Journal of Organometallic Chemistry, 132 (1977) 243—254

CARBONYL (η^3-ALLYL) ANIONS OF MOLYBDENUM AND TUNGSTEN

G. DOYLE

Corporate Research Laboratories, Exxon Research and Engineering Company, Linden, New Jersey 07036 (U.S.A.)

(Received November 4th, 1976)

Summary

Anionic complexes of the type $[M(CO)_2(diket)(\eta^3\text{-allyl})Cl]^-$ (where M is Mo or W and diket is a β-diketonate group) are readily prepared by the addition of allyl chloride to $[M(CO)_4(diket)]^-$ anions. NMR measurements indicate an equilibrium between two conformers due to rotation of the allyl groups. $[M(CO)_5(OC(=O)R)]^-$ anions also react with allyl chloride to form η^3-allyl complex anions. Some structural aspects of both the diketonate and carboxylate derivatives are discussed.

Introduction

The number and variety of allyl complexes of the Group VI transition metals are surprisingly large [1—10]. Many of these compounds, which are relatively stable, can be prepared quite easily from a large number of simple metal complexes. This, together with their interesting structural chemistry, has contributed to the interest in such compounds.

In our work with tetracarbonyl diketonate anions, $[M(CO)_4(diket)]^-$, and pentacarbonyl carboxylate anions, $[M(CO)_5(OC(=O)R)]^-$, of molybdenum and tungsten we have found that these species can also be easily converted to η^3-allyl derivatives. In contrast to most of the other compounds which have previously been reported, the allyl derivatives forming the subject of this communication are anionic complexes rather than neutral molecules.

Results and discussion

When any of several $[M(CO)_4(diket)]^-$ anions [11] react with allyl or substituted allyl chlorides, they are very rapidly and quantitatively converted to anions of the general type $[M(CO)_2(\eta^3\text{-allyl})(diket)Cl]^-$. The reactions take place in a matter of seconds at room temperature by merely mixing the reactants in an open flask and allowing the resulting CO to escape. The overall reaction (eq. 1) can be described as an oxidative addition-ligand elimination reac-

$$[M(CO)_4(diket)]^- + allyl\text{-}Cl \rightarrow [M(CO)_2(\eta^3\text{-}allyl)(diket)Cl]^- + 2\,CO \qquad (1)$$

tion where the metal is formally oxidized from the 0 to the +2 state.

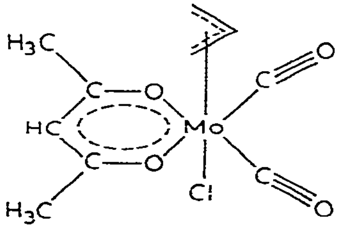
Allylic halides undergo similar oxidative additions with neutral complexes and such reactions are used effectively in the synthesis of $(MeCN)_2Mo(CO)_2(\eta^3\text{-allyl})X$ complexes from $Mo(CO)_6$ [6]. Neutral complexes containing bidentate ligands such as $W(CO)_4(bipy)$ also react similarly, but much more vigorous conditions are required (only negligible amounts of $W(CO)_2(\eta^3\text{-allyl})(bipy)Cl$ are obtained after several hours reflux in THF) [1]. While this oxidative addition—ligand elimination process is not an unexpected reaction for the $[M(CO)_4(diket)]^-$ anions, other metal carbonyl anions often react with allyl chlorides in a different manner. The $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ anion reacts by simple chloride substitution to form $(\eta^5\text{-}C_5H_5)Mo(CO)_3(\eta^1\text{-allyl})$ [5]. The complex anions $[R_2B(pz)_2Mo(CO)_4]^-$ and $[RB(Pz)_3Mo(CO)_3]^-$ (containing the bi- and tri-dentate pyrazolylborate ligands respectively) undergo loss of a CO molecule in addition to substitution, forming neutral η^3-allyl derivatives with a non-inert gas configuration [9]. The simple $[M(CO)_5X]^-$ (X = halide) anions undergo a more complex reaction, forming binuclear derivatives [2], while with $[M(CO)_4(SCH_2CH_2Ph_2)]^-$ anions, allyl chloride reacts with the coordinated ligand [12]. Although the formation of the $[M(CO)_2(\eta^3\text{-allyl})(diket)Cl]^-$ anions proceeds quite readily, in many cases it does appear to be very sensitive to the composition of the reactants. Relatively minor changes in one of the components can have an enormous effect on the manner in which the reaction proceeds while other seemingly major changes have no noticeable effect. For instance, there appears to be no restriction on the diketonate ligand bound to the metal, and the normal allyl derivatives were obtained from acetylacetonate, hexafluoroacetylacetonate, dibenzoylmethanide and several other diketonate and related ligands with equal facility. Of the three Group VI metals however, only the Mo and W complexes react to form the allyl complexes. The corresponding $[Cr(CO)_4(diket)]^-$ aions do react with allyl chloride, forming green solids which have not been identified. These green products are insoluble in the usual organic solvents and do not appear to contain CO.

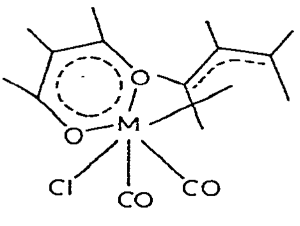
A large number of different quaternary ammonium, phosphonium or arsonium salts of the $[M(CO)_4(diket)]^-$ anions have been used without a noticeable difference in the course of the reaction. When the $[Na(diglyme)_2]^+$ salt was treated with allyl chloride, an entirely different reaction took place, leading to the quantitative formation of $Na(diglyme)_2[Mo_2(\eta^3\text{-allyl})_2(CO)_4Cl_3]$. This type of influence by a cation appears to be most unusual and is not understood.

In addition to allyl chloride, methylallyl chloride and crotyl chloride will also react to form the analogous η^3-methallyl and η^3-crotyl derivatives. Of the allylic halides only the chlorides will react with the $[M(CO)_4(diket)]^-$ anions to form the $[M(CO)_2(\eta^3\text{-allyl})(diket)X]^-$ complexes. Allyl bromide, for instance, reacts with $[W(CO)_4(acac)]^-$ to give what appears to be a mixture of unidentified products. Allyl iodide reacts with the same anion to give a blue-black crystalline compound whose NMR and infrared spectra indicate that it contains neither an allyl or acetylacetonate group. However, three CO stretching bands at 2053, 1980 and 1938 cm^{-1} are observed. Its elemental analysis gives an empirical composition of $(C_6H_5)_4PW(CO)_3I_3$, although its structure is not known.

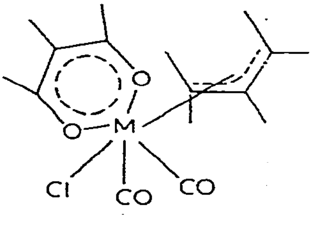
When one allows allyl chloride to react with anions of the type $[M(CO)_3(acac)L]^-$, where L is a typical Lewis base such as pyridine, triphenylphosphine, etc., two different products are possible if the reaction proceeds in the usual manner. As might be expected, only the $[M(CO)_2(acac)(\eta^3\text{-allyl})Cl]^-$ anions have been observed in all the cases examined thus far.

Since the structures of some closely related neutral complexes have been determined by X-ray crystallography [13,14], we wished to ascertain by infrared and NMR spectroscopy if the ligand arrangement in our anionic species was similar. The structure of $Mo(CO)_2(\eta^3\text{-allyl})(dipy)NCS$ [14], which is typical of those determined, is that of a distorted octahedron with the two CO groups and the two donor atoms of the chelating ligand roughly defining a plane with the metal being located slightly out of that plane. The allyl group and the thiocyanate occupy the other two remaining sites. If $[Mo(CO)_2(\eta^3\text{-allyl})(acac)Cl]^-$ had a similar structure (see below) it should be easily distinguished since a plane of symmetry bisects the acetylacetonate ligand, and the two methyl groups should be equivalent by NMR. All other reasonable structures would be of lower symmetry and two separate resonances should be seen for the non-equivalent methyl groups. Unlike the neutral complexes, however, the anions have NMR spectra which are temperature-dependent, making a simple analysis impossible, at least for the simple allyl derivatives. The temperature dependency is most likely due to the dynamic nature of the allyl group causing the interconversion of conformational isomers I and II. This type of behavior has been noted for $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_3H_5)$ [15] and several halo(η^3-allyl)carbonyl complexes of tungsten [7]. (Often more complex rearrangements leading to similar NMR spectra are possible and have been observed for several $R_2B(Pz)_2Mo(CO)_3(\eta^3\text{-allyl})$ and $RB(Pz)_3Mo(CO)_2(\eta^3\text{-allyl})$ complexes [9]). In order to simplify the spectra and to facilitate interpretation, certain anions containing substituted ligands such as methallyl (η^3-C_4H_7) and 3-methyl-2,4-pentanedionate (3-Meacac) or 1,1,1-trifluoro-2,4-pentanedionate (tfacac) in place of the unsubstituted li-





(I)



(II)

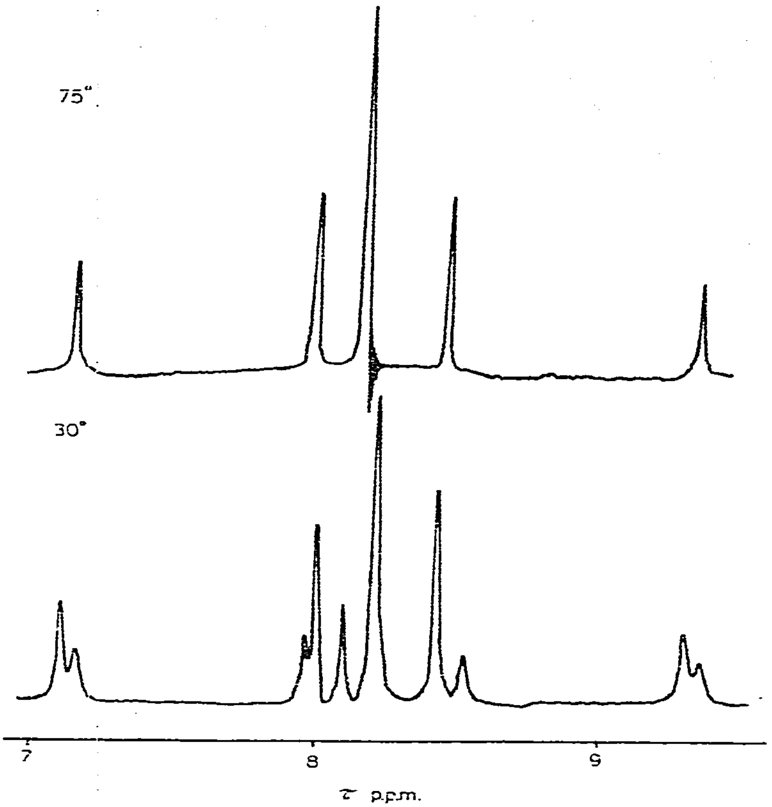


Fig. 1. High and low temperature limiting NMR spectra of the [Mo(CO)$_2$(η^3-C$_4$H$_7$)(3-Meacac)Cl]$^-$ ion.

gands were examined. The high and low temperature limiting spectra of the [Mo(CO)$_2$(η^3-C$_4$H$_7$)(3-Meacac)Cl]$^-$ anion are shown in Fig. 1 and are typical of that expected for conformation equilibrium. At 75° C the methallyl group is freely rotating, rapidly interconverting the two different conformers and an average spectrum is observed. As the temperature is lowered the signals broaden until finally in the low temperature limit two superimposable sets of signals are observed, each set corresponding to one of the conformers. It can be noted that only one resonance signal for the methyl groups on the 3-methyl-2,4-pentanedionate ligand are observed, supporting the symmetriacl structure postulated. The analogous tungsten anion has a very similar spectrum. However, the conformers appear to be nearly equal in concentration at 30° C whereas in the molybdenum species one conformer seems to be in about five times the concentration of the other.

Although the simple allyl complexes exhibit the same type of behavior, their spectra are inherently more complex. Figure 2 illustrates the spectra of the [W(CO)$_2$(η^3-allyl)(tfacac)Cl]$^-$ ion at various temperatures where the temperature dependence can most clearly be seen. At the high temperature limit the allyl spectrum is quite typical, consisting of a complex multiplet for the central proton and doublets for the *syn* and *anti* protons. The coupling constants for the *syn* and *anti* protons are approximately 6 and 9 Hz, respectively. As the

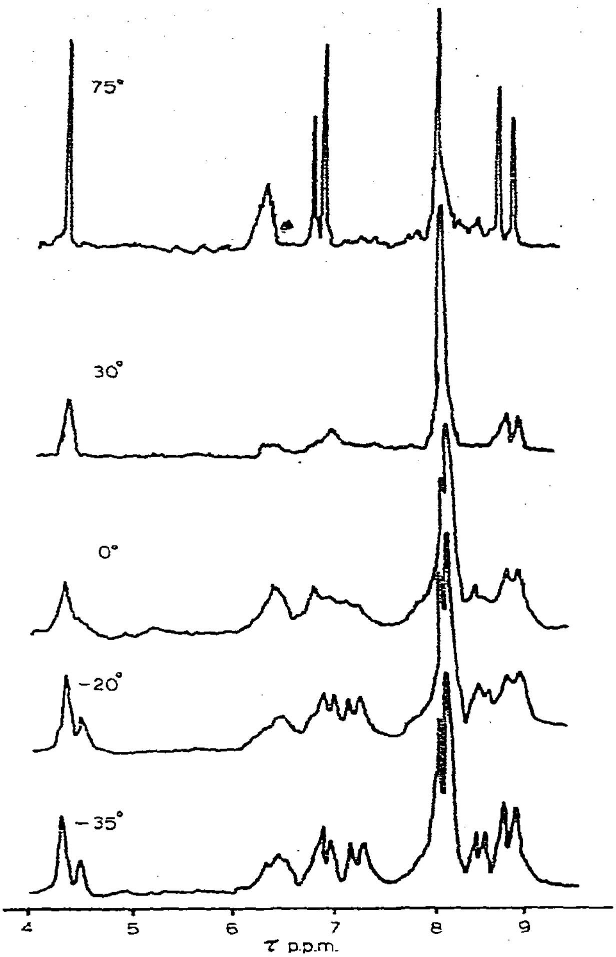


Fig. 2. NMR spectrum of the $[W(CO)_2(\eta^3\text{-allyl})(tfacac)Cl]^-$ ion at various temperatures.

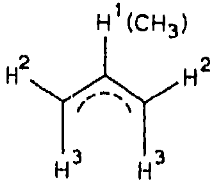
temperature is lowered, separate sets of signals can be distinguished for each of the conformers. With minor variation, this behavior is seen for all the allyl anions investigated and it is suggested that all have the same structure containing a relatively mobile allyl group. (NMR data for a number of these complexes are given in Table 1).

The infrared spectra of all the $[M(CO)_2(\eta^3\text{-allyl})(diket)Cl]^-$ anions (see Table 1) show only two very strong CO stretching bands which are of nearly equal intensity. No evidence is seen for separate bands for different conformers, as has been observed in some cases [15]. This is not too unusual since one would expect only slight differences in frequencies which might not be discerned with such broad intense bands. As expected, the bands are at considerable lower frequency than the related neutral species [1]. By placing electronegative groups such as $[CF_3]^-$ on the diketonate ligands, which would tend to draw electron density from the metal, the CO stretching frequencies tend to increase, partially offsetting the effect of the negative change.

(continued on p. 250)

TABLE 1

NMR (τ, ppm) AND IR DATA (cm^{-1}) FOR SOME $[M(CO)_2(diket)(\eta^3\text{-allyl})Cl]^-$ ANIONS



Anion	τ (H^1(CH$_3$))	τ (H^2$_{syn}$)	τ (H^3$_{anti}$)	τ (Diketonate ligand)	ν(CO) (cm^{-1})
$[W(CO)_2(\eta^3\text{-}C_3H_5)(acac)Cl]^-$	~6.9		8.82	8.21 CH$_3$, 4.74 CH	1887, 1770
$[W(CO)_2(\eta^3\text{-}C_3H_5)(tfacac)Cl]^-$	~7.1	6.55	8.95	8.26 CH$_3$, 4.56 CH	1894, 1776
$[W(CO)_2(\eta^3\text{-}C_3H_5)(hfacac)Cl]^-$	~7.1	6.88	8.60	4.72 CH	1912, 1805
$[Mo(CO)_2(\eta^3\text{-}C_3H_5(acac)Cl]^-$	~7.2		9.05	8.20 CJ$_3$, 4.82 CH	1894, 1783
$[Mo(CO)_2(\eta^3\text{-}C_3H_5)(3\text{-Meacac})Cl]^-$	~6.5	6.78	~9.1	8.09 CH$_3$C(=O), 8.29 CCH$_3$	1892, 1780
$[W(CO)_2(\eta^3\text{-}C_4H_7)(acac)Cl]^-$	7.76	7.18	8.87	8.18 CH$_3$, 4.74 CH	1894, 1786
$[W(CO)_2(\eta^3\text{-}C_4H_7)(hfacac)Cl]^-$	7.73	7.03	8.61	4.56 CH	1912, 1821
$[W(CO)_2(\eta^3\text{-}C_4H_7)(3\text{-Meacac})Cl]^-$	7.87	7.30	8.96	8.11 CH$_3$C(=O), 8.33 CCH$_3$	1895, 1785
$[Mo(CO)_2(\eta^3\text{-}C_4H_7)(acac)Cl]^-$	7.98	7.00	9.15	8.23 CH$_3$, 4.88 CH	1894, 1795
$[Mo(CO)_2(\eta^3\text{-}C_4H_7)(hfacac)Cl]^-$	8.03	6.88	8.96	4.23 CH	1919, 1828
$[Mo(CO)_2(\eta^3\text{-}C_4H_7)(3\text{-Meacac})Cl]^-$	7.84	6.96	9.14	8.07 CH$_3$C(=O), 8.25 CCH$_3$	1895, 1792
$[Mo(CO)_2(\eta^3\text{-}C_4H_7)(dbzm)Cl]^-$	7.78	6.77	9.01	~2.0 C$_6$H$_5$, 2.47 CH	1892, 1790

TABLE 2

ANALYTICAL DATA AND INFRARED DATA FOR SOME $[M(CO)_3(O_2CR)(allyl)Cl]^-$ SALTS

Compound	Anal. (Found (calcd.)(%))				$\nu(CO)$ (cm^{-1})	Decomp. point (°C)
	C	H	P	Cl		
$(C_6H_5)_4P[Mo(CO)_3(O_2CCH_3)(\eta^3\text{-}C_3H_5)Cl]$	58.20	4.66	4.86	6.08	1292, 1826	83
	(58.29)	(4.31)	(4.73)	(5.41)		
$(C_6H_5)_4P[Mo(CO)_3(O_2CC_4H_9)(\eta^3\text{-}C_3H_5)Cl]$	60.14	4.97	4.19	5.78	1936, 1830	129
	(60.33)	(4.92)	(4.44)	(5.08)		
$(C_5H_5)_4P[Mo(CO)_3(O_2CCH_3)(\eta^3\text{-}C_4H_7)Cl]$	59.13	4.60	4.65	5.29	1929, 1821	126
	(59.25)	(4.52)	(4.63)	(5.30)		
$(C_6H_5)_4P[Mo(CO)_3(O_2CC_4H_9)(\eta^3\text{-}C_4H_7)Cl]$	60.97	5.07	4.59	5.47	1920, 1813	77
	(60.82)	(5.10)	(4.36)	(4.99)		
$(C_6H_5)_4P[W(CO)_3(O_2CCH_3)(\eta^3\text{-}C_3H_5)Cl]$	51.27	3.96	4.05	4.49	1907, 1808	101
	(51.76)	(3.80)	(4.17)	(4.77)		
$(C_6H_5)_4P[W(CO)_3(O_2CH)(\eta^3\text{-}C_3H_5)Cl]$	50.59	3.25	4.59	4.86	1895, 1815	120
	(51.08)	(3.59)	(4.25)	(4.86)		
$(C_6H_5)_4P[W(CO)_3(O_2CCF_3)(\eta^3\text{-}C_3H_5)Cl]$	48.63	3.06	3.88	3.89	1910, 1831	139
	(48.22)	(3.16)	(3.88)	(4.45)		
$(C_6H_5)_4P[W(CO)_3(O_2CC_4H_9)(\eta^3\text{-}C_3H_5)Cl]$	54.22	4.32	3.98	4.00	1902, 1808	105
	(53.99)	(4.36)	(3.95)	(4.52)		
$(C_6H_5)_4P[W(CO)_3(O_2CCH_3)(\eta^3\text{-}C_4H_7)Cl]$	52.00	3.35	4.36	4.92	1910, 1821	143
	(52.35)	(3.99)	(4.09)	(4.68)		
$(C_6H_5)_4P[W(CO)_3(O_2CC_4H_9)(\eta^3\text{-}C_4H_7)Cl]$	53.95	3.85	3.77	4.41	1910, 1820	97
	(54.12)	(4.54)	(3.88)	(4.44)		
$(C_6H_5)_4P[W(CO)_3(O_2CCH_3)(\eta^3\text{-Crotyl})Cl]$	52.05	3.45	4.36	5.30	1926, 1833	131
	(52.35)	(3.99)	(4.09)	(4.68)		
$(C_6H_5)_4P[W(CO)_3(O_2CCH_3)(\eta^3\text{-}C_6H_5C_3H_4)Cl]$	55.75	3.76	3.78	4.54	1913, 1830	144
	(55.77)	(3.94)	(3.78)	(4.33)		

In a manner completely analogous to the reaction of $[M(CO)_4(diket)]^-$ anions with allyl chlorides, the metal pentacarbonyl carboxylate anions, $[M(CO)_5(OC(=O)R)]^-$ [16], react to form complex anions of the type $[M(CO)_3(\eta^3\text{-allyl})(OC(=O)R)Cl]^-$. These reactions are very facile. However, they seem to suffer from the same restrictions as those of the diketonate complexes.

Infrared and NMR spectral data are of little help in determining the structure of the $[M(CO)_3(\eta^3\text{-allyl})(OC(=O)R)Cl]^-$ anions. The infrared spectra of these anions show two very intense bands, one somewhat more intense than the other, in the CO stretching region (Table 2). This type of pattern is more consistent with a *facial* arrangement of the three CO groups, as shown below, rather than one of the three possible *meridional* arrangements. The NMR spectra of all

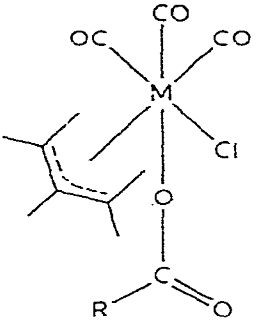
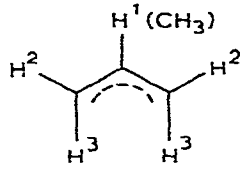


TABLE 3

NMR SPECTRA (τ, ppm) FOR SOME $[M(CO)_3(O_2CR)(allyl)Cl]^-$ ANIONS

Anion				
	τ ($H^1(CH_3)$)	τ (H^2_{syn})	τ (H^3_{anti})	Carboxylate protons
$[Mo(CO)_3(O_2CCH_3)(\eta^3\text{-}C_3H_5)Cl]^-$	~6.8	~6.8	9.16	8.46
$[Mo(CO)_3(O_2CC_4H_9)(\eta^3\text{-}C_3H_5)Cl]^{-\,a}$	~6.8	~6.8	~9.1	9.08
$[Mo(CO)_3(O_2CCH_3)(\eta^3\text{-}C_4H_7)Cl]^-$	8.05	7.11	9.35	8.44
$[Mo(CO)_3(O_2CC_4H_9)(\eta^3\text{-}C_4H_7)Cl]^{-\,a}$	8.04	7.12	9.33	9.05
$[W(CO)_3(O_2CCH_3)(\eta^3\text{-}C_3H_5)Cl]^-$	~7.4	6.92	8.90	8.40
$[W(CO)_3(O_2CC_4H_9)(\eta^3\text{-}C_3H_5)Cl]^{-\,a}$	6.33	6.92	8.89	9.02
$[W(CO)_3(O_2CCF_3)(\eta^3\text{-}C_3H_5)Cl]^-$	~6.33	6.98	8.85	
$[W(CO)_3(O_2CCF_3)(\eta^3\text{-}C_3H_5)Cl]^-$	~6.3	6.98	~8.8	
$[W(CO)_3(O_2CCH_3)(\eta^3\text{-}C_4H_7)Cl]^-$	7.89	7.23	9.03	8.42
$[W(CO)_3(O_2CC_4H_9)(\eta^3\text{-}C_4H_7)Cl]^-$	7.87	7.23	~9.0	9.01

[a] $O_2CC_4H_9$ represents the $[(CH_3)_3CCO_2]^-$ group.

the anions of this type prepared (both allyl and methallyl) showed no temperature dependency over the temperature range of +75 to −45°C. The spectra of the tungsten allyl derivatives show a complex multiplet of the central protons and doublets with the normal coupling constants for the *syn* and *anti* protons (see Table 3 for chemical shift data). The chemical shifts and coupling constants are such that very complicated patterns result with the molybdenum analogs. The methallyl complex anions of both metals give the expected spectra consisting of three sharp singlets for the *syn*, methyl, and *anti* protons. Presumably in the carboxylate derivatives there is sufficiently less steric interaction than in the diketonate complexes, allowing relatively free rotation of the allyl or methallyl group even at low temperatures. In no case was there any evidence for the existence of separate conformers.

Experimental

General

Reagents. The preparation of the $[M(CO)_4(diket)]^-$ [11] and $[M(CO)_5(OC(=O)R)]^-$ [16] salts has previously been described. All other reagents were obtained from commercial sources.

Analyses. Elemental analyses were carried out by the Analytical and Information Division, Exxon Research and Engineering Co. and by Clark Micro Analytical Laboratory, Urbana, Illinois. The results for a number of $[M(CO)_2(diket)(\eta^3\text{-allyl})Cl]^-$ and related salts are given in Table 4 while the results for some $[M(CO)_3(\eta^3\text{-allyl})(OC(=O)R)Cl]^-$ salts are given in Table 2.

Spectra. Infrared spectra were obtained on a Beckman Model 20 Infrared Spectrometer as Nujol mulls or methylene chloride solutions. NMR spectra were obtained as solutions in acetonitrile on a Varian A-60 spectrometer.

Preparation of the complexes

All preparations were carried out in a nitrogen filled glove box. The complexes in general are moderately stable in air, but slowly decompose after several days exposure.

Preparation of the $[M(CO)_2(\eta^3\text{-allyl})(diket)Cl]^-$ salts. To a flask containing 0.005 mol of the $[M(CO)_4(diket)]^-$ salt dissolved in a minimum amount of THF, is added 5 ml of allyl chloride (or 5 ml of 3-chloro-2-methylpropene or 1-chloro-2-butene for the corresponding η^3-methallyl or η^3-crotyl derivatives). After the very vigorous CO evolution ceases, the solution is warmed and filtered to remove any solid impurities. The filtrate is then added to 100 ml pentane, precipitating the solid $[M(CO)_2(\eta^3\text{-allyl})(diket)Cl]^-$ salt which is collected on a filter and dried. Yields are quantitative.

These same salts can be prepared starting from $[M(CO)_3L(diket)]^-$ salts (L = Lewis base ligand) in exactly the same manner.

Reaction of $(C_6H_5)_4P[W(CO)_4(acac)]$ with allyl iodide. A solution containing 1 g $(C_6H_5)_4P[W(CO)_4(acac)]$ dissolved in 25 ml CH_2Cl_2 was prepared. Ten ml allyl iodide were added. A slow evolution of gas took place and in a short time a dark colored solid formed. This was collected on a filter, washed with pentane and dried. Yield was 1.2 g of a compound which analyzed for $(C_6H_5)_4PW(CO)_3I_3$. Found: C, 33.10; H, 2.33; P, 3.07; I, 39.27. $C_{27}H_{20}I_3O_3PW$ calcd.: C, 32.82; H, 2.04; P, 3.13; I, 38.53%.

(continued on p. 254)

TABLE 4

ANALYTICAL DATA FOR SOME $[M(CO)_2(allyl)(diket)Cl]^-$ SALTS

Compound [a]	Anal. (Found (calcd.)(%))				Decomp. point (°C)
	C	H	N(P)	Cl	
$(C_2H_5)_4N[W(CO)_2(\eta^3\text{-}C_3H_5)(acac)Cl]^-$	38.55	5.96	2.57	6.50	153
	(38.76)	(5.78)	(2.51)	(6.35)	
$(C_6H_5)_4P[W(CO)_2(\eta^3\text{-}C_3H_5)(tfacac)Cl]^-$	50.22	3.70	3.90	4.33	108
	(50.48)	(3.62)	(3.83)	(4.38)	
$(C_6H_5)_4As[W(CO)_2(\eta^3\text{-}C_3H_5)(hfacac)Cl]^-$	45.07	3.72		4.24	86
	(45.03)	(2.89)		(3.81)	
$(C_6H_5)_4P[W(CO)_2(\eta^3\text{-}C_3H_5)(MeAcet)Cl]^-$	51.95	3.84	4.11		129
	(51.65)	(2.84)	(3.96)		
$(C_2H_5)_4N[W(CO)_2(\eta^3\text{-}C_3H_5)(trop)Cl]^-$	41.97	5.20	2.19	6.62	114
	(42.30)	(5.29)	(2.47)	(6.25)	
$(C_6H_5)_4P[W(CO)_2(\eta^3\text{-}C_3H_5)(dbzm)Cl]^-$	59.77	4.41	3.49	4.12	105
	(60.10)	(4.24)	(3.52)	(4.07)	
$(C_6H_5)_4P[W(CO)_2(\eta^3\text{-}C_3H_5)(3Meacac)Cl]^-$	54.50	4.50	3.77	4.37	159
	(54.68)	(4.46)	(4.03)	(4.61)	
$(C_6H_5)_4As[W(CO)_2(\eta^3\text{-}C_4H_7)(acac)cl]^-$	51.65	4.76		4.60	95
	(51.70)	(4.22)		(4.36)	
$(C_6H_5)_4As[W(CO)_2(\eta^2\text{-}C_4H_7)(hfacac)cl]^-$	45.58	3.14		4.21	121
	(45.65)	(3.06)		(3.85)	
$(C_6H_5)_4P[W(CO)_2(\eta^3\text{-}C_4H_7)(3\text{-}Meacac)Cl]^-$	54.12	4.80	3.92	4.51	157
	(54.52)	(4.58)	(3.90)	(4.47)	

$(C_6H_5)_4As[W(CO)_2(\eta^3\text{-Crotyl})(\text{hfacac})Cl]^-$	45.98	3.04		4.04	94
	(45.65)	(3.06)		(3.85)	
$(C_2H_5)_4N[Mo(CO)_2(\eta^3\text{-}C_3H_5)(\text{acac})Cl]^-$	44.57	7.29	3.81	8.20	139
	(44.29)	(7.43)	(3.22)	(8.17)	
$(C_6H_5)_4As[Mo(CO)_2(\eta^3\text{-}C_3H_5)(\text{hfacac})Cl]^-$	50.30	3.44		4.30	103
	(49.86)	(3.94)		(4.38)	
$C(_6H_5)_4P[Mo(CO)_2(\eta^3\text{-}C_3H_5)(3\text{-Meacac})Cl]^-$	61.12	5.23	4.34	5.26	170
	(61.76)	(5.03)	(4.55)	(5.20)	
$(C_4H_9)_4N[Mo(CO)_2(\eta^3\text{-}C_4H_7)(\text{acac})Cl]^-$	55.47	8.75	2.39		79
	(55.69)	(8.62)	(2.39)		
$(C_6H_5)_4As[Mo(CO)_2(\eta^3\text{-}C_4H_7)(\text{hfacac})Cl]^-$	50.95	3.82		3.95	126
	(50.47)	(3.38)		(4.20)	
$(C_6H_5)_4P[Mo(CO)_2(\eta^3\text{-}C_4H_7)(3\text{-Meacac})Cl]^-$	62.35	5.36	4.46	5.99	133
	(62.22)	(5.22)	(4.46)	(5.10)	
$(C_2H_5)_4N[Mo(CO)_2(\eta^3\text{-Crotyl})(\text{acac})Cl]^-$	47.97	7.70	3.17		110
	(48.36)	(7.27)	(2.96)		
$(C_6H_5)_4As[Mo(CO)_2(\eta^3\text{-Crotyl})(\text{hfacac})Cl]^-$	50.17	3.69		4.51	114
	(50.47)	(3.38)		(4.26)	

---

[a] η^3-C_3H_5 and η^3-C_4H_7 designates the η^3-allyl and η^3-methallyl groups respectively.

Reaction of Na(diglyme)$_2$[Mo(CO)$_4$(acac)] with allyl chloride. Allyl chloride (3 ml) was added to 1 g of liquid Na(diglyme)$_2$[Mo(CO)$_4$(acac)] in a small flask. After the vigorous CO evolution ceased another 10 ml allyl chloride was added and the resulting solution was filtered. The filtrate was evaporated to dryness on a rotary evaporator and the residue was washed with several portions of pentane. The remaining brown solid residue was collected in a filter and dried. Analysis, IR and NMR spectra indicate the product to be Na(diglyme)$_2$-[Mo$_2$(CO)$_4$(allyl)$_2$Cl$_3$]. Found: C, 33.18; H, 4.86; Cl, 13.64. $C_{22}H_{38}Cl_3NaMo_2O_{10}$ calcd.: C, 33.72; H, 4.89; Cl, 13.67%.

Preparation of [M(CO)$_3$(η^3-allyl)(O$_2$CR)Cl]$^-$ salts. Ten ml allyl chloride (3-chloro-2-methylpropene or 1-chloro-2-butene for the η^3-methallyl or η^3-crotyl derivatives) were added to 0.003 mol of the solid [M(CO)$_5$(O$_2$CR)]$^-$ salt in a small flask. After the vigorous gas evolution has ceased the mixture was warmed, then filtered to remove any solid impurities. The filtrate was added to 100 ml pentane precipitating the solid yellow-orange salts which were collected on a filter and dried. Yields are quantitative.

Acknowledgement

I wish to express my sincere thanks to Mr. J.W. Swirczewski for his very able experimental assistance throughout the course of this work.

References

1 C.G. Hull and M.H.B. Stiddard, J. Organometal. Chem., 9 (1967) 519.
2 H.D. Murdoch, J. Organometal. Chem., 4 (1965) 119;
H.D. Murdoch and R. Henzi, J. Organometal. Chem., 5 (1966) 552.
3 A.T.T. Hsieh and B.O. West, J. Organometal. Chem., 112 (1976) 285.
4 M. Cousins and M.L.H. Green, J. Chem. Soc., (1963) 889.
5 M.L.H. Green and A.N. Stear, J. Organometal. Chem., 1 (1964) 230.
6 H.T. Dieck and H. Frieder, J. Organometal. Chem., 14 (1968) 375.
7 C.E. Holloway, J.D. Kelley and M.H.B. Stiddard, J. Chem. Soc. A, (1969) 931.
8 K.C. Ramey, D.C. Lini and W.B. Wise, J. Amer. Chem. Soc., 91 (1968) 4275.
9 S. Trofimenko, J. Amer. Chem. Soc., 91 (1969) 588; 91 (1969) 3183; Inorg. Chem., 9 (1970) 2493.
10 M.L.H. Green, J. Knight, L.C. Mitchard, G.G. Roberts and W.E. Silverthorn, Chem. Commun., (1971) 1619.
11 G. Doyle, J. Organometal. Chem., 61 (1973) 235.
12 G. Doyle, J. Organometal. Chem., 101 (1975) 85.
13 A.J. Graham and R.H. Fenn, J. Organometal. Chem., 25 (1970) 173.
14 A.J. Graham and R.H. Fenn, J. Organometal. Chem., 17 (1969) 405.
15 J.W. Faller and M.J. Incorvia, Inorg. Chem., 7 (1968) 840;
A. Davison and W.C. Rode, Inorg. Chem., 6 (1967) 1224.
16 G. Doyle, J. Organometal. Chem., 84 (1975) 323.