cr(CO)_5]$.[49,115] I relayed these comments to the Associate Editor handling the manuscript, and the paper was accepted![176]

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

Scheme 7. Shock-Sensitive Pentacarbonylmetalates(3−) of Nb and Ta



$Na[M(CO)_6] + 3Na \xrightarrow[-70\ ^\circ C]{NH_3} Na_3[M(CO)_5] \xrightarrow[NH_3,\ -70\ ^\circ C]{3\ CsI} Cs_3[M(CO)_5]\downarrow + 3NaI$

$Cs_3[Nb(CO)_5]$, $Cs_3[Ta(CO)_5]$: Pure deep red-brown pyrophoric and explosive solids, which immediately inflame in perfluorocarbons!

Comment in the notebook of Garry Warnock who first prepared $Cs_3[Nb(CO)_5]$:
"The main sample (~0.9 g) completely exploded when I attempted to powder the big lumps. An enormous BANG, louder than any I ever experienced before [occurred during this operation]."

IR, ν(CO), silicone fluid mull $Cs_3[Nb(CO)_5]$

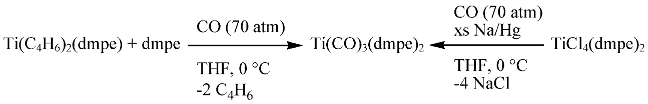
there were many opportunities for the discovery of fundamentally new metal carbonyl chemistry in this poorly explored area in the early 1980s.[177]

Zerovalent and Lower-Valent Carbonyls of Ti, Zr, and Hf

When we began this new quest in metal carbonyl chemistry, only three well-defined isolable zerovalent carbonyls of group 4 elements were known: Zr(butadiene)$_2$(dmpe)(CO), a pyrophoric solid, which readily lost CO at room temperature,[179] and the more thermally robust Ti(CO)$_3$(dmpe)$_2$[180,181] and Ti(CO)$_2$(PF$_3$)(dmpe)$_2$,[180] which were structurally authenticated. Earlier Ozin and co-workers reported on the cocondensation of Ti atoms with excess CO at 10−15 K and, on the basis of IR and UV−vis spectral data, identified the highest stoichiometry titanium carbonyl as Ti(CO)$_6$, a green substance, which decomposed at about 40−50 K.[182] Because the latter was a 16-electron, low-spin d^4 species, a reasonable first target for our atmospheric-pressure naphthalene-mediated reductive carbonylation method was the unknown 18-electron, low-spin d^6 [Ti(CO)$_6$]$^{2-}$. This species promised to be significantly more robust than the neutral hexacarbonyl. However, many attempts to access this compound in the early 1980s from non-carbonyl precursors were uniformly unsuccessful. There was also a great interest in exploring zerovalent group 4 carbonyl chemistry, but I was hesitant to enter this area because Wreford had only recently published his definitive study on Ti(CO)$_3$(dmpe)$_2$ in 1982.[181] Also, he had recently moved from the University of Toronto to become a group leader in the Central Research Department, Experimental Station, of E. I. duPont de Nemours and Company, and I had no desire to compete with duPont in basic research! However, I had the good fortune to meet with him at duPont in July 1983 and discovered that he (and the Company) no longer had any research interests in this area.

Wreford's original routes to Ti(CO)$_3$(dmpe)$_2$ involved relatively high-pressure (ca. 70 atm) carbonylations of Ti(C$_4$H$_6$)$_2$(dmpe), where C$_4$H$_6$ = 1,3-butadiene, or reductive carbonylations of TiCl$_4$(dmpe) with sodium amalgam in THF, both in the presence of additional dmpe at 0 °C (Scheme 8).[180] Yields for these procedures were a respectable 55% and 28%, respectively, but the relatively high-pressure and subambient-temperature conditions required special equipment, which made this novel substance poorly accessible. However, we soon found that by mixing THF solutions of TiCl$_4$(dmpe)$_2$[183] and 4 equiv of sodium naphthalene at −60 °C under an Ar atmosphere, followed by the addition of CO at atmosphere pressure and slow warming over a period of 6−12 h, 70−80% isolated yields of satisfactorily pure Ti(CO)$_3$(dmpe)$_2$ could be obtained (eq 16). But our most

Scheme 8. Wreford's Original Routes to Ti(CO)$_3$(dmpe)$_2$, where dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$



$$TiCl_4(dmpe)_2 + 4NaC_{10}H_8 \xrightarrow[THF]{Ar,\ -80\ ^\circ C} \xrightarrow[-80\ to\ -20\ ^\circ C,\ -4NaCl]{CO\ (1\ atm)} Ti(CO)_3(dmpe)_2 + 4C_{10}H_8 \quad (16)$$

surprising discovery in this study was that the crowded seven-coordinate Ti(CO)$_3$(dmpe)$_2$ underwent facile atmospheric-pressure carbonylation at 20 °C in THF to give an unprecedented pentacarbonyltitanium(0) complex, Ti(CO)$_5$(dmpe). Treatment of the equilibrium mixture of the two carbonyl complexes with BH$_3$·THF, an effective organophosphane "sponge", under an atmosphere of CO, caused Ti(CO)$_3$(dmpe)$_2$ to disappear within 24 h and more Ti(CO)$_5$(dmpe) to form. Because the other product, dmpe·2BH$_3$, is poorly soluble in THF, filtration of the reaction mixture at 0 °C, followed by removal of THF, provided spectroscopically pure, bright-red Ti(CO)$_5$(dmpe) (eq 17).[184] Although the

$$Ti(CO)_3(dmpe)_2 + 2CO + 2BH_3{\cdot}THF \xrightarrow{THF,\ 0\ ^\circ C} Ti(CO)_5(dmpe) + dmpe{\cdot}2BH_3 \quad (17)$$

highly fluxional Ti(CO)$_5$(dmpe) was too thermally unstable at 20 °C to obtain elemental analyses, its composition was unambiguously established by ^{13}C and ^{31}P NMR spectra of the 99% ^{13}C-labeled pentacarbonyl.[185] From a synthetic inorganic chemist's view, however, the most exciting property of Ti(CO)$_5$(dmpe) was its facile interaction with a variety of good donor ligands to afford a number of new titanium(0) carbonyls (Scheme 9). In contrast, Ti(CO)$_3$(dmpe)$_2$ proved to be inert to all of these Lewis bases.

We were also very interested in syntheses of carbonyltitanates, other than [Ti(CO)$_6$]$^{2-}$, as none were known at the time. Because CpV(CO)$_4$ was well established and thermally robust,[186] reductive carbonylations of CpTiCl$_3$ were examined by Beatrice Kelsey Stein as a possible route to the isoelectronic [CpTi(CO)$_4$]$^-$. Efforts to effect this conversion with Na, NaK, K, Na−Hg, Mg, and KC$_8$ under a variety of

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(177) See: Sikora, D. J.; Macomber, D. W.; Rausch, M. D. *Adv. Organomet. Chem.* **1986**, *25*, 317.
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(180) Wreford, S. S.; Fischer, M. B.; Lee, J.-S.; James, E. J.; Nyburg, S. C. *J. Chem. Soc., Chem. Commun.* **1981**, 458.
(181) Domaille, P. J.; Harlow, R. L.; Wreford, S. S. *Organometallics* **1982**, *1*, 935.
(182) Busby, R.; Klotzbücher, W.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 822.
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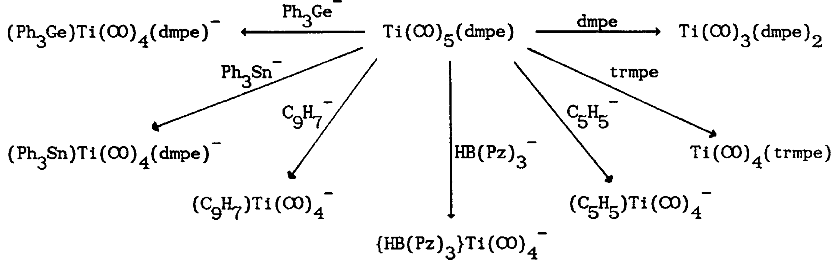
(184) Chi, K.-M.; Frerichs, S. R.; Stein, B. K.; Blackburn, D. W.; Ellis, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 163.
(185) Ellis, J. E. *Polyhedron* **1989**, *8*, 1611.
(186) Fischer, E. O.; Hafner, W. *Z. Naturforsch.* **1954**, *9B*, 503.

Scheme 9. Reactions of Main-Group Nucleophiles with $Ti(CO)_5(dmpe)$, a Synthon for the Unknown $Ti(CO)_7$



conditions were entirely unproductive. However, she discovered that reductions of $CpTiCl_3$ by sodium naphthalene, carried out by the same two-step procedure as that developed for $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$, vide supra, provided the desired substance, as thermally stable complex salts (eq 18), where $R_4E^+ = Et_4N^+$ or Ph_4As^+, the latter of which was structurally characterized (Figure 5).[187] Soon thereafter, the

$$\mathrm{CpTiCl_3 + 4NaC_{10}H_8 \xrightarrow[-3NaCl]{THF,\ -70\ ^{\circ}C} \xrightarrow[\substack{2.\ R_4E^+Cl^- \\ -NaCl,\ -4C_{10}H_8}]{1.\ CO\ (1\ atm)} [R_4E][CpTi(CO)_4]} \tag{18}$$

first isolable zerovalent zirconium carbonyl, $[CpZr(CO)_4]^-$,[187] and the related $[Cp^*M(CO)_4]^-$, where $Cp^* = C_5Me_5$ and M = Ti and Zr,[188] were obtained by the same route.[189]

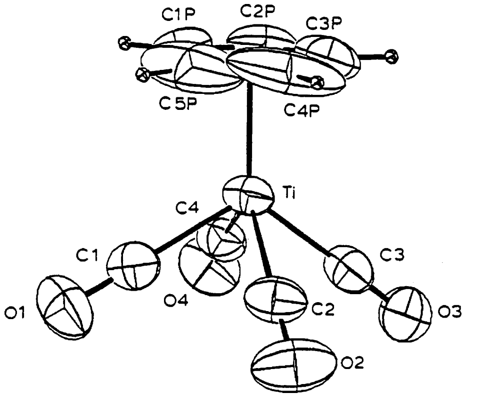


Figure 5. Structure of $[\eta^5\text{-}C_5H_5Ti(CO)_4]^-$ (from ref 187).

Carlo Floriani had previously shown that vanadocene monocarbonyl underwent reductive cleavage by Na metal under a CO atmosphere to give good yields of $CpV(CO)_4$ (eq 19).[190] We wondered whether titanocene dicarbonyl, the

$$\mathrm{Cp_2V(CO) + 2CO + Na \xrightarrow[THF,\ 20\ ^{\circ}C]{1\ atm\ of\ CO} CpV(CO)_4 + NaCp} \tag{19}$$

first known group 4 carbonyl,[191] would undergo an analogous reduction because no previous attempts to reduce this species had been reported. It proved to be inert under Floriani conditions (eq 19), but the addition of naphthalene afforded $[CpTi(CO)_4]^-$, albeit in only 20% (unoptimized) isolated yields. Also, an analogous reduction carried out in the presence of dmpe, instead of CO, provided $[CpTi(CO)_2(dmpe)]^-$, which could be protonated by acetic acid to give an unprecedented carbonyl hydride of Ti, $CpTi(CO)_2(dmpe)H$ (eq 20).[192] Titanocene dicarbonyl was thereby

$$\mathrm{Cp_2Ti(CO)_2 + 2KC_{10}H_8 + dmpe \xrightarrow[\substack{-60\ ^{\circ}C \\ -KCp}]{THF} K[CpTi(CO)_2(dmpe)] \xrightarrow[-KOAc]{HOAc} CpTi(CO)_2(dmpe)H} \tag{20}$$

established to be a useful precursor to half-sandwich carbonyl anions of zerovalent Ti. However, Scott Frerich's discovery that alkali-metal salts of $[CpTi(CO)_2(dmpe)]^-$ could not be isolated without the addition of crown ethers or cryptands really opened our eyes to the importance of effective alkali-metal complexants in the stabilization of early-transition-metal carbonyl anions.[193] Cooper and co-workers had also reported that $[Na(cryptand\ 221)]^+$ salts of the pentacarbonylmetalate dianions of Mo and W appeared to be substantially more thermally stable in the solid state than the unsolvated $Na_2[M(CO)_5]$.[194] We then considered the possible importance of crown ethers or cryptands in the synthesis of $[Ti(CO)_6]^{2-}$.

Hafnium(0) carbonyls were also of particular interest because none were known before 1987. Several attempts were made to reductively carbonylate Wreford's $HfCl_4(dmpe)_2$[195] to form the unknown $Hf(CO)_3(dmpe)_2$. These reactions provided very thermally unstable deep-red solutions at −70 °C in THF, suggestive of the presence of hafnium carbonyls, but none could be spectrally characterized or isolated. However, when we changed from dmpe to the electron-rich tripodal phosphane, i.e., 1,1,1-tris(dimethylphosphanomethyl)ethane (trmpe),[196] $Hf(CO)_4(trmpe)$ was isolated, along with the Ti and Zr analogues (eq 21).[197] Interestingly, these remain the only examples of

$$\mathrm{MCl_4{\cdot}2THF + trmpe + 4KC_{10}H_8 \xrightarrow[\substack{-60\ ^{\circ}C \\ -KCl}]{DME} \xrightarrow[\substack{-60\ to\ 0\ ^{\circ}C \\ -4C_{10}H_8}]{CO\ (1\ atm)} M(CO)_4(trmpe)} \quad \mathrm{M = Ti,\ Zr,\ and\ Hf} \tag{21}$$

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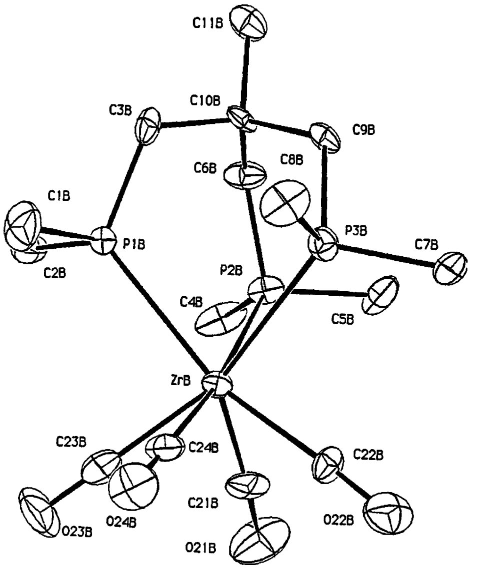

Figure 6. Structure of $Zr(CO)_4(trmpe)$, where trmpe = $CH_3C(CH_2PMe_2)_3$, with H atoms omitted for clarity.

zerovalent phosphane carbonyls known for all three group 4 metals. Structural authentication was achieved for $Zr(CO)_4(trmpe)$ (Figure 6). We were anxious to report on the Hf complex, but Geoffrey Cloke "beat us to the punch" with his description of the first hafnium(0) carbonyl, $Hf(\eta^6\text{-arene})_2CO$, where arene = 1,3,5-tri-*tert*-butylbenzene.[198] Also, soon thereafter, Frerichs completed the triad of half-sandwich carbonylmetalates with the synthesis and isolation of $[C_5R_5Hf(CO)_4]^-$, where R = H and Me.[199] Later on, Anthony DiMaio was able to obtain related 1,4,7-triazacyclononane (tacn) carbonyl complexes, $M(CO)_4(tacn)$, where M = Ti, Zr, and Hf, the first N-substituted derivatives of the unknown $M(CO)_7$, for Zr and Hf.[200] The five hafnium(0) carbonyls mentioned in this paragraph are the only ones known to date, so there remain many opportunities in this very poorly explored area.

After a good route to $Ti(CO)_3(dmpe)_2$ had been developed,[184] many unsuccessful attempts were made to reduce this substance under an atmosphere of CO to afford salts of $[Ti(CO)_6]^{2-}$. We had almost given up hope of obtaining this species when Frerichs established the "magical" ability of crown ethers or cryptands to stabilize $[CpTi(CO)_2(dmpe)]^-$, as mentioned above. I then proposed to Kai-Ming Chi that he conduct the reaction of $Ti(CO)_3(dmpe)_2$ with 2 equiv of $[Na(cryptand\ 222)][C_{10}H_8]$, produced by reacting Na metal with naphthalene in the presence of cryptand 222 in THF, followed by the addition of CO. In the absence of crown ethers or cryptands, the identical reaction invariably produced unattractive yellow to dark-brown insoluble substances devoid of metal carbonyl units. Amazingly, the next morning, he obtained a homogeneous red-brown solid, which was taken up in acetonitrile and precipitated by the addition of THF to afford bright-red-violet microcrystals! To make a long story short, this proved to be satisfactorily pure $[Na(cryptand\ 222)]_2[Ti(CO)_6]$ and was obtained in 76% yield. Soon Chi also obtained $[Ti(CO)_6]^{2-}$ and $[Zr(CO)_6]^{2-}$ directly from the respective $MCl_4(THF)_2$ by exactly the same alkali-metal naphthalene route previously employed for the group 5 hexacarbonylmetalates(1−), except very effective alkali-metal complexants, i.e., crown ethers or cryptands, had to be added prior to the carbonylation step (eq 22), where L = crown ether or cryptand and M = Ti and Zr. Interestingly,

$$MCl_4(THF)_2 + 6AC_{10}H_8 \xrightarrow[-4ACl]{\substack{\text{THF or DME}\\ -60\ ^\circ\text{C}}} \xrightarrow{nL} \xrightarrow[-60\text{ to }+20\ ^\circ\text{C}]{\text{CO (1 atm)}} [AL_n]_2[M(CO)_6] \quad (22)$$

identical reductive carbonylations carried out in the presence of triglyme, tetraglyme, or even tris[2-(2-methoxyethoxy)-ethyl]amine, which has been described as "an acyclic cryptand",[201] do not afford any $[M(CO)_6]^{2-}$. Also, quite inexplicably, corresponding cryptand or crown ether mediated reductions of $HfCl_4(THF)_2$ failed to provide any $[Hf(CO)_6]^{2-}$. Initially, we were unable to grow suitable single crystals of hexacarbonylmetalates(2−) for structural authentication. However, syntheses of 99% ^{13}CO-enriched hexacarbonylmetalates(2−) were readily carried out. Stephen Philson, director of the Departmental NMR laboratory, was able to acquire Ti-47,49 and Zr-91 NMR spectra, which showed binomial septets (Scheme 10) consistent with the presence of octahedral metal hexacarbonyl complexes. These results provided unambiguous evidence for the syntheses of the first stable binary carbonyls of Ti[202] and Zr.[203] Chi also examined analogous reductive carbonylations of the 1,1,1-tris(dimethylphosphanomethyl)ethane carbonyl complexes, $M(CO)_4(trmpe)$, where M = Ti, Zr, and Hf,[197] and found that all three gave high yields of the respective $[M(CO)_6]^{2-}$. Of particular significance was the synthesis of $[Hf(CO)_6]^{2-}$ because this species has not been obtained by any other route to date. Single-crystal X-ray studies on $[K(cryptand\ 222)]_2[M(CO)_6]$ were carried out by Doyle Britton of our Department for M = Ti, Zr, and Hf to provide proof for the existence of hexacarbonylmetalates(2−) in the solid state (Figure 7).[204] Interestingly, $[Hf(CO)_6]^{2-}$ remains the only example of a compound containing Hf in a formally negative oxidation state. Also, Paul Fischer and Robert Jilek have recently developed a convenient high-yield, "one-pot" synthesis for $[K(18\text{-crown-}6)]_2[Ti(CO)_6]$, which should help facilitate explorations of the reaction chemistry of this still poorly investigated carbonylmetalate.[205] Chemical properties of the group 4 carbonylmetalates will be described in detail elsewhere, but it should be emphasized that they have a bright future as precursors for the general exploration of the low-valent chemistry of Ti, Zr, and Hf and promise to provide strikingly new substances. For example, Eugenijus Urnezius recently showed that the interaction of white phosphorus, P_4, with $[Ti(CO)_6]^{2-}$ was the first route to a decaphosphatitanocene dianion (Figure 8),[206] the only "all-inorganic" metallocene reported to date (eq 23).[207]

$$[Ti(CO)_6]^{2-} + 2.5P_4 \xrightarrow[7\text{ days}]{\text{THF, 20 °C}} [Ti(\eta^5\text{-}P_5)_2]^{2-} + 6CO \quad (23)$$
$$\text{ca. 20\% yield}$$

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(198) Cloke, F. G. N.; Lappert, M. F.; Lawless, G. A.; Swain, A. C. *J. Chem. Soc., Chem. Commun.* **1987**, 1667.

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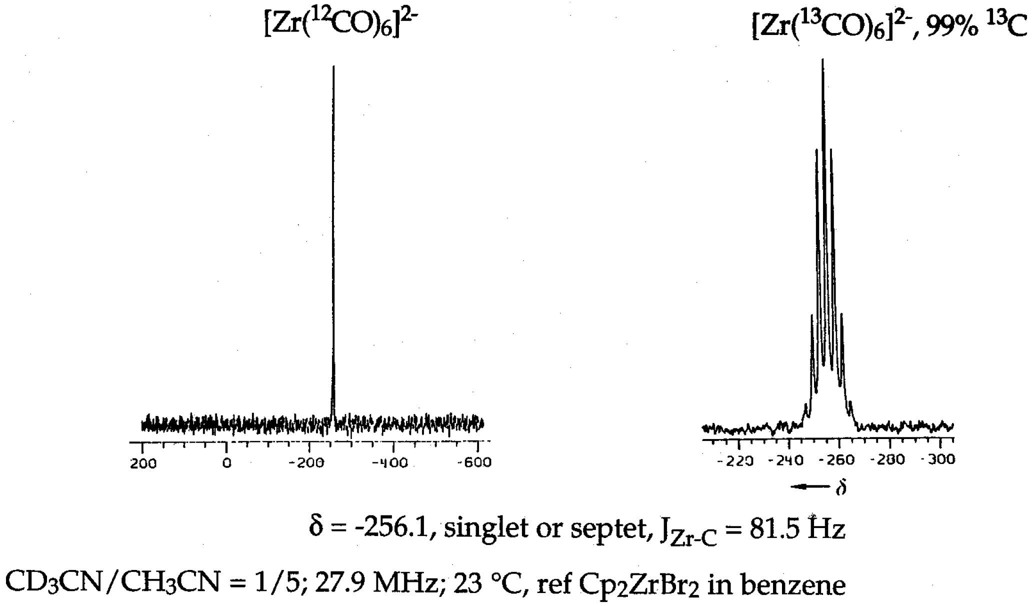
(201) Soula, G. *J. Org. Chem.* **1985**, *50*, 3717. This inexpensive ionophore, available from Aldrich, is about as effective as 18-crown-6 for the complexation of a K cation.

(202) Chi, K.-M.; Frerichs, S. R.; Philson, S. B.; Ellis, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 303.

Scheme 10. Proof for the Existence of $[Zr(CO)_6]^{2-}$ in Solution via ^{91}Zr NMR Spectra



New Classes of Transition-Metal Arene Complexes

Although the first study on the interaction of alkali-metal polyarenes with transition-metal halides was disclosed in a U.S. Patent in 1939,[208] more than 25 years elapsed before Chatt and Davidson established that arene- and polyarene-incorporated products could be accessed by this facile procedure. For example, by mixing *trans*-$RuCl_2(dmpe)_2$ with sodium naphthalene in THF, they obtained a novel naphthyl hydride complex, *cis*-$RuH(2\text{-}C_{10}H_7)(dmpe)_2$, in 68% isolated yields.[209] Jonas subsequently reported in 1974 that Ni(dcpe)-Cl, where dcpe = 1,2-bis(dicyclohexylphosphano)ethane, was reduced by lithium naphthalene in diglyme at 0 °C to afford a substance that analyzed as $Ni(dcpe)(C_{10}H_8)$.[210] The nature of the naphthalene−Ni interaction was not determined in this study, but subsequently a very closely related, formally zerovalent Ni species, $Ni(dippe)(\eta^2\text{-}C_{10}H_8)$, where dippe = 1,2-bis(diisopropylphosphano)ethane, was structurally authenticated.[211] Wreford then showed that early-transition-metal arene complexes could be isolated by the action of arene anions on respective halides with his synthesis and structural characterization of $Ta(\eta^4\text{-}C_{10}H_8)(dmpe)_2Cl$, the initial naphthalene complex of a 5d-block element (eq 24).[212]

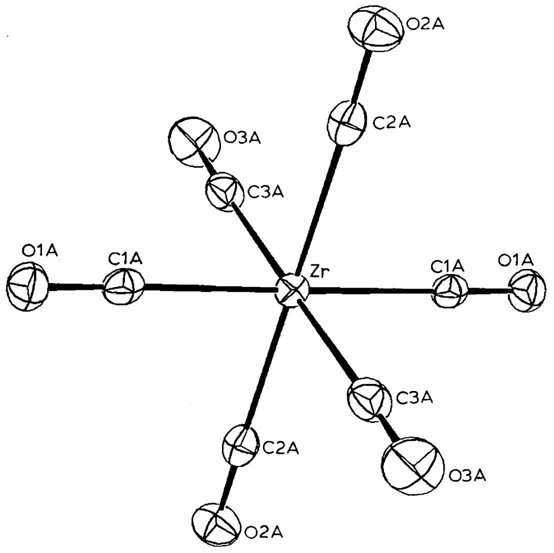


Figure 7. Structure of $[Zr(CO)_6]^{2-}$.

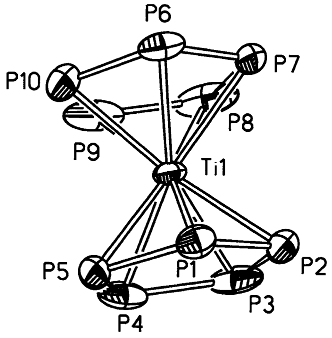


Figure 8. Structure of $[Ti(\eta^5\text{-}P_5)_2]^{2-}$.

$$TaCl_4(dmpe)_2 + 3NaC_{10}H_8 \xrightarrow[-3NaCl]{THF,\ 20\ °C} Ta(\eta^4\text{-}C_{10}H_8)(dmpe)_2Cl + 2C_{10}H_8 \quad (24)$$

Soon thereafter, Timms and co-workers discovered that a

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(203) Chi, K.-M.; Frerichs, S. R.; Philson, S. B.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1190. Despite the earlier publication date on this paper, $[Ti(CO)_6]^{2-}$ was prepared several months before $[Zr(CO)_6]^{2-}$ in our laboratory.

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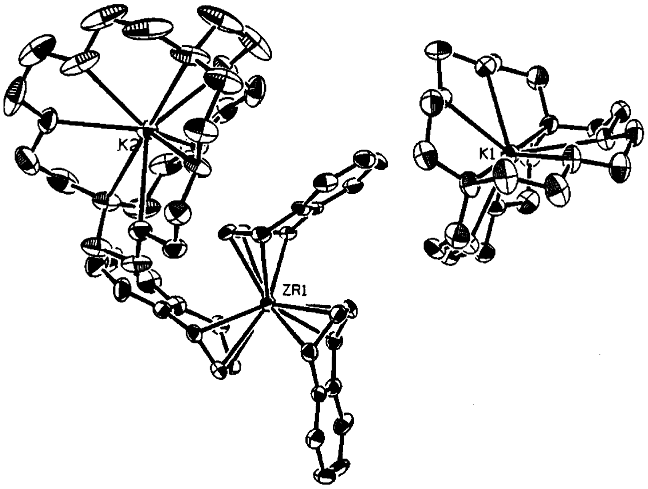

Figure 9. Structure of [K(cryptand 222)]$_2$[Zr(η^4-$C_{10}H_8$)$_3$], with H atoms omitted for clarity.

variety of bis(arene)metal(0) complexes, including bis(toluene)titanium and bis(1-methylnaphthalene)molybdenum, could be isolated from the reactions of excess K atoms in vacuo with appropriate early-transition-metal halides in THF at −110 °C in the presence of excess arene.[213] Timms noted that, “We have not attempted to determine the mechanism of reduction by potassium atoms although it seems likely that the arenes are activated by conversion into radical anions.”[213a] On this basis, it was clear that the Timms route was really an unconventional and rather difficult variant of Chatt’s original procedure. Thus, Chatt’s synthetic method held substantial promise for the creation of new classes of transition-metal arene complexes that were not available directly by the Fischer−Hafner or usual metal atom vapor methods.[214]

Because of these prior results, we felt it was important to isolate and characterize the labile, presumed naphthalenemetalate, intermediates in the aforementioned carbonylmetalate syntheses,[168,202,203] particularly because homoleptic polyarenemetalates were unknown at the time. This “new project” and its extension to other metals and polyarenes remain key aspects of our present research program. I am still amazed that no one followed up on the original Olivé report on bis(naphthalene)metal complexes[166] until nearly 30 years later. Marie Pomije, Mikhail Barybin, and co-workers then showed for the first time that this method, closely related to Chatt’s original procedure, was useful for conventional syntheses and the isolation of bis(naphthalene)metal(0) complexes of V, Cr, and Mo.[178] Interestingly, a prior statement in the literature claimed that alkali-metal naphthalene reductions of $CrCl_3$ “*failed to yield the elusive naphthalene sandwich compound*.”[215]

Our first breakthrough in polyarenemetalate chemistry involved the isolation, characterization, and structural authentication of the naphthalenezirconate intermediate, implicated in the first synthesis of $[Zr(CO)_6]^{2-}$ (eq 22).[203] Meehae Jang was very surprised to discover that the complex was tris(η^4-naphthalene)zirconate(2−) (Figure 9), both in solution and in the solid state, rather than the still unknown bis(η^6-naphthalene)zirconate(2−), isoelectronic with bis(naphthalene)molybdenum(0).[163] The zirconate(2−) was of interest as the initial example of a complex containing three aromatic hydrocarbons bound to one transition metal. For this reason, the article was dedicated[80] to E. O. Fischer, in whose laboratory the first rational synthesis of a bis(arene)metal complex, $Cr(C_6H_6)_2$, had been carried out nearly 40 years earlier![216]

We were also vigorously pursuing the intermediate in the naphthalene-mediated synthesis of $[Ta(CO)_6]^-$.[168] Only one homoleptic arene complex of Ta was known, i.e., bis(benzene)tantalum(0), prepared exclusively by the metal atom vapor route,[217] and low-valent Ta chemistry, sans carbonyl groups, was generally a very poorly explored area.[218] In the early 1990s, Pomije had isolated a microcrystalline solid, which was analyzed for [K(cryptand 222)][Ta($C_{10}H_8$)$_3$] and gave NMR spectra in good agreement with those of $[Zr(C_{10}H_8)_3]^{2-}$.[219] However, publication of these preliminary results was delayed for nearly a decade until unambiguous structural evidence and a reproducible synthesis were obtained for this substance.[220] Recently, a facile procedure for the synthesis of multigram quantities of thermally robust, but very pyrophoric [Na(THF)][Ta(η^4-$C_{10}H_8$)$_3$] in 60−65% yields (eq 25), has been developed by Victor Sussman.[221] Chemical properties of $[Ta(C_{10}H_8)_3]^-$ indicate that it is an effective synthon in many reactions for “naked” atomic Ta^-, but a tremendous amount of basic research remains to understand its myriad of reactivity patterns.[220] Attempts to isolate a homoleptic naphthaleneniobate(1−) from the reductions of $NbCl_5$ or $NbCl_4(THF)_2$ by alkali-metal naphthalenes have been unsuccessful to date, but corresponding anthracene anion reductions were originally shown by Sergey Roush, a summer undergraduate student from Russia, to afford quite robust salts of [Nb(1−4-η^4-anthracene)$_3$]$^-$ (eq 26; Figure 10).[222] Although the reaction chemistry of this species has been examined much less than that of tris(naphthalene)tantalate(1−), all anthracenes in the niobate are readily displaced by CO, PF_3, and COT, as depicted in Scheme 11.[222] Thus, tris(anthracene)niobate(1−) promises to be a useful

$$TaCl_5 + 6NaC_{10}H_8 \xrightarrow[-60\text{ to }+20\ °C \atop -5NaCl,\ -3C_{10}H_8]{DME} \xrightarrow{THF} [Na(THF)][Ta(\eta^4\text{-}C_{10}H_8)_3] \quad (25)$$

$$NbCl_4(THF)_2 + 5KC_{14}H_{10} + 18\text{-crown-6} \xrightarrow[-4KCl,\ -2C_{14}H_{10}]{THF,\ -60\text{ to }+20\ °C} [K(18\text{-crown-6})(THF)][Nb(C_{14}H_{10})_3] \quad (26)$$

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(213) (a) Hawker, P. N.; Kündig, E. P.; Timms, P. L. *J. Chem. Soc., Chem. Commun.* **1978**, 730. (b) Hawker, P. N.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1983**, 1123.

(214) See: Reference 57, pp 343−345.

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(218) Calderazzo, F.; Pampaloni, G. *J. Organomet. Chem.* **1995**, *500*, 47. Calderazzo and Pampaloni have been key pioneers in the exploration of low-valent chemistry of the group 4 and 5 elements. This review provides a particularly cogent account of their remarkable progress in this area up to the early 1990s.

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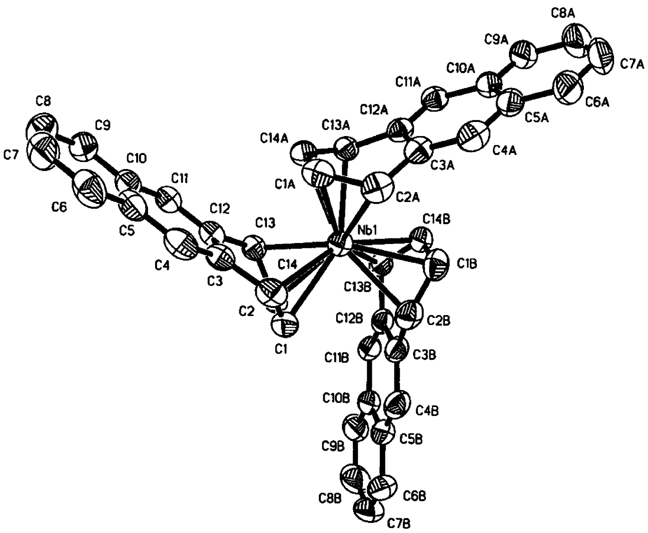
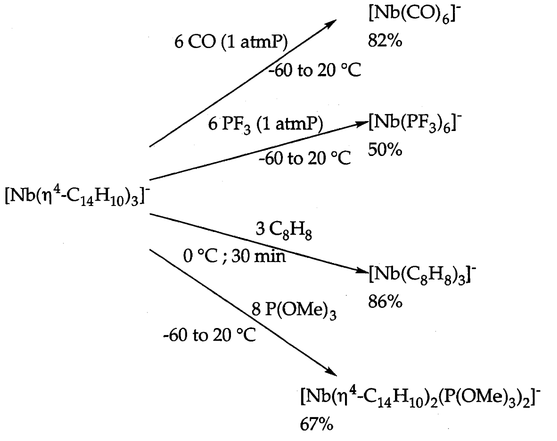


Figure 10. Structure of tris(1−4-η^4-anthracene)niobate(1−), with H atoms omitted for clarity.

Scheme 11. Substitution Reactions of Tris(1−4-η^4-anthracene)niobate(1−), a Synthon for Spin-Paired Atomic Nb Anion



precursor for the exploration of low-valent Nb chemistry. We were surprised to discover that there were no prior reports on polyaromatic hydrocarbon complexes of Nb. This circumstance also emphasizes the substantial opportunities for significant new results in this area. For example, homoleptic polyarene complexes of Hf, W, and Re are presently unknown but should be accessible by similar conventional routes. Such species promise to function as effective synthons for charged or neutral atoms of these highly refractory elements under mild conditions.

Because neutral or anionic homoleptic polyarene transition-metal complexes had only been isolated for certain group 4−6 metals, the possibility of obtaining related complexes of the later d-block elements was examined. The existence of the cationic naphthaleneruthenium species, $[Ru(\eta^6\text{-}C_{10}H_8)_2]^{2+}$, the first established bis(naphthalene)metal complex and the only one obtained via the classic Fischer−Hafner route,[223] as well as unconfirmed reports that bis(naphthalene)iron(0) could be obtained by metal atom vapor syntheses,[224] suggested that related anionic complexes of the later d-block elements might be possible. Indeed, Cooper reported that reduction of cobaltocene by 3 equiv of potassium naphthalene gave a useful synthon for "naked" atomic Co(I−) and one that was more readily available than Jonas' $[Co(C_2H_4)_4]^-$.[225] Cooper speculated that the unstable cobalt complex might be $[Co(\eta^6\text{-}C_{10}H_8)(THF)]^-$ or $[Co(\eta^4\text{-}C_{10}H_8)_2]^-$, but apparently all attempts to characterize or isolate this species failed. Because certain early-transition-metal anthracene complexes, i.e., $[Cp^*Ti(\eta^4\text{-}C_{14}H_{10})(\eta^2\text{-}C_{14}H_{10})]^-$ and $Ti(dmpe)(\eta^6\text{-}C_{14}H_{10})(\eta^4\text{-}C_{14}H_{10})$, proved to be far more stable in solution and in the solid state than presumably analogous naphthalene species, which defied isolation and characterization,[226] the possibility of preparing an anthracene-stabilized Co(I−) species was examined by William Brennessel. He found that the best synthesis involved the reaction of anhydrous $CoBr_2$ in THF with 3 equiv of potassium anthracene, followed by the addition of 18-crown-6 or cryptand 222. With these conditions, he was able to isolate 80−87% yields of deep-red to nearly black microcrystalline K salts of $[Co(1-4\text{-}\eta^4\text{-}C_{14}H_{10})_2]^-$ (eq 27).

$$\mathrm{CoBr_2 + 3KC_{14}H_{10} + L \xrightarrow[-78\ to\ +20\ ^\circ C,\ -2KBr]{THF} [KL(THF)_x][Co(C_{14}H_{10})_2]} \qquad (27)$$

Both salts were thermally robust and structurally characterized, with the assistance of Victor G. Young, Jr., director of our X-ray facility. Their unit cells showed essentially identical anions (Figure 2). Although heteroleptic Ti complexes containing two coordinated anthracenes had been previously isolated,[226] vide supra, and bis(anthracene)chromium(0), admixed with free anthracene, was known,[227] $[Co(C_{14}H_{10})_2]^-$ was the first homoleptic complex of this type to be isolated in pure form. Because a previously known monoanthracenecobalt complex, $Co(\eta^4\text{-}C_{14}H_{10})(PMe_3)_2(SnPh_3)$ was inert toward CO under ambient conditions,[228] we were pleased to discover that both anthracene groups in the cobaltate were rapidly displaced by CO at normal pressures above −30 °C in THF to afford a high isolated yield (87%) of $[Co(CO)_4]^-$. To further establish its utility in synthesis as a synthon for "spin-paired" atomic Co(I−), several ligand substitution reactions were examined, as shown in Scheme 12.[229] Most certainly other homoleptic polyarenemetalates of the later transition metals will prove to be accessible and isolable. Because no species of this type are known for later 4d- or 5d-block metals, one can anticipate many new and interesting results in this relatively uncharted, yet fundamentally important, area of transition-metal chemistry. One only hopes that funding opportunities will continue to exist for basic inorganic chemistry research of this type.

Closing Comments

One important area of our recent research, not discussed in this account, involves isocyanide complexes of the early

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(227) Elschenbroich, C.; Möckel, R.; Bilger, L. *Z. Naturforsch* **1984**, *39B*, 375. This substance was obtained by condensation of Cr atoms with excess anthracene and could not be freed from the latter without decomposition.

(228) Klein, H.-F.; Ellrich, K.; Lamac, S.; Lull, G.; Zsolnai, L.; Huttner, G. *Z. Naturforsch.* **1985**, *40B*, 1377.

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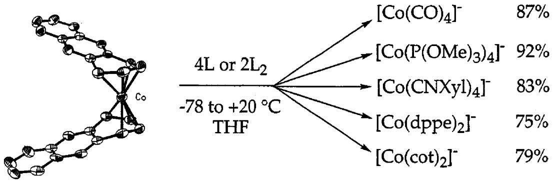
Scheme 12. Substitution Reactions of Bis(1−4-η^4-anthracene)cobaltate(1−), a Synthon for "Naked" Atomic Co(1−)



dppe = 1,2-bis(diphenylphosphano)ethane

cot = 1,3,5,7-cyclooctatetraene

transition metals. Barybin initiated this project in our laboratory several years ago with his synthesis of the first homoleptic isocyanides of Nb and Ta,[230] as well as significant excursions into related V systems.[231] A review on this and related metal isocyanide chemistry is in preparation.[232]

Acknowledgment. I sincerely thank Professor Richard Eisenberg for the opportunity to contribute this paper. Our research has been supported for more than 30 years by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society. I am very thankful to my students, postdocs, and other collaborators, whose names have been mentioned in this paper and/or in the references. Without their vital contributions, very little of the research recognized by the F. Albert Cotton Award would have been possible. I must also acknowledge individuals for their wonderful friendship and strong support for many years, including my wife, Lynda Ellis, former graduate advisor, Alan Davison, and colleagues Fred Basolo, Wolfgang Beck, Fausto Calderazzo, Marcetta Darensbourg, the late Paul Gassman, Wayne Gladfelter, Roald Hoffmann, Tobin Marks, and Dietmar Seyferth. Finally, I greatly thank Ms. Christine Lundby for her expert assistance in the preparation of the manuscript, which was not an easy task, and Victor Sussman for the cover artwork.

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