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CARBONYL-π-ALLYL COMPLEXES OF MOLYBDENUM AND TUNGSTEN

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In spite of current interest in allyl complexes of transition metals, little work has been reported on derivatives of the Group VI metals. Reported data may be summarised as follows:

1. $Na[C_5H_5M(CO)_3]$ + allyl chloride $\rightarrow C_5H_5M(CO)_3(\sigma\text{-allyl}) \xrightarrow{UV} C_5H_5M(CO)_2(\pi\text{-allyl})$
   $M = Mo$ or W (Refs. 1 and 2)
2. $Et_4N[M(CO)_5Y]$ + allyl-X $\rightarrow Et_4N[M_2(CO)_4(\pi\text{-allyl})_2X_3]$
   $M = Mo$ or W; $Y = Cl$, Br, or I; $X = Cl$ or Br (ref. 2)
3. $Et_4N[Mo_2(CO)_4(2\text{-Me-}\pi\text{-allyl})Cl_3] + L \rightarrow Mo(CO)_2L(2\text{-Me-}\pi\text{-allyl})Cl$
   $L = 2$ pyridine, 2,2′-bipyridine, or 1,2-diaminoethane (Ref. 4)
4. $CrCl_3$ + allyl-MgBr $\rightarrow Cr(\pi\text{-allyl})_3$ (Refs. 5 and 6)
   (π-Allyl derivatives of Mo and W were also prepared by related methods.)

In addition, it has been reported that an attempt to prepare allyl derivatives of chromium, molybdenum, and tungsten by treating the hexacarbonyls with allyl bromide was unsuccessful[7].

As an extension of our studies[8,9] on the oxidation of 2,2′-bipyridine (Bipy) substituted hexacarbonyls, it was decided to investigate the reaction of the latter with allyl halides. Reaction occurs in boiling tetrahydrofuran with the compounds $Mo(CO)_4$(Bipy) and $Mo(CO)_4$(Phen), (Phen = 1,10-phenanthroline), to yield complexes of the type $Mo(CO)_2L(\pi\text{-allyl})X$, ($L$ = Bipy or Phen; $X = Cl$, Br, or I). A similar reaction occurs using 2-methyl-3-chloro-1-propene to yield the analogous 2-methyl-π-allyl complexes. Alternatively, pyridine (Py) and carbon monoxide are displaced readily from the complexes $Mo(CO)_3$(Bipy)(Py) and $Mo(CO)_3$(Phen)(Py) on reaction with allyl halides to yield π-allyl derivatives identical with those mentioned above.

Allyl halides oxidise the compounds $W(CO)_4$(Bipy) and $W(CO)_4$(Phen) less readily than their molybdenum analogues and negligible reaction occurs in boiling tetrahydrofuran. Reaction of allyl halides with the trisubstituted derivatives $W(CO)_3$(Bipy)(Py) and $W(CO)_3$(Phen)(Py) proceeds readily, however, to yield the expected products. Even under these conditions, very little reaction occurred using 2-methyl-3-chloro-1-propene.

Some reactions of these π-allyl complexes have been investigated. No reaction with boiling pyridine could be detected, suggesting that the carbonyl groups are rather resistant to substitution. The chloride ion in the chloro complexes is easily replaced, however, in boiling acetone with another anion such as SCN^- or $SC_6F_5^-$, or with pyridine in the presence of BF_4^- or BPh_4^-.

All of the complexes (see Table 1) are air-stable crystalline solids which vary in colour from deep orange to deep maroon. The non-ionic complexes are slightly soluble and the ionic complexes are very soluble in polar solvents such as acetone or nitrobenzene to form stable solutions. The complexes are insoluble in non-polar solvents. The infrared spectra of the complexes in the C–O stretching region contain two bands of approximately equal intensity. In the spectra of some of the tungsten complexes, the bands were split, suggesting the possible existence of isomers. In order to check that this observation was not due to crystal effects, the solution

TABLE 1

PHYSICAL PROPERTIES OF COMPLEXES

Complex	*No.*	*Colour*	*ν(C–O)*[a]	*ν(C–N)*[a]	*Cond.*[b]
Mo(CO)$_2$(Bipy)(π-allyl)Cl	1	red	1934, 1845		0.10
Mo(CO)$_2$(Bipy)(π-allyl)Br	2	dark red	1927, 1845		0.17
Mo(CO)$_2$(Bipy)(π-allyl)I	3	maroon	1923, 1845		0.39
Mo(CO)$_2$(Bipy)(π-allyl)NCS	4	crimson	1927, 1848	2075	0.05
Mo(CO)$_2$(Bipy)(π-allyl)SC$_6$F$_5$	5	red	1927, 1852		0.08
Mo(CO)$_2$(Bipy)(2-Me-π-allyl)Cl	6	maroon	1927, 1852		0.07
Mo(CO)$_2$(Bipy)(2-Me-π-allyl)NCS	7	red	1946, 1852	2079	0.07
[Mo(CO)$_2$(Bipy)(Py)(π-allyl)]BPh$_4$	8	deep orange	1957, 1869		18.4
[Mo(CO)$_2$(Bipy)(Py)(π-allyl)]BF$_4$	9	crimson	1953, 1883		31.9
[Mo(CO)$_2$(Bipy)(Py)(2-Me-π-allyl)]BF$_4$	10	red	1953, 1876		29.0
Mo(CO)$_2$(Phen)(π-allyl)Cl	11	dark red	1938, 1859		0.51
Mo(CO)$_2$(Phen)(π-allyl)Br	12	dark red	1931, 1848		0.21
Mo(CO)$_2$(Phen)(π-allyl)I	13	deep maroon	1944, 1875		0.65
Mo(CO)$_2$(Phen)(π-allyl)NCS	14	crimson	1927, 1852	2079	0.05
Mo(CO)$_2$(Phen)(2-Me-π-allyl)Cl	15	maroon	1923, 1848		0.13
Mo(CO)$_2$(Phen)(2-Me-π-allyl)NCS	16	crimson	1934, 1848	2070	0.07
[Mo(CO)$_2$(Phen)(Py)(π-allyl)]BF$_4$	17	pale crimson	1942, 1866sh 1848		28.6
W(CO)$_2$(Bipy)(π-allyl)Cl	18	maroon	1919, 1818		0.78
W(CO)$_2$(Bipy)(π-allyl)Br	19	deep maroon	1919, 1835		0.94
W(CO)$_2$(Bipy)(π-allyl)I	20	deep maroon	1919, 1838		1.6
W(CO)$_2$(Bipy)(π-allyl)NCS	21	red	1931, 1842	2088	0.03
W(CO)$_2$(Bipy)(π-allyl)SC$_6$F$_5$	22	maroon	1923, 1838		0.05
[W(CO)$_2$(Bipy)(Py)(π-allyl)]BPh$_4$	23	red	1934, 1855 1923, 1838		19.4
[W(CO)$_2$(Bipy)(Py)(π-allyl)]BF$_4$	24	dark red	1938, 1876		30.2
W(CO)$_2$(Phen)(π-allyl)Cl	25	maroon	1927, 1845		0.10
W(CO)$_2$(Phen)(π-allyl)Br	26	deep maroon	1919, 1852 1821		0.33
W(CO)$_2$(Phen)(π-allyl)I	27	deep maroon	1938, 1852 1919, 1821		1.0
W(CO)$_2$(Phen)(π-allyl)NCS	28	dark red	1927, 1852		0.16
[W(CO)$_2$(Phen)(Py)(π-allyl)]BF$_4$	29	maroon	1931, 1859 1838		29.7

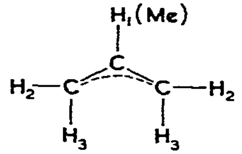
[a] Infrared spectra (cm^{-1}) in Nujol, [b] Conductivity Λ_M ($ohm^{-1} \cdot cm^2 \cdot mole^{-1}$) of 10^{-3} *M* solutions in PhNO$_2$.

spectrum of the compound $[W(CO)_2(Bipy)(Py)(\pi\text{-allyl})]BPh_4$ was measured. A spectrum essentially identical with that observed in the solid state was found. Comparison of the infrared spectra of the compounds $Mo(CO)_2(Bipy)(\pi\text{-allyl})NCS$ and $Mo(CO)_2(Bipy)(\pi\text{-allyl})Cl$ shows two additional peaks in the spectrum of the former compound. A strong band at 2080 cm^{-1} may be assigned to $\nu(C{-}N)$ and a weak band at 825 cm^{-1} to $\nu(C{-}S)$. On the basis of the position of the latter mode, it may be inferred that the thiocyanate is N-bonded to molybdenum. There is no evidence in the spectra of these compounds for bands resulting from $\nu(C{=}C)$ in the region 1500–1700 cm^{-1}, which is consistent with their formulation as π-allyl derivatives. Measurement of the magnetic moments of a selection of the complexes demonstrates that they are diamagnetic. This is also verified by the sharply resolved bands in the nuclear magnetic resonance spectra. Owing to their low solubility in suitable solvents, it was only possible to measure the molecular weight of one non-ionic compound by osmometry. The value found for the compound $Mo(CO)_2(Bipy)(\pi\text{-allyl})NCS$ in acetone was 404 (calcd. 407).

Nuclear magnetic resonance spectroscopy can demonstrate conclusively that a metal complex contains a π-allyl group. As was noted previously[4], the complex $Mo(CO)_2(Bipy)(2\text{-Me-}\pi\text{-allyl})Cl$ (and similar compounds) is insufficiently soluble for its NMR spectrum to be measured in conventional solvents. However, the thiocyanates and the saltlike derivatives of molybdenum are sufficiently soluble in liquid sulphur dioxide. The aliphatic PMR spectra are typical of those reported previously for π-allyl and 2-Me-π-allyl complexes[10] and are presented in Table 2. The spectrum

TABLE 2

NUCLEAR MAGNETIC RESONANCE DATA IN LIQUID SO_2



No.	τ[a]	Complexity	Relative peak area	Assignment	J(cps)	$H_{arom.}/H_{aliph.}$
4	~6.5	multiplet	1	H_1 coupled to H_2+H_3		8:5
	6.69	doublet	2	H_2 coupled to H_1	6	
	8.50	doublet	2	H_3 coupled to H_1	9	
7	6.97	singlet	2	H_2		8:7
	8.53	singlet	2	H_3		
	8.99	singlet	3	Me		
9	~6.5	multiplet	1	H_1 coupled to H_2+H_3		13:5
	6.44	doublet	2	H_2 coupled to H_1	6	
	8.20	doublet	2	H_3 coupled to H_1	9	
10	6.67	singlet	2	H_2		13:7
	8.23	singlet	2	H_3		
	8.85	singlet	3	Me		
16	6.80	singlet	2	H_2		8:7
	8.45	singlet	2	H_3		
	9.28	singlet	3	Me		
17	~6.5	multiplet	1	H_1 coupled to H_2+H_3		13:5
	6.30	doublet	2	H_2 coupled to H_1	6	
	8.12	doublet	2	H_3 coupled to H_1	9	

[a] Relative to HMDS (τ = 9.95) as internal standard.

of the compound $Mo(CO)_2(Phen)(\pi\text{-allyl})NCS$ proved very complicated and comparison of the aromatic resonances with those in the spectrum of the compound $Mo(CO)_2(Phen)(2\text{-Me-}\pi\text{-allyl})NCS$ clearly demonstrates the presence of two isomers.

EXPERIMENTAL

Halo complexes

Complexes of the type $M(CO)_2L(\pi\text{-allyl})X$ and $Mo(CO)_2L(2\text{-Me-}\pi\text{-allyl})Cl$ (M = Mo or W; L = Bipy or Phen; X = Cl, Br or I) were prepared by one of the two methods outlined below. More precise details are summarised in Table 3. In Table 4 analytical data for all compounds are presented.

TABLE 3

PREPARATION OF π-ALLYL HALIDE COMPLEXES

No.	*Method*	*Allyl X (ml)*	*Substituted carbonyl (g)*	*THF (ml)*	*Product (g)*
1	*a*	25	5.0	150	4.6
1	*b*	5	0.73	50	0.50
2	*a*	5	1.0	40	1.0
3	*a*	5	1.0	40	1.1
6	*a*	5	1.1	40	1.0
11	*a*	5	1.0	40	0.81
12	*a*	5	1.0	40	0.85
13	*a*	5	1.0	40	0.90
15	*a*	5	1.1	40	1.1
18	*b*	15	2.9	100	2.2
19	*b*[a]	5	0.93	40	0.26
20	*b*	5	0.62	40	0.35
25	*b*[a]	10	1.1	40	0.36
26	*b*[a]	10	1.1	40	0.20
27	*b*[a]	10	0.92	40	0.15

[a] Also crystallised from acetone/water and dried *in vacuo* at 100°.

Method (*a*). A mixture of the tetracarbonyl complex $M(CO)_4L$ and an excess of the allyl halide were heated in boiling tetrahydrofuran with vigorous stirring for 2 h under nitrogen. The product, which separated, was filtered off from the cold solution, washed with light petroleum, and dried *in vacuo*.

Method (*b*). A mixture of the complex $M(CO)_3LPy$ and the allyl halide were heated in boiling tetrahydrofuran for 2 h under nitrogen. The product, which separated, was filtered off, washed with light petroleum, and dried *in vacuo*.

Isothiocyanato complexes

All of the isothiocyanato complexes were prepared by a direct metathetical reaction as described for the following typical compound.

Isothiocyanatodicarbonyl-2,2'-bipyridine-π-allylmolybdenum. The complex $Mo(CO)_2(Bipy)(\pi\text{-allyl})Cl$ (0.94 g) and NaSCN (1.0 g) were heated in boiling acetone (100 ml) with stirring for 3 h. On cooling, NaCl was filtered off. The product (0.51 g),

TABLE 4

ANALYTICAL DATA

No.	Yield (%)	Found (%)						Calcd. (%)					
		C	H	N	X	S	M	C	H	N	X	S	M
1	86	46.6	3.5	7.2	9.1		24.8	46.8	3.4	7.3	9.2		25.0
2	88	42.6	2.9	6.5	19.2		22.6	42.0	3.0	6.5	18.6		22.4
3	86	37.9	2.6	5.9	26.8		20.4	37.8	2.75	5.9	26.7		20.15
4	51	47.4	3.4	10.2		7.8	23.7	47.2	3.2	10.3		7.9	23.55
5	72	46.3	2.4	5.0	17.3		17.5	46.0	2.4	5.1	17.3		17.5
6	87	47.9	4.0	7.2	8.9		24.2	48.2	3.8	7.0	8.9		24.1
7	46	48.3	3.7	10.0		7.4	22.3	48.4	3.6	10.0		7.6	22.8
8	37	70.6	5.2	6.2			11.4	70.6	5.1	5.6			12.8
9	49	46.8	3.6	8.3	14.9		18.1	46.6	3.5	8.2	14.8		18.6
10	15	48.0	3.8	7.9	14.2		18.1	47.65	3.8	7.95	14.4		18.15
11	77	49.9	3.1	7.0	8.6		23.3	49.9	3.2	6.9	8.7		23.5
12	73	46.3	3.6	6.0	17.7		20.9	45.0	2.9	6.2	17.6		21.2
13	70	41.0	2.4	5.7	25.7		19.1	40.8	2.6	5.6	25.4		19.2
14	63	50.2	3.35	9.6		7.3	21.6	50.1	3.05	9.75		7.45	22.25
15	92	51.1	3.5	6.6	8.6		22.4	51.1	3.6	6.6	8.4		22.7
16	73	50.9	3.3	9.0		6.7	20.8	51.2	3.4	9.45		7.2	21.55
17	39	49.1	3.5	7.9	13.9		17.6	49.0	3.4	7.8	14.1		17.8
18	72	37.7	3.0	6.1	7.8		38.9	38.1	2.8	5.9	7.5		38.9
19	33	34.5	2.7	5.5	16.5		34.9	34.8	2.5	5.4	15.5		35.6
20	49	31.9	2.1	4.8	22.6		32.6	31.9	2.3	5.0	22.5		32.6
21	31	38.5	2.8	8.8		6.8	37.1	38.8	2.6	8.5		6.5	37.1
22	43	39.5	2.1	4.5	15.9		29.0	39.6	2.1	4.4	14.9		28.9
23	15	63.4	5.0	5.1			21.7	63.2	4.6	5.0			22.0
24	18	39.1	3.1	7.2	11.8		30.2	39.8	3.0	7.0	12.6		30.5
25	36	40.7	2.9	5.6	7.1		37.0	41.1	2.6	5.6	7.1		37.0
26	18	37.7	2.2	5.0	14.8		34.2	37.7	2.4	5.2	14.8		34.0
27	15	34.6	2.4	4.6	21.4		31.5	34.7	2.2	4.8	21.6		31.3
28	59	41.7	2.5	8.0		6.0	35.2	41.6	2.5	8.1		6.2	35.4
29	21	42.6	2.9	6.6	12.1		29.2	42.1	2.9	6.7	12.1		29.3

which was precipitated by addition of water (300 ml), was filtered off, washed with boiling water (1 l), crystallized from acetone/water, and dried *in vacuo* at 100°.

Pentafluorothiophenolato complexes

Complexes of the type $M(CO)_2(Bipy)(\pi\text{-allyl})SC_6F_5$ (M = Mo or W) were prepared by the method described for the following compound.

Pentafluorothiophenolatodicarbonyl-2,2'-bipyridine-π-allylmolybdenum. A mixture of $Mo(CO)_2(Bipy)(\pi\text{-allyl})Cl$ (0.50 g) and $TlSC_6F_5$ (1.0 g) were heated in boiling acetone (100 ml) for 2 h. After filtration, water was added dropwise to the cooled solution until the product began to separate. The solution was set aside at room temperature for 3 days to complete crystallisation of the product (0.51 g), which was dried *in vacuo* at 100°.

Dicarbonyl-2,2'-bipyridinepyridine-π-allylmolybdenum tetraphenylborate

The complex $Mo(CO)_2(Bipy)(\pi\text{-allyl})Cl$ (0.53 g), $NaBPh_4$ (0.73 g) and pyridine

(5 ml) were heated in boiling acetone (100 ml) for 2 h. After separation of the suspension of NaCl by filtration through Kieselguhr, water (20 ml) was added. Evaporation of the solvent yielded a yellow oil, which was redissolved in acetone/water. The product (0.38 g), which was deposited from solution at 0°, was filtered off and dried at 100° *in vacuo*.

Dicarbonyl-2,2′-bipyridinepyridine-π-allyltungsten tetraphenylborate

The complex $W(CO)_2(Bipy)(\pi\text{-allyl})Cl$ (0.59 g), $NaBPh_4$ (0.74 g) and pyridine (5 ml) were heated in boiling acetone (100 ml) for 3 h. The solution was filtered and water (20 ml) was added. The solvent was partially evaporated under reduced pressure and unreacted starting material separated. The latter was filtered off, and the product (0.16 g), which was isolated after further reduction of the volume of the solution, was filtered off and dried *in vacuo* at 100°.

Tetrafluoroborate complexes

These were prepared by methods entirely analogous to that described for the following compound.

Dicarbonyl-2,2′-bipyridinepyridine-π-allylmolybdenum tetrafluoroborate. A mixture of $Mo(CO)_2(Bipy)(\pi\text{-allyl})Cl$ (1.77 g), $NaBF_4$ (0.23 g), and pyridine (10 ml) were heated in boiling acetone (100 ml) for 5 h. The cooled solution was filtered through Kieselguhr. Water (30 ml) was added and the volume of solution was reduced until the onset of crystallisation. The product (1.50 g) which separated after 5 days at 0° was dried *in vacuo* at 100°.

Physical measurements

Common physical measurements were carried out as described in other publications[9,11]. Nuclear magnetic resonance spectra were recorded using a Varian HA-100 spectrometer.

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SUMMARY

Allyl halides and 2-methylallyl halides react with the substituted carbonyls $Mo(CO)_4(Bipy)$ and $Mo(CO)_4(Phen)$, (Bipy = 2,2′-bipyridyl and Phen = 1,10-phenanthroline), in boiling tetrahydrofuran to yield derivatives of the type $Mo(CO)_2(Bipy)(\pi\text{-allyl})X$ and $Mo(CO)_2(Phen)(\pi\text{-allyl})X$, (X = Cl, Br, or I). Identical products result respectively from reaction of the compounds $Mo(CO)_3(Bipy)(Py)$ and $Mo(CO)_3(Phen)(Py)$, (Py = pyridine), with allyl halides. Good yields of the tungsten π-allyl compounds can be obtained only by the latter route. Replacement of the chloride in the molybdenum and tungsten compounds may be effected readily by other anions (SCN^- or $SC_6F_5^-$) or by pyridine in the presence BF_4^- or BPh_4^-. The existence of the π-allyl system in the thiocyanates and salt-like compounds has been demonstrated by PMR measurements in liquid SO_2.

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