DICARBONYL ALLYL DERIVATIVES OF MOLYBDENUM AND TUNGSTEN CONTAINING β-DIKETONATE SUBSTITUENTS

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Summary

A number of complexes of the type $M(CO)_2(\eta^3\text{-allyl})(\text{diket})L$ (where M is Mo or W, diket is a β-diketonate group and L is pyridine, tetrahydrofuran or acetonitrile) have been prepared and characterized by elemental analysis and IR and NMR spectroscopy. These complexes apparently adopt an octahedral configuration similar to related neutral species but spectroscopic data indicate an equilibrium between two conformers probably due to rotation of the allyl groups.

Introduction

In a recent communication [1] we reported the preparation and characterization of several anionic complexes of the general type $[M(CO)_2(\eta^3\text{-allyl})(\text{diket})Cl]^-$ where M is Mo or W, and (diket) is a β-diketonate ligand. These complexes exhibited a number of interesting properties, consequently we wished to compare the behavior of the anionic complexes with similar uncharged species where the chlorine is replaced with a neutral ligand such as pyridine. Uncharged complexes of this specific type with both allylic and diketonate substituents had not yet been prepared, although a large number of rather similar complexes were well known [2—10]. In all of the complexes, however, the bidentate rather than the unidentate ligand was uncharged.

Results and discussion

The reaction of metal complexes containing halide substituents with thallium-(I) salts of β-diketones has proven to be an excellent method for the preparation of β-diketonate complexes. A number of possible precursors to the desired $M(CO)_2(\text{diket})(\eta^3\text{-allyl})L$ complexes have been prepared such as $W(CO)_2(\eta^3\text{-allyl})py_2Cl$ [2] and $Mo(CH_3CN)_2(\eta^3\text{-methallyl})(CO)_2Cl$ [4]. When either of these, or any of several related complexes were exposed to a variety of thallium(I)

TABLE 1

NMR DATA (τ, ppm) FOR SOME TYPICAL [M(CO)$_2$(diket)(allyl)L] COMPLEXES

acac and dpm are the anions of 2,4-pentanedione and 2,2,6,6-tetramethyl-3,5-heptanedione respectively. NMR spectra obtained at ambient temperature in toluene-d_8.

Allyl Protons
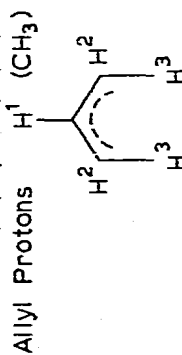
| Complex	τ(H^1(CH$_3$))	τ(H^2 syn)	τ(H^3 anti)	τ(Diketonato ligand)	τ(Other protons)
Mo(CO)$_2$(acac)(η^3-C$_3$H$_5$)(py)	~6.4	6.65	8.58	8.15 CH$_3$, 4.92 CH	1.61, 2.24, 2.65 py
Mo(CO)$_2$(acac)(η^3-C$_3$H$_5$)(THF)	~6.01		8.72	8.05 CH$_3$, 4.66 CH	6.50, 8.28 THF
Mo(CO)$_2$(acac)(η^3-C$_4$H$_7$)(CH$_3$CN)	7.88	6.89	8.91	8.06 CH$_3$, 4.70 CH	7.88 CH$_3$CN
Mo(CO)$_2$(acac)(η^3-C$_4$H$_7$)(THF)	7.89	6.88	~9.0	8.06 CH$_3$, 4.68 CH	6.46, 8.27 THF
Mo(CO)$_2$(dpm)(η^3-C$_4$H$_7$)(py)	7.02	6.90	~8.9	8.98 CH$_3$, 4.50 CH	1.78, 2.33, 2.68 py
W(CO)$_2$(acac)(η^3-C$_3$H$_5$)py	~7.3	~7.1	8.38	8.13 CH$_3$, 4.84 CH	1.63, 2.21, 2.67 py
W(CO)$_2$(dpm)(η^3-C$_3$H$_5$)py	~6.95	7.27	8.21	9.04 CH$_3$, 4.50 CH	1.80, 2.90, 3.35 py

diketonate salts, they reacted smoothly and rapidly even at room temperature. For example the reaction of Tl(acac) and $W(CO)_2(\eta^3\text{-allyl})py_2Cl$ proceeds as follows:

$$W(CO)_2(\eta^3\text{-allyl})py_2Cl + Tl(acac) \xrightarrow[25^\circ C]{THF} W(CO)_2py(\eta^3\text{-allyl})(acac) + TlCl + py$$
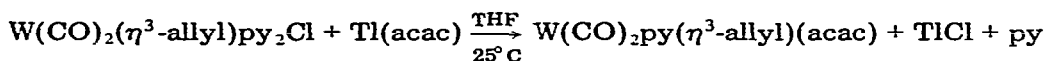
The yellow crystalline products are usually obtained in good yields and are somewhat air sensitive. Although an exhaustive study was not made, all the different diketonate ligands used have reacted with equal facility.

Because of the ready displacement of the acetonitrile ligands, the reaction of the acetonitrile complexes must be carried out in acetonitrile or a non-coordinating solvent. If, for instance, Tl(acac) reacts with $Mo(CH_3CN)_2(\eta^3\text{-methallyl})(CO)_2Cl$ in THF the product obtained is $Mo(acac)(\eta^3\text{-methallyl})(CO)_2(THF)$ whereas $Mo(acac)(\eta^3\text{-methallyl})(CO)_2(CH_3CN)$ is obtained using acetonitrile as the solvent. The CO ligands appear to be strongly bound during the course of the reaction and show no evidence at all of being displaced in competition with the acetonitrile (or pyridine in the case of the reaction of $M(\eta^3\text{-allyl})(CO)_2py_2Cl$ complexes). An indication of this is the fact that complexes containing bidentate ligands such as $Mo(CO)_2(bipy)(\eta^3\text{-allyl})Cl$ proved to be completely inert to Tl(acac) even at elevated temperatures and long reaction times. Presumably the energy required to displace CO, or to make one of the chelating ligands monodentate, is sufficiently high to make the reaction unfavorable.

Although the stereochemistry of the $M(CO)_2(\eta^3\text{-allyl})(diket)L$ complexes cannot be assigned without ambiguity, some predictions can be made based on spectroscopic evidence and analogies to structures of complexes with similar compositions which have previously been determined. All of the complexes of this type which contain diether or diamine chelating ligands which have been examined thus far possess a pseudooctahedral geometry where the two carbonyls and the chelating group lie in a horizontal plane and the allyl group and the remaining ligands lie above and below the plane respectively [10—13]. This type of structure as shown in configuration I has also been proposed for the $[M(CO)_2(\eta^3\text{-allyl})(diket)Cl]^-$ anions, based on infrared and NMR spectroscopic evidence [1]. In complexes which contain chelating diphosphines the bidentate ligands span an axial and equatorial position as in configuration II [9].
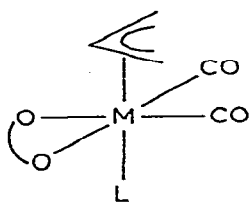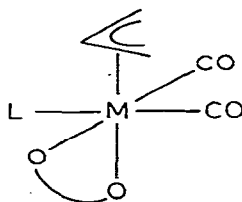
(I)   (II)

A symmetrical structure for the $M(CO)_2(\eta^3\text{-allyl})(diket)L$ complexes as in I seems most consistent with the available spectroscopic data. The room temperature proton NMR spectra of the acetylacetonate complexes exhibit a single resonance for the methyl groups on the acetylacetonate groups and patterns typical of symmetrical η^3-allyl groups. These complexes show a temperature
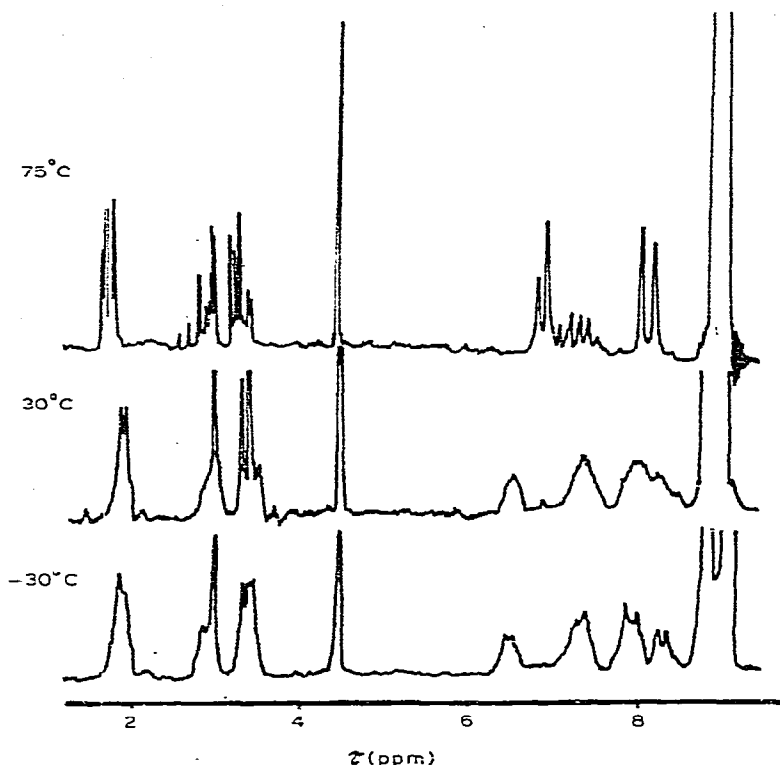
Fig. 1. NMR Spectrum of W(dpm)(CO)$_2$(η^3-allyl)py in toluene-d_8.

dependence reminiscent of the anionic derivatives [1]. At elevated temperatures sharp "average" signals are observed for the allyl protons (see Table 1 for chemical shift data) and as the temperature is lowered the signals broaden, but unlike the anionic complexes, they remain as very broad unresolved signals even at —60°C. It has not been possible to lower the temperature sufficiently in order to "freeze out" the spectra of the individual components for the acetylacetonate complexes although somewhat better results were obtained with complexes containing the sterically more demanding dipivaloylmethanide (dpm) ligand (see Fig. 1). At low temperatures signals for two separate conformers are easily observed for the methyl protons on the dpm ligand and to some extent for the allyl protons although incomplete resolution and signal overlap make assignments for the allyl protons impossible. The η^3-methallyl complexes behave similarly, giving sharp resonances for the methyl, *syn* and *anti* protons at elevated temperatures and a broad unresolved signal at low temperatures.

The temperature dependency seems to be most consistent with a mechanism which involves the rotation of the allyl group interconverting conformer I with an isomer in which the open end of the η^3-allyl group is oriented toward the diketonate ligand. Other more complex rearrangements leading to similar NMR spectra are possible and cannot be ruled out, for example a twisting mechanism interconverting conformers I and II.

The appearance of additional bands in the infrared spectra, in the CO stretch-

TABLE 2

INFRARED SPECTRA OF THE $M(CO)_2(\eta^3$-allyl)(diket)L AND SOME RELATED COMPLEXES

Complex	$\nu(CO)$ (cm^{-1})	Cotton—Kraihazel force parameter [a]		Reference
		k	ki	
$Mo(CO)_2(\eta^3$-$C_3H_5)(acac)py$	1912, 1825	14.11	0.65	This work
$Mo(CO)_2(\eta^3$-$C_3H_5)(acac)THF$	1923, 1832	14.24	0.69	This work
$Mo(CO)_2(\eta^3$-$C_3H_5)(bzac)py$	1916, 1821	14.11	0.71	This work
$Mo(CO)_2(\eta^3$-$C_3H_5)(dpm)py$	1927, 1837	14.31	0.69	This work
$Mo(CO)_2(\eta^3$-$C_4H_7)(acac)py$	1923, 1818	14.14	0.79	This work
$Mo(CO)_2(\eta^3$-$C_4H_7)(acac)THF$	1923, 1825	14.19	0.75	This work
$Mo(CO)_2(\eta^3$-$C_4H_7)(acac)CH_3CN$	1923, 1828	14.21	0.72	This work
$Mo(CO)_2(\eta^3$-$C_4H_7)(dpm)py$	1919, 1825	14.16	0.71	This work
$Mo(CO)_2(\eta^3$-$C_4H_7)(bzac)py$	1919, 1815	14.09	0.78	This work
$W(CO)_2(\eta^3$-$C_3H_5)(acac)py$	1908, 1815	14.00	0.70	This work
$W(CO)_2(\eta^3$-$C_3H_5)(bzac)py$	1901, 1808	13.90	0.69	This work
$W(CO)_2(\eta^3$-$C_3H_5)(dpm)py$	1919, 1825	14.16	0.71	This work
$[Mo(CO)_2(\eta^3$-$C_3H_5)(acac)Cl]^-$	1894, 1783	13.66	0.82	1
$[W(CO)_2(\eta^3$-$C_3H_5)(acac)Cl]^-$	1887, 1770	13.51	0.87	1
$Cr(CO)_2(\eta^3$-$C_3H_5)(bipy)Cl$	1932, 1848	14.43	0.64	6
$Mo(CO)_2(\eta^3$-$C_3H_5)(bipy)Cl$	1934, 1845	14.42	0.68	2
$W(CO)_2(\eta^3$-$C_3H_5)(bipy)Cl$	1919, 1818	14.11	0.76	2
$[W(CO)_2(\eta^3$-$C_3H_5)(bipy)py]^+$	1938, 1876	14.69	0.48	2

[a] m/dynes/Å.

ing region especially, has been useful in certain cases in detecting the presence of rotational isomers [14,15]. The IR spectra of all the $M(CO)_2(\eta^3$-allyl)(diket)L complexes are quite similar in this region (see Table 2). All have two very intense bands of approximately equal intensity in the CO stretching region which is characteristic of *cis*-dicarbonyl complexes but no additional peaks in that region were observed for any of the complexes. These additional peaks would be difficult to observe since the frequencies of the CO stretches for the two rotamers would be expected to be very close (all the complexes prepared thus far have bands which vary from 1915 and 1825 cm^{-1} by only ± 15 cm^{-1} even for large changes in composition) and the CO stretching bands are fairly broad and very intense making closely spaced bands difficult to detect. For complexes containing the acetonitrile group, the $C\equiv N$ stretching bands, which are much sharper and less intense, have proven to be more useful. For instance, solutions of the complex $Mo(CO)_2(acac)(\eta^3$-methallyl)(CH_3CN)$ have two CN stretching bands at 2309 and 2283 cm^{-1} supporting the argument for the presence of two isomeric species in solution although no conclusions can be made regarding the stereochemistry of these species.

As can be seen from the data, the frequencies and force constants for the CO stretching vibrations for these neutral complexes are substantially higher than the negatively charged analogs but considerably lower than similar cationic species as would be predicted. The expected trend toward lower force constants is also observed as one goes from the first and second to third row transition metal.

These complexes are generally soluble in most of the usual polar organic sol-

vents, however, as was mentioned previously, in some cases ligand exchange reactions will occur in solvents which can act as good coordinating ligands. No evidence, either chemical or spectroscopic, has been seen for solvent induced ionization as has been observed for $Mo(CO)_2(\eta^3\text{-allyl})(CH_3CN)_2Cl$ [16]. All the complexes are stable indefinitely at room temperature in an inert atmosphere but at elevated temperatures ($>80°C$) they gradually decompose without melting over a wide temperature range.

Experimental

General

Reagents. The preparation of thallium diketonate salts was accomplished by the reaction of a slight excess of the β-diketone with thallium ethoxide in benzene. All other reagents not described 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 are given in Table 3.

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 toluene-d_8 on a Varian A60 spectrometer.

TABLE 3

ANALYTICAL DATA FOR SOME [M(CO)$_2$(diket)(allyl)L] COMPLEXES

Complex	Analysis (Found (calcd.) (%))		
	C	H	N
$Mo(CO)_2(\eta^3\text{-}C_3H_5)(acac)py$	48.77 (48.52)	4.87 (4.62)	4.26 (3.78)
$Mo(CO)_2(\eta^3\text{-}C_3H_5)(acac)THF$	46.45 (46.20)	5.40 (5.69)	
$Mo(CO)_2(\eta^3\text{-}C_3H_5)(bzac)py$	55.79 (55.52)	4.69 (4.56)	3.55 (3.24)
$Mo(CO)_2(\eta^3\text{-}C_3H_5)(dpm)py$	55.53 (55.38)	6.61 (6.58)	3.50 (3.08)
$Mo(CO)_2(\eta^3\text{-}C_4H_7)(acac)py$	50.09 (49.88)	4.93 (4.97)	3.80 (3.63)
$Mo(CO)_2(\eta^3\text{-}C_4H_7)(acac)THF$	47.45 (47.63)	5.47 (5.96)	
$Mo(CO)_2(\eta^3\text{-}C_4H_7)(acac)CH_3CN$	44.89 (44.96)	4.87 (4.94)	4.02 (4.03)
$Mo(CO)_2(\eta^3\text{-}C_4H_7)(dpm)py$	55.87 (56.28)	6.66 (6.65)	2.99 (2.99)
$Mo(CO)_2(\eta^3\text{-}C_4H_7)(bzac)py$	56.01 (56.38)	5.01 (4.73)	2.94 (3.13)
$W(CO)_2(\eta^3\text{-}C_3H_5)(acac)py$	39.04 (39.23)	3.70 (3.70)	3.45 (3.06)
$W(CO)_2(\eta^3\text{-}C_3H_5)(bzac)py$	46.10 (46.09)	4.07 (3.85)	2.44 (2.69)
$W(CO)_2(\eta^3\text{-}C_3H_5)(dpm)py$	46.85 (46.42)	5.38 (5.38)	2.71 (2.57)

Preparation of complexes

All preparations were carried out in a nitrogen-filled glove box.

M(CO)$_2$(η^3-allyl)(diket)py complexes. The complex Mo(CO)$_2$py$_2$(η^3-allyl)Cl was prepared either by the method of Murdoch and Henzi [3] or by the reaction of allyl chloride with Mo(CO)$_4$py$_2$. (The tungsten analogs and also the π-methallyl derivatives can be prepared similarly.) This M(CO)$_2$(η^3-allyl)py$_2$Cl complex (0.01 mol) was added to a flask containing an exactly equivalent amount of the thallium diketonate salt plus 50 ml THF. The filtrate was evaporated to dryness on a rotary evaporator and the residue was washed with several portions of pentane before being collected on a filter and dried. The products could be recrystallized from toluene/ether mixtures but with no noticeable increase in purity. The yields are usually greater than 80%.

M(CO)$_2$(η^3-allyl)(diket)THF. These complexes are prepared in a manner similar to that described above except that the M(CH$_3$CN)$_2$(CO)$_2$(η^3-allyl)Cl [4] complexes are used as the starting materials. The solid residue obtained after filtration and evaporation was dissolved in boiling heptane and on cooling of the heptane solution fine yellow crystals of the M(CO)$_2$(η^3-allyl)(diket)THF complex formed which were collected on a filter and dried. Yields are about 50%.

M(CO)$_2$(η^3-allyl)(diket)(CH$_3$CN) complexes. These complexes were obtained in a manner similar to that described immediately above except that CH$_3$CN was used as a solvent. The solid residue obtained upon evaporation was simply washed with pentane, then collected on a filter and dried. Yields are usually greater than 75%.

Acknowledgement

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