

Preliminary communication

A NEW METHOD OF PREPARATION OF THE ANIONIC DECACARBONYLS
 $M_2(CO)_{10}^{2-}$ (M = Cr, Mo, W) AND SYNTHESSES AND PROPERTIES OF
 $Mg(THF)_2[M_2(CO)_{10}]$

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Summary

The anionic decacarbonyls $M_2(CO)_{10}^{2-}$ were synthesized via reduction reactions of $CrCl_3$, $MoCl_5$ and WCl_6 with metallic magnesium or sodium amalgam under carbon monoxide. Chemical properties and IR characteristics of the magnesium salt $Mg(THF)_2[M_2(CO)_{10}]$ are described.

The $M_2(CO)_{10}^{2-}$ (M = Cr, Mo or W) compounds were usually prepared by reduction of $M(CO)_6$ by alkali metals in liquid ammonia [1–3], tetrahydrofuran [4–6] (THF) or hexamethylphosphoramide [7]. Only compounds of the $K_2[M_2(CO)_{10}]$ type (K = Na^+ , Li^+ , K^+ , Cs^+ , NR_4^+ , PPN^+) could be synthesized. Anionic decacarbonyls $M_2(CO)_{10}^{2-}$ with a +2-charged cation were unknown.

We have tried to obtain the anionic decacarbonyls by direct reduction of $CrCl_3$, $MoCl_5$ or WCl_6 (MCl_n) in THF with metallic magnesium or sodium amalgam under carbon monoxide. E.g.; MCl_n (3 g) was dissolved in 75 cm³ THF under carbon monoxide and an excess of magnesium turnings (4 g) was added upon stirring. After 15 min the solution changed its colour to black, with fixation of CO. After 18 h the stoichiometric amount of CO was fixed and the yellow precipitate liberated [8]. Magnesium excess was removed from the solution by decantation; the precipitate was filtered off and washed with THF (5 × 10 cm³). The precipitates were then dried under vacuo (yield ≈ 60%). Elemental analysis showed that the obtained species contained $MgCl_2$ [9] (eq. 1).

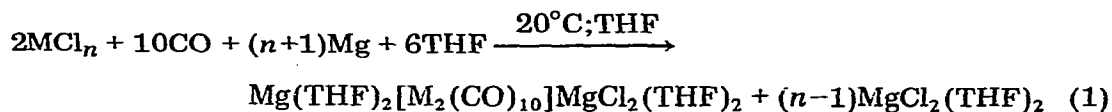
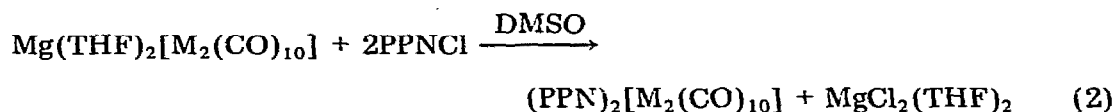


TABLE 1
INFRARED DATA FOR $M_2(CO)_{10}^{2-}$ IN THE CARBONYL STRETCHING FREQUENCY REGION

Salt	Solvent	$\nu(CO)$ (cm^{-1})
$Mg(THF)_2[Cr_2(CO)_{10}]MgCl_2(THF)_2$	DMSO	1914m, 1993vs, 1785m
	Nujol	2035vw, 1900vs, 1720s
$Mg(THF)_2[Mo_2(CO)_{10}]MgCl_2(THF)_2$	DMSO	1931s, 1887vs, 1785s
	Nujol	2040vw, 1941(sh), 1900vs
		1878(sh), 1720s, 1678(sh)
$Mg(THF)_2[W_2(CO)_{10}]MgCl_2(THF)_2$	DMSO	1931s, 1886vs, 1785s
	Nujol	2040vw, 1960(sh), 1880vs
		1724s, 1680(sh)

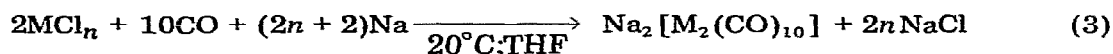
The magnesium chloride cannot be totally removed with THF. Application of methanol or ethanol results in formation of the corresponding hydride $[4,10] Mg(THF)_2[M_2H(CO)_{10}]_2$.

The shape of absorption bands in the IR spectra, as well as their frequencies (Table 1) are characteristic for $M_2(CO)_{10}^{2-}$ ions of the D_{4d} symmetry [11]. The absorption bands in Nujol are broad and more complex, which is indicative of interaction of $MgCl_2$ with CO groups. Moreover, the IR spectra exhibit symmetric and asymmetric $\nu(C-O-C)$ frequencies at 970 and 1020 cm^{-1} from the coordinated THF molecules, but it is difficult to determine how many THF molecules are fixed with Mg^{2+} and how many with $MgCl_2$. The assigned amounts are taken from earlier observations [12].



The magnesium cation in the compound obtained can be replaced by other cations, e.g. PPN^+ , by dissolving 1 g of the magnesium salt in DMSO (10 cm^3) and addition of the stoichiometric amount of $PPNCl$ in CH_2Cl_2 (10 cm^3). Then the mixture is distilled off under vacuum until dry and the precipitate extracted with methanol. $(PPN)_2[M_2(CO)_{10}]$ in 70% yield was formed.

The $M_2(CO)_{10}^{2-}$ anionic decacarbonyls can also be obtained directly with alkali metals, e.g. sodium. The reaction was carried out under similar conditions to those for the reaction 1, MCl_n (3 g) was dissolved in 100 cm^3 THF under CO



$MCl_n = MoCl_5$ or WCl_6

and excess sodium as Na/Hg was added under stirring for 10 h. The solution was filtered off on Celite filter and evaporated under vacuum to 30 cm^3 ; 15 cm^3 cyclohexane was added. The crystalline compound $Na_2[M_2(CO)_{10}]$ precipitated slowly in 20% yield.

References

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- 8 If CrCl_3 was used, 1 mg $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was added to the reaction mixture, to accelerate the reaction. Such a solution changed in colour after 2 h under formation of a yellow-green precipitate.
- 9 Elemental analysis: $\text{Mg}(\text{THF})_2[\text{Cr}_2(\text{CC})_{10}]\text{MgCl}_2(\text{THF})_2$, found: C, 39.31; H, 4.29; Cl, 9.26; Mg, 6.38; Cr, 13.38; calcd.: C, 39.81; H, 4.08; Cl, 9.06; Mg, 6.20; Cr, 13.27%. $\text{Mg}(\text{THF})_2[\text{Mo}_2(\text{CO})_{10}]\text{MgCl}_2(\text{THF})_2$, found: C, 36.07; H, 3.64; Cl, 8.07; Mg, 5.43; Mo, 21.83; calcd.: C, 35.47; H, 3.64; Cl, 8.07; Mg, 5.53; Mo, 21.83%. $\text{Mg}(\text{THF})_2[\text{W}_2(\text{CO})_{10}]\text{MgCl}_2(\text{THF})_2$, found: C, 33.05; H, 3.51; Cl, 7.65; Mg, 5.29; W, 39.38, calcd.: C, 33.34; H, 3.40; Cl, 7.50; Mg, 5.19; W, 39.29%.
- 10 ^1H NMR: $\delta(\text{M}-\text{H})$: Cr, -19.1 ppm; Mo, 12.1 ppm, W, -12.5 ppm.
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