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PENTACARBONYLCARBOXYLATE ANIONS OF THE GROUP VI TRANSITION METALS

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Summary

Pentacarbonylcarboxylate anions of Cr, Mo and W were prepared either directly from the metal hexacarbonyls or by reaction of a thallium(I) carboxylate with the pentacarbonyl halide ions. The infrared spectra indicate that the complexes deviate significantly from C_{3v} symmetry. Cotton–Kraihanzel force constants for a number of complexes were calculated and compared.

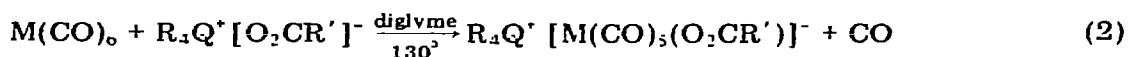
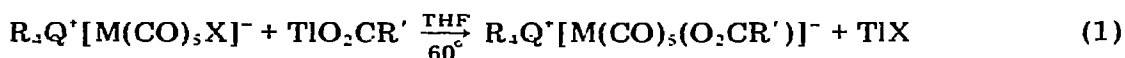
Introduction

There have been quite a variety of pentacarbonyl complexes of the Group VI metals containing monodentate, uninegatively charged ligands which have been prepared and characterized [1,2]. Many of these have proven to be active catalyst components for the olefin metathesis reaction [3,4]. Our work in this area has led us to the investigation of anionic carboxylate complexes of the Group VI metal carbonyls which we describe here. Several of these $[RCO_2M(CO)_5]^-$ complexes of Cr and W had previously been prepared by Schlientz and coworkers [5] either by the reaction of $[M_2(CO)_{10}]^{2-}$ with Hg or Ag carboxylates or directly from the metal carbonyl and tetraalkylammonium carboxylates. Only one of the analogous molybdenum complexes, which were of most interest from a catalyst standpoint was mentioned. In addition to the anionic complexes the isoelectronic neutral complexes of Mn and Re have also been prepared [6,7].

Results and discussion

The preparation of the $[M(CO)_5(O_2CR)]^-$ complexes (where M is either Cr, Mo or W) were easily prepared by either of two routes analogous to the preparation of the $[M(CO)_4(diket)]^-$ anions described previously [8]. These are illu-

strated by the following equations:



Method two, which is similar to one of the methods used by Schlientz [5], is the preferred method if the starting carboxylate is available which, unfortunately, is usually not the case. Method one gives excellent yields but is somewhat hampered by the relative insolubility of the thallium(I) carboxylate salts (and also to some extent of the products) in a suitable solvent which makes purification quite difficult if care is not taken to insure complete reaction. This method is probably the most general and experimentally the simplest of any of the procedures, since the starting materials are very easily prepared in large quantities and in high purity. In general, these complexes are somewhat more air sensitive than the diketonate complexes although they, too, are indefinitely stable under dry nitrogen. There appears to be no severe limitations on the type of carboxylate groups used. Thus, complexes have been prepared containing such diverse groups as acetate, trichloroacetate, pentafluoropropionate, trimethylacetate, stearate and benzoate. There also seems to be no severe limitation on the quaternary ammonium or phosphonium cation that is used.

Although the acetate ion and other carboxylate ions are capable of functioning as bidentate [9] ligands, this possibility was not observed even for the Mo complexes where the possibility of replacing a CO group would be more likely. As a monodentate ligand the carboxylate group is a one electron donor thus giving the $[M(CO)_5(O_2CR)]^-$ complexes the expected 18 electron configuration about the metal. If it were functioning as a bidentate ligand, it would be a three electron donor requiring the replacement of a CO ligand if the 18 electron configuration were to be maintained. Since no gas evolution was observed during the reaction of TiO_2CR and $[M(CO)_5X]^-$ anions, and elemental analyses of the products are in agreement only with a pentacarbonyl species, it is fairly certain that no tetracarbonyl complexes with bidentate carboxylate groups were formed.

NMR spectra were obtained for the acetate and trimethylacetate complexes for all three metals and in all cases the expected singlets were observed. For acetonitrile solutions of the acetate complexes, the resonances occurred at τ values of 8.43, 8.28, and 8.27 ppm (TMS = 10.0) and for the trimethylacetates at 9.02, 9.00 and 8.98 ppm for the Cr, Mo and W complexes respectively. This trend, a shift to lower fields as one goes down the Periodic Table, was also observed in the resonances of diketonate ligands for the $[M(CO)_5(diket)]^-$ anions [8].

The infrared spectra of the $[M(CO)_5(O_2CR)]^-$ anions, of which that shown in Fig. 1 is typical, in the carbonyl stretching region appear considerably more complex than expected with four or more bands being observed (see Table 1).

If one discounts any contamination due to impurities or sample decomposition, the lowering of symmetry of the complex anions may account for the appearance of the additional bands. For a $M(CO)_5X$ type molecule with C_{4v} symmetry it is predicted that there will be only three infrared active bands

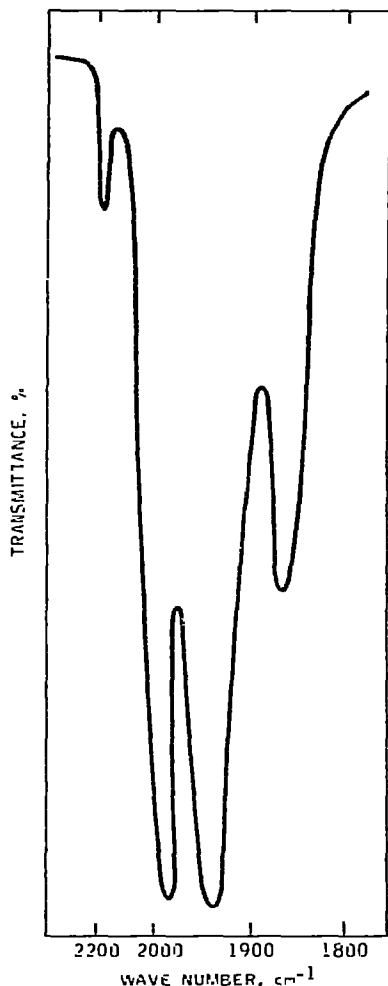


Fig. 1. Infrared spectrum of $(n\text{-C}_4\text{H}_9)_4\text{N}[\text{Mo}(\text{CO})_5(\text{O}_2\text{CC}_2\text{F}_5)]$ in the CO stretching region (CH_2Cl_2 solution).

$(2A_1 + E)$ in the CO stretching region. Because of the unsymmetrical nature of the carboxylate groups and effects due to crystal packing however, the overall symmetry of the molecule could be lowered to a point where an additional band (the B_1 mode) would appear and possibly the E band could be split giving rise to a total of five bands*. This type of behavior is, indeed, found for most of the carboxylate complexes prepared. In general, the spectra consists of a very weak band of A_1 symmetry at high frequency, followed by the B_1 band of weak to medium intensity, often occurring as a shoulder on the very intense E band which follows. This band is usually very broad and is sometimes split. The lowest frequency band of A_1 species is usually quite intense. Because of the

* It has also been pointed out by a referee that in weak donor solvents considerable cation-anion interaction can occur which can also effectively lower the symmetry of the octahedral anion.

TABLE 1

FREQUENCIES^a AND CALCULATED FORCE CONSTANTS FOR SOME [M(CO)₅(CARBOXYLATE)] ANIONS

Anion	A ₁ (1)	A ₁ (2)	B ₁	E	k ₁	k ₂	k ₃
[Cr(CO) ₅ (O ₂ CCH ₃)] ⁻	2050	1850	1989	{ 1965 1915	13.26	15.98	0.39
[Cr(CO) ₅ (O ₂ CCF ₃)] ⁻	2083	1848	1995	1930	13.18	16.07	0.52
[Cr(CO) ₅ (O ₂ CC(CH ₃) ₃)] ⁻	2020	1850	1975	1930	13.13	15.75	0.35
[Mo(CO) ₅ (O ₂ CCH ₃)] ⁻	2035	1857	1985	1930	13.00	15.91	0.43
[Mo(CO) ₅ (O ₂ CCF ₃)] ⁻	2078	1860	1991	1920	13.16	16.01	0.56
[Mo(CO) ₅ (O ₂ CC ₂ F ₅)] ⁻	2075	1860	1990	1936	13.65	15.99	0.42
[Mo(CO) ₅ (O ₂ CCCl ₃)] ⁻	2062	1853	1982	1927	13.44	15.86	0.43
[Mo(CO) ₅ (O ₂ CC ₁₈ H ₃₅)] ⁻	2079	1852	1981	1920	13.54	15.85	0.48
[W(CO) ₅ (O ₂ CCH ₃)] ⁻	2070	1831	1973	{ 1912 1890	12.87	15.72	0.56
[W(CO) ₅ (O ₂ CCF ₃)] ⁻	2078	1848	1995	1930	13.10	16.07	0.52
[W(CO) ₅ (O ₂ CC(CH ₃) ₃)] ⁻	2008	1840	1955	{ 1910 1870	12.50	15.43	0.50
[W(CO) ₅ (O ₂ CH)] ⁻	2059	1831	1970	1910	12.80	15.67	0.55

^a Obtained as Nujol mulls.

nature of the bands, the frequencies are often known only to $\pm 15 \text{ cm}^{-1}$. In the complexes reported in this work and also by Schlientz [5] the position of the bands are usually in agreement within this range. However the effect of different cations or the method of obtaining the spectra appear to account for fairly large differences and may be the main source of discrepancies. Because of these relatively large discrepancies the calculated force constants should not be regarded as being precise to more than 0.2 mdynes/Å. The force constants were calculated by the approximate method of Cotton and Kraihanzel [10]. In general the force constants are quite low (especially k_1) as compared to similar neutral complexes such as $\text{M}(\text{CO})_5\text{py}$ etc. [11], which is as expected for a negatively charged complex.

Although many exceptions can be noted, the force constants increase as the electron withdrawing properties of the substituents on the carboxylate groups increase. A decrease in electron density on the metal should consequently lead to less back bonding between the metal orbitals and CO antibonding orbitals and therefore a higher CO stretching force constant as is observed.

Another trend, which was also observed in the $[\text{M}(\text{CO})_5(\text{diket})]^-$ complexes, is that there is a rather uniform decrease in k_1 on going from Cr to the Mo to the W complexes.

The only reaction of the $[\text{M}(\text{CO})_5(\text{O}_2\text{CR})]^-$ anions which was studied was the oxidative elimination reaction with allyl chloride. For the Mo and W pentacarbonylcarboxylate anions this proceeds as follows:



Although the Cr complexes react with allyl chloride, no well-defined products could be obtained. The $[\text{M}(\text{CO})_3(\pi\text{-allyl})(\text{O}_2\text{CR})\text{Cl}]^-$ complexes will be described in more detail in a forthcoming paper.

Experimental

General

Analyses. Elemental analyses were carried out by the Analytical and Information Division, Esso Research and Engineering Company. The results for a number of $[M(\text{CO})_5(\text{O}_2\text{CR})]^-$ salts are given in Table 2.

Spectra. Infrared spectra were obtained either on a Perkin-Elmer Model 521 Infrared Spectrometer or on a Beckman Model 20 Infrared Spectrometer. Spectra were obtained either as solutions in CH_2Cl_2 or as Nujol mulls between KBr plates. NMR spectra were obtained on a Varian Model A-60 NMR spectrometer as solutions in CD_3CN .

Preparation of $[M(\text{CO})_5(\text{O}_2\text{CR})]^-$ salts

All work was carried out in a dry box under a nitrogen atmosphere and carefully dried solvents were used throughout.

The metal pentacarbonylhalide salts were prepared by the method of Abel, Butler and Reid [12]. Silver(I) acetate was obtained from commercial sources and the thallium(I) carboxylates were synthesized by treating exactly equivalent amounts of thallium(I) ethoxide and the appropriate carboxylic acid in benzene.

Tetrabutylammonium carboxylates were prepared by adding stoichiometric amounts of the carboxylic acids to a solution of tetrabutylammonium hy-

TABLE 2
ANALYTICAL DATA FOR $[M(\text{CO})_5(\text{O}_2\text{CR})]^-$ SALTS

Compound	Found (calcd.)(%)		
	C	H	N(P)
$(\text{C}_6\text{H}_5)_4\text{P}[\text{Cr}(\text{CO})_5(\text{O}_2\text{CCH}_3)]$	62.70 (63.06)	3.96 (3.92)	5.15 (5.24)
$(\text{C}_6\text{H}_5)_4\text{P}[\text{Cr}(\text{CO})_5(\text{O}_2\text{CC}_4\text{H}_9)]$	63.96 (64.56)	4.34 (4.62)	5.28 (4.89)
$(\text{C}_6\text{H}_5)_4\text{P}[\text{Cr}(\text{CO})_5(\text{O}_2\text{CCF}_3)]$	56.96 (57.77)	3.08 (3.13)	4.89 (4.81)
$(\text{C}_2\text{H}_5)_4\text{N}[\text{Mo}(\text{CO})_5(\text{O}_2\text{CC}_6\text{H}_5)]$	49.84 (49.30)	5.43 (5.17)	2.60 (2.87)
$(\text{C}_2\text{H}_5)_4\text{N}[\text{Mo}(\text{CO})_5(\text{O}_2\text{CCH}_3)]$	42.53 (42.37)	5.72 (5.45)	3.91 (3.30)
$(\text{C}_4\text{H}_9)_4\text{N}[\text{Mo}(\text{CO})_5(\text{O}_2\text{CCF}_3)]$	46.92 (46.75)	6.74 (6.12)	2.37 (2.37)
$(\text{C}_4\text{H}_9)_4\text{N}[\text{Mo}(\text{CO})_5(\text{O}_2\text{CC}_2\text{F}_5)]$	45.39 (44.97)	5.88 (5.66)	2.58 (2.18)
$(\text{C}_4\text{H}_9)_4\text{N}[\text{Mo}(\text{CO})_5(\text{O}_2\text{CCl}_3)]$	42.64 (43.10)	5.35 (5.66)	2.42 (2.19)
$(\text{C}_4\text{H}_9)_4\text{N}[\text{Mo}(\text{CO})_5(\text{O}_2\text{CC}_{18}\text{H}_{35})]$	61.24 (61.50)	9.18 (9.40)	1.71 (1.84)
$(\text{C}_6\text{H}_5)_4\text{P}[\text{W}(\text{CO})_5(\text{O}_2\text{CCH}_3)]$	51.24 (51.55)	3.60 (3.21)	4.69 (4.29)
$(\text{C}_6\text{H}_5)_4\text{P}[\text{W}(\text{CO})_5(\text{O}_2\text{CCF}_3)]$	47.76 (47.97)	2.60 (2.59)	4.25 (3.99)
$(\text{C}_6\text{H}_5)_4\text{P}[\text{W}(\text{CO})_5(\text{O}_2\text{CC}_4\text{H}_9)]$	52.54 (52.88)	3.87 (3.78)	4.31 (4.01)
$(\text{C}_6\text{H}_5)_4\text{P}[\text{W}(\text{CO})_5(\text{O}_2\text{CH})]$	50.47 (50.89)	2.96 (2.99)	4.65 (4.37)

dioxide in methanol. After evaporating the solvent on a rotary evaporator under vacuum the resulting solids were dried in a vacuum desiccator and used without further purification.

Method A. To a solution of 0.01 mol of an appropriate salt of the metal pentacarbonyl halide ion in 40 ml THF, is added an exactly equivalent amount of very finely ground thallium(I) or silver(I) carboxylate. This mixture is slowly brought to reflux with stirring and held at reflux for 15-20 minutes until it is certain that the reaction is complete. The hot solution is filtered through a fine fritted glass funnel. On cooling of the filtrate, the orange-yellow solid usually begins to partially crystallize, but more complete recovery can be accomplished by the addition of pentane. The solid compound is collected on a funnel and dried. The yield is quantitative.

Method B. This procedure is essentially the same as that of Schlientz and coworkers [5]. A mixture of 0.02 mol of a tetraalkylammonium carboxylate salt and a slight excess of the metal hexacarbonyl are heated with stirring in 50 ml diglyme at 125° until CO is no longer evolved. The hot reaction mixture is filtered and, after the filtrate has cooled, is added to 250 ml pentane. The solvent is removed by decantation and the yellow solid is washed with several additional portions of pentane, then collected on a filter and dried. Excess carbonyl not removed by washing can be sublimed off under vacuum with gentle warming. The yields of the pentacarbonyl carboxylate salts are usually greater than 95%.

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