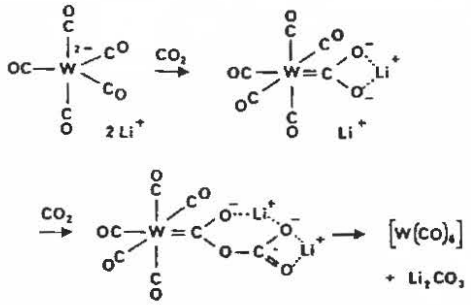
Highly Reduced Metal Carbonyls

Daniel G. Brown Literature Seminar April 21, 1992

Anionic metal carbonyls, or carbonylmetalates, have been known since Hieber synthesized $[HFe(CO)_4]^-$ in 1932 [1]. Carbonylmetalates such as Collman's reagent $Na_2[Fe(CO)_4]$ [2] and $Na_2[Cr(CO)_5]$ [3] are well known in organic synthesis. Less well known is the inorganic chemistry of this class of compounds.

Metal carbonyls with the metal in a formal oxidation state of 2- are known to form Fischer type carbene complexes with a M=C bond. In 1990 Cooper reduced a carbene complex with potassium napthalenide to form $[(OC)_4Cr{=}C(OCH_3)(Ph)]^{2-}$ [4], the first stable carbene complex with a 2- charge. Anionic metal carbonyls can also react to form complexes with an M = Si bond [5].

Carbonylmetalates can reduce CO_2 to CO [6]. Based on infrared and ^{13}C NMR studies, Cooper proposed a mechanism for the reduction of CO_2 by $Li_2[W(CO)_5]$ to Li_2CO_3 and $W(CO)_6$ [7].

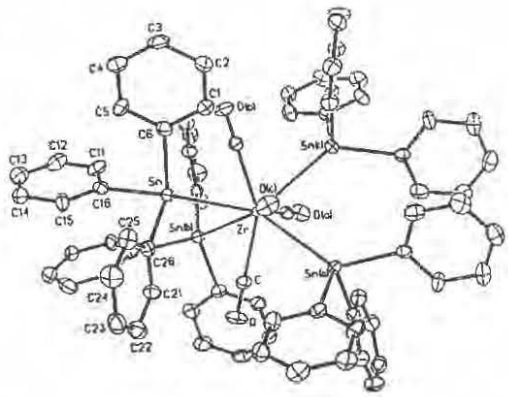


Reductions of heterallenes X=C=Y to form M=C≡X, where X=N or O, have also been reported [8].

Anionic metal carbonyls can react with other metal carbonyls. In 1991 Atwood did some infrared kinetic studies on the reactions of $Na_2Fe(CO)_4$ with various manganese carbonyls. Based on his results he proposed single electron transfer mechanisms with a $[Fe(CO)_4]^{\bullet-}$ intermediate for some of these reactions. Other reactions could be interpreted as occurring via CO^{2+} transfers [9].

While $Na_2[Fe(CO)_4]$ and $Na_2[Cr(CO)_5]$ do react similarly in many cases, they do not always react in the same manner. The presence of bulky ligands on a phosphorus halide, for example, causes $[Fe(CO)_4]^{2-}$ to coordinate differently than the larger $[Cr(CO)_5]^{2-}$ [10]. This implies that other, less well known anionic metal carbonyls could form their own distinct products.

Until recently carbonylmetalates with the metal in the 2- state were only known for group 6 and 8 elements. In 1987 Ellis synthesized $[K\text{-}15\text{-crown-}5]_2[Zr(CO)_6]$, the first known anionic carbonyl compound in group 4 [11]. Using single crystal X-ray diffraction, Ellis then determined the structure of the $[Hf(CO)_6]^{2-}$ anion [12]. While the chemistry of group 4 dianionic metal carbonyls is not as well studied as that of groups 6 and 8, some reactions have been studied [13,14], including one forming an 8-coordinate zirconium carbonyl; with only monodentate ligands.



Structure of $[((C_6H_5)_3Sn)_4Zr(CO)_4]^{2-}$

Carbonylmetalates with the metal in a 3- or 4-oxidation state are also known. These were synthesized by Ellis in the late 1970's and early 1980's [15]. Although the chemistry of these superreduced species is less well studied, reactions with these can produce different products than reactions with dianionic metal carbonyls [16]. Reactions of tri- and tetraanionic metal carbonyls as well as synthesis of other anionic carbonyls such as the unknown $Na_3[Tc(CO)_4]$ could be subjects for further studies.

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