(1—3-η-Allyl)dicarbonyl-molybdenum(II) and -tungsten(II) Complexes and their Reactions with some Chelating Anions

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Complexes $[MX(\eta\text{-}C_3H_5)(CO)_2L_2]$ [M = Mo or W; L_2 = 2,2′-bipyridyl (bipy) or di(2-pyridyl)amine (dpa); X = Cl, Br, I, NCS, $MeCO_2$, CF_3CO_2, $PhSO_2$, or $p\text{-}MeC_6H_4SO_2$] have been prepared by one or more of four preparative routes. The oxo-anions are all unidentate and *O* bonded. Reaction of the molybdenum complexes with sodium pentane-2,4-dionate and dimethyl- or diethyl-dithiocarbamate in the presence of pyridine results in displacement of halide and bipy or dpa and formation of $[Mo(\eta\text{-}C_3H_5)(CO)_2(A)(py)]$ (A = pd, $Me_2NCS_2^-$, or $Et_2NCS_2^-$). The salicylaldehyde anion (sal) reacts similarly with molybdenum dpa complexes but behaves as a unidentate ligand towards the corresponding bipy complexes with formation of $[Mo(\eta\text{-}C_3H_5)(CO)_2(sal)(bipy)]$.

COMPLEXES $[MX(\eta\text{-}C_3H_5)(CO)_2L_2]$ (X = halogen and M = Mo or W) have been known for more than ten years, but only recently have some been found to act as catalysts for the polymerisation of certain dienes.[1,2] As few reactions of these formally seven-co-ordinate molybdenum- and tungsten-(II) derivatives have been reported,[3-7] we recently initiated investigations into the preparation and reactions of a range of complexes of this type. These studies led to the isolation of previously unknown chromium analogues,[8] while this paper summarises synthetic methods available for the molybdenum and tungsten complexes and describes their reactions with some anionic three-electron donors.

EXPERIMENTAL

All solvents were purified and dried by standard procedures, and reactions were carried out in an atmosphere of dry nitrogen gas. The starting materials tricarbonyl(η-cycloheptatriene)molybdenum and *cis*-$[M(CO)_4L_2]$ [Mo = Mo or W; L_2 = 2,2′-bipyridyl (bipy) or di(2-pyridyl)amine (dpa)] were prepared by literature methods or extensions of them.[9,10] The salts $[R_4E][MX(CO)_3L_2]$ (E = P or As, X = halide) were prepared either by Behrens method,[11] or more conveniently by the reaction of $[M(CO)_4L_2]$ with an excess of tetraphenyl-phosphonium or -arsonium halide in refluxing toluene–acetonitrile for 3 h.

^1H N.m.r. spectra were recorded on a JEOL PS100 spectrometer using tetramethylsilane as internal reference. I.r. spectra were recorded on a Perkin-Elmer 237 spectrophotometer using Nujol and hexachlorobutadiene mulls.

Preparation of Complexes $[MX(\eta\text{-}C_3H_5)(CO)_2L_2]$.—Complexes (I)—(IV) (Table 1) were prepared by one or more of four synthetic methods. Typical experimental procedures are given for one complex prepared by each method, and significant variations in experimental detail are noted in Table 1 for the others.

(*a*) *From the hexacarbonyl*. The complex $Mo(CO)_6$ (2.64 g, 10 mmol), dpa (1.71 g, 10 mmol), and allyl bromide (9 cm³, 100 mmol) were allowed to react in refluxing tetrahydrofuran (thf) (40 cm³) for 3 h. The *product* $[MoBr(\eta\text{-}C_3H_5)(CO)_2(dpa)]$ [Table 1, (II; X = Br)] was filtered off from the cooled solution, washed with thf, and vacuum dried (yield 91%).

(*b*) $[M(CO)_4L_2]$ + *allyl compound*. The complex $[Mo(CO)_4(dpa)]$ (0.47 g, 1.24 mmol) and allyl isothiocyanate (2.5 cm³, 30 mmol) were allowed to react in boiling thf (20 cm³) for 2 h. The product was precipitated on addition of light petroleum (100 cm³) followed by refrigeration at 0 °C for 2 h. The *complex* was filtered off, washed with light petroleum, and dried *in vacuo* (yield 88%).

(*c*) *Anion exchange*. The complex $[MoCl(\eta\text{-}C_3H_5)(CO)_2(bipy)]$, (I; X = Cl) (0.50 g, 1.3 mmol), and $Na[O_2CCF_3]$ (0.41 g, 3.0 mmol) were stirred in acetone (20 cm³) at room temperature for 3 d. The solution was filtered and the product precipitated on slow addition of water. The dark red *solid* was washed with water and dried *in vacuo* (yield 98%).

(*d*) $[MX(CO)_3L_2]^-$ + *allyl compound*. The salt $[Ph_4P][WBr(bipy)(CO)_3]$ (2.10 g, 2.5 mmol) was added to allyl bromide (2.5 cm³, 30 mmol) in methanol (25 cm³), and the mixture stirred for 1 h at room temperature. The *product*, $[WBr(\eta\text{-}C_3H_5)(CO)_2(bipy)]$ (III; X = Br), was filtered off, washed with methanol followed by water, and dried *in vacuo* (yield 78%).

Reactions with Three-electron Donors.—The complexes $[MX(\eta\text{-}C_3H_5)(CO)_2L_2]$ were treated in acetone with a *ca.* 4M excess of sodium pentane-2,4-dionate (pd), dialkyldithiocarbamate, or salicylaldehydate (sal) in the presence of pyridine (py). In a typical experiment, (I; X = Cl) (0.35 g, 0.91 mmol), Na(pd) (0.44 g, 3.60 mmol), and py (5 cm³) were stirred in acetone (20 cm³) for 3 d at room temperature. The solution was filtered, water (10 cm³) added to the filtrate, and the solvent evaporated at room temperature until the *product* started to separate out as an oil. On standing at 0 °C, the oil crystallised and the complex $[Mo(\eta\text{-}C_3H_5)(CO)_2(pd)(py)]$, (V; A = pd, L = py) (Table 3), was filtered off under nitrogen, washed with water, and dried (yield 86%). Other complexes (V) (Table 3) were prepared by similar procedures.

RESULTS AND DISCUSSION

A summary of the complexes prepared and the procedures used is given in Table 1. Complexes (I) and (III) (X = Cl, Br, I, and NCS) have been prepared previously, and their spectroscopic properties were in accord with literature values.[3,12] Analytical results for all the new

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complexes are given in Tables 2 and 3, together with selected i.r. data.

TABLE 1

Preparative procedures for $[MX(\eta\text{-}C_3H_5)(CO)_2L_2]$ complexes

Substituent X	$[MoX(\eta\text{-}C_3H_5)(CO)_2(bipy)]$, (I)	$[MoX(\eta\text{-}C_3H_5)(CO)_2(dpa)]$, (II)	$[WX(\eta\text{-}C_3H_5)(CO)_2(bipy)]$, (III)	$[WX(\eta\text{-}C_3H_5)(CO)_2(dpa)]$, (IV)
Cl	a (i), b, d	a (i), b, d	d	d
Br	a, b	a, b	d	d
I	a, b, c (ii)	a, b, c	c (iii)	c (iii)
NCS	a (i), b (iv), c, d	a (iv), b (iv), c	c (iii)	c (iii)
CH_3CO_2	a (i), b (i), c (v), d (vi)	a (i), b, c (ii), (v)	c (ii), (iii), (v)	
CF_3CO_2	c	c		
$C_6H_5SO_2$	c (v)	c (v)	c (ii), (iii), (v)	
$MeC_6H_4SO_2$	c (v)	c (v)	c (ii), (iii), (v)	

(i) Toluene as solvent, (ii) product precipitated during reaction, (iii) reaction carried out under reflux, (iv) product precipitated by light petroleum (b.p. 40—60 °C), (v) methanol as solvent, and (vi) product precipitated on cooling in ice.

TABLE 2

Analytical and selected i.r. data for $[MX(\eta\text{-}C_3H_5)(CO)_2L_2]$ complexes

Complex	Analysis */%			I.r. data (4 000—650 cm^{-1})			
	C	H	N	$\nu(CO)$	$\nu(CO_2)$	$\nu(SO)$	$\nu(SOM)$
(I; X = $MeCO_2$)	50.2	4.1	7.0	1 852	1 315		
	(50.0)	(3.9)	(6.9)	1 943	1 620		
(I; X = CF_3CO_2)	44.5	3.3	6.1	1 855	1 417		
	(44.1)	(2.8)	(6.1)	1 948	1 690		
(I; X = $PhSO_2$)	51.6	3.9	5.8	1 854		1 089	864
	(51.4)	(3.7)	(5.7)	1 936		1 076 (sh)	
						1 059	
(I; $MeC_6H_4SO_2$)	51.6	4.1	5.4	1 832		1 085 (sh)	870
	(52.4)	(4.0)	(5.5)	1 932		1 075 (sh)	860 (sh)
						1 054	
(II; X = Cl)	45.0	3.7	10.5	1 842			
	(45.1)	(3.5)	(10.5)	1 928			
(II; X = Br)	40.4	3.2	9.3	1 844			
	(40.5)	(3.2)	(9.5)	1 930			
(II; X = I)	37.0	3.0	8.6	1 816			
	(36.7)	(2.9)	(8.6)	1 834			
				1 924			
(II; X = NCS)	45.6	3.5	13.2	1 838			
	(45.5)	(3.3)	(13.3)	1 928			
(II; X = $MeCO_2$)	47.8	4.2	9.8	1 850	1 330		
	(48.3)	(4.0)	(9.9)	1 937	1 595		
(II; X = CF_3CO_2)	42.8	4.1	9.3	1 842	1 420		
	(42.8)	(2.9)	(8.8)	1 935	1 665		
(II; X = $PhSO_2$)	49.5	4.1	8.1	1 852		1 033	918
	(49.9)	(3.8)	(8.3)	1 933		1 049	
(II; X = $MeC_6H_4SO_2$)	49.2	4.4	7.8	1 843		1 037	907
	(50.9)	(4.0)	(8.1)	1 937			
(III; X = $MeCO_2$)	41.1	3.5	5.6	1 831	1 316		
	(41.1)	(3.2)	(5.6)	1 930	1 630		
(III; X = $PhSO_2$)	43.5	3.4	4.9	1 836		1 078 (sh)	856
	(43.6)	(3.1)	(4.8)	1 921		1 092	
(III; X = $MeC_6H_4SO_2$)	43.0	3.8	4.7	1 819		1 060	855 (sh)
	(44.6)	(3.4)	(4.7)	1 921		1 069 (sh)	865
						1 092	
(IV; X = Cl)	36.7	3.2	8.5	1 828			
	(36.9)	(2.9)	(8.6)	1 918			
(IV; X = Br)	33.6	2.8	7.9	1 830			
	(33.8)	(2.6)	(7.9)	1 919			
(IV; X = I)	31.6	2.7	7.4	1 803			
	(31.1)	(2.4)	(7.3)	1 820			
				1 918			
(IV; X = NCS)	38.7	3.4	10.9	1 824			
	(37.6)	(2.8)	(11.0)	1 915			

* Calculated values are given in parentheses.

Of the four preparative routes used, (a) was the most convenient for molybdenum halide complexes as a high yield of product (65—100%) could be obtained directly from the hexacarbonyl without prior isolation of the tetracarbonyl complex $[Mo(CO)_4L_2]$. Complexes containing oxo-anions other than acetate were not formed by methods (a) or (b), but were readily obtained by anion exchange [method (c)]. The tungsten complexes [(III) and (IV)] were in general less readily prepared. Very little reaction occurred between allyl halides and the tetracarbonyl derivatives (or hexacarbonyl–bidentate ligand mixtures) under the conditions used to form the molyb-

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denum complexes, and on using more forcing conditions extensive decomposition occurred. Reaction of allyl halides with the salts $[Ph_4E][WX(CO)_3L_2]$ at room temperature [method (d)] provided a quicker and more convenient synthesis of the tungsten halide complexes than those used previously.[3,13] Oxo-anion-exchange reactions on the tungsten complexes proceeded slowly, and for the bipy complexes only, at room temperature. At elevated temperatures yields in excess of 80% were obtained for these complexes, but attempts to isolate the corresponding dpa complexes under these conditions resulted in partial oxidation of the products with formation of tungsten oxo-species.

TABLE 3

Analytical and selected i.r. data on the reaction products of $[MoX(\eta\text{-}C_3H_5)(CO)_2L_2]$ with three-electron donors

$[Mo(\eta\text{-}C_3H_5)(CO)_2(A)L]$,(V)		Analysis *(%)			Carbonyl-stretching wave-numbers (cm^{-1})
A	L	C	H	N	
pd	py	49.2	5.1	3.9	1 918
		(48.5)	(4.6)	(3.8)	1 830
Me_2NCS_2	py	39.8	4.4	7.3	1 918
		(39.8)	(4.1)	(7.1)	1 822
Et_2NCS_2	py	42.1	5.3	6.6	1 923
		(42.9)	(4.8)	(6.6)	1 838
sal (bidentate)	py	52.2	4.2	3.8	1 932
		(51.9)	(3.8)	(3.6)	1 840
					1 630 (sal)
sal (unidentate)	bipy	56.5	4.4	6.0	1 930
		(56.2)	(3.8)	(6.0)	1 842
					1 665 (sal)

* Calculated values are given in parentheses.

Crystal-structure determinations have been carried out on five complexes of the type under investigation,[1,14-17] and all have very similar stereochemistries. The ligand arrangement is basically octahedral with the two *cis*-carbonyl groups and the donor atoms of the bidentate ligand approximately coplanar, while the allyl group is *trans* to the unidentate ligand. The similarities in spectra of all the complexes listed in Table 1 indicate that their stereochemistries are all probably based on this ligand arrangement.

The *cis*-carbonyl groups give rise to two strong bands of approximately equal intensity centred at *ca.* 1 930 and *ca.* 1 840 cm^{-1} for the molybdenum and some 10 cm^{-1} lower for the corresponding tungsten complexes. These bands can be assigned to A_1 and B_1 carbonyl modes, and Cotton–Kraihanzel force-constant calculations show that the C–O stretching force constants are some 1—2% smaller for tungsten compared with the corresponding molybdenum complexes.[2] Besides the two main carbonyl bands, additional weak shoulders were evident in solid-state spectra of several of the dpa complexes, and for (II) and (IV) (X = I) these features could be just resolved into separate bands. Unfortunately the low solubility of these complexes in suitable solvents precluded a thorough investigation of the possible causes.

The positions of the CO_2 symmetric and asymmetric stretches (Table 2), and the appearance of three C–F stretching modes in the spectrum of the CF_3CO_2 complexes, indicate that both the acetate and trifluoroacetate groups are unidentate.[18] The Mo^{II} and W^{II} sulphinate complexes appear to be *O* bonded from i.r. evidence, in contrast to the closely related $[Mo(\eta\text{-}C_5H_5)(CO)_3(SO_2R)]$ in which *S* bonding is normally found although *O*-bonded intermediates are formed initially.[19] A similar preference for the more polarisable donor atom of an ambidentate ligand is shown by tungsten in $[W(\eta\text{-}C_5H_5)(CO)_3(SCN)]$, whereas both linkage isomers can be isolated for the molybdenum complex.[20] *X*-Ray studies on complex (I; X = NCS) and $[Mo(NCS)(\eta\text{-}C_3H_4Me)(CO)_2(phen)]$ have shown *N*-bonded thiocyanate groups in both cases,[14,15] and i.r. data on all the thiocyanates listed in Table 1 are consistent with this mode of bonding. However, Mo^{II} and W^{II} are obviously borderline with regard to a 'hard' or 'soft' classification and some preparations of $[Mo(NCS)(\eta\text{-}C_3H_5)(CO)_2(dpa)]$, (II; X = NCS), and $[W(NCS)(\eta\text{-}C_3H_5)(bipy)(CO)_2]$, (III; X = NCS), showed additional bands in the C–N and C–S stretching regions of their i.r. spectra, although analytically pure. It is tempting to suggest that linkage or some other form of isomerism is responsible for these bands, but so far we have been unable to define the precise conditions under which these bands appear and consequently no firm conclusions can yet be reached.

Reactions with Three-electron Donors.—In the presence of py, the pd and dialkyldithiocarbamate anions displaced both the halide ion and the neutral bidentate ligands bipy or dpa from the molybdenum (but not the tungsten) complexes under very mild conditions. Free ligand was recovered from the reaction mixture, so that the overall reaction scheme can be represented as in (1).

$$[MoX(\eta\text{-}C_3H_5)(CO)_2L_2] + Na[A] + py \longrightarrow [Mo(\eta\text{-}C_3H_5)(CO)_2(py)(A)] + NaX + L_2 \qquad (1)$$

The products were shown to contain η-bonded allyl groups by n.m.r. spectroscopy (Table 4), while the i.r. data (Table 3) indicate that the complexes still contain *cis*-dicarbonyl groups. Of the various bonding modes of the pd ligand, *viz.* unidentate enolic, bidentate ketonic, *C*-bonded, and chelated enolic, the i.r. data are only consistent with the chelated enolate form of the ligand,[21] while both the i.r. (single C–N and CS_2 stretching modes) and n.m.r. data confirmed that the dialkyldithiocarbamate ligands were also chelating.[22,23]

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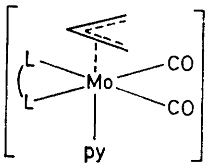
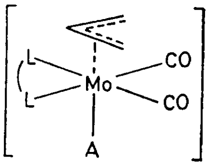
Since the initial complexes $[MoX(\eta\text{-}C_3H_5)(CO)_2L_2]$ are known to undergo anion exchange as well as form stable


(A)


(B)

A = pd, Me_2NCS_2, Et_2NCS_2, or sal

cationic species in the presence of py and non-co-ordinating anions,[3] either (A) or (B) or both appear to be the most likely intermediates formed in the reaction with anionic three-electron donors. Attempts to isolate either intermediate using pd or dialkyldithiocarbamates were unsuccessful; however, when the reaction was carried out using Na(sal) as the three-electron donor, dpa was readily replaced with formation of $[Mo(\eta\text{-}C_3H_5)(CO)_2(py)(sal)]$, (V; A = sal, L = py), but under the same experimental conditions bipy was not displaced and the product $[Mo(\eta\text{-}C_3H_5)(CO)_2(sal)(bipy)]$, (V; A = sal, L = py), containing unidentate sal (Table 3) was isolated. The spectra of the latter complex were very similar to that of complexes known to have structure (B),[1,14] and the n.m.r. data (Table 4) shows the 1 : 2 : 2 η-allyl splitting pattern expected for this ligand arrangement. This provides strong evidence that intermediate (B) is formed as a precursor of products (V).

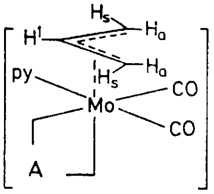
TABLE 4

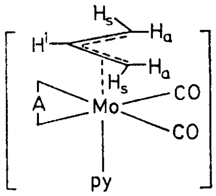
^{1}H N.m.r. data on the reaction products of $[MoX(\eta\text{-}C_3H_5)(CO)_2L_2]$ with three-electron donors

Complex	δ [a]/p.p.m.	Relative peak area	Assignment
(V; A = pd, L = py) [b]	1.42 (d)	2	H_a
	3.35 (m)	3	$H^1 + H_s$
	1.87 (s)	6	Me (pd)
	5.12 (s)	1	H (pd)
	7.35 (m), 7.78 (m), 8.35 (d)	5	H_m, H_p, H_o (py)
(V; A = $Me_2NCS_2^-$, L = py) [c]	1.32 (d)	2	H_a
	ca. 3.08 (d) [d]	2	H_s
	3.16 (s)	6	$Me(Me_2NCS_2)$
	4.14 (m)	1	H1
	7.36 (m), 7.84 (m), 8.72 (d)	5	H_m, H_p, H_o (py)
(V; A = sal, L = py) [e]	1.52 (m)	2	H_a
	3.18 (br, s)	1	H^1
	3.44 (br, s)	2	H_s
	7.20 (m), 6.72 (m), 8.40 (d)	5	H_m, H_p, H_o (py)
	6.37 (t), 6.72 (d), 6.98 (d), 7.20 (m)	4	H(aromatic) (sal)
	8.90 (s)	1	H(aldehyde) (sal)
(V; A = sal, L = bipy) [e]	1.30 (d)	2	H_a
	3.19 (s)	2	H_s
	3.52 (m)	1	H^1
	6.52 (t), 6.98 (d), 7.42 (m), 7.95 (m)	12	H(aromatic) (sal + bipy)
	8.50 (d), 8.85 (d), 9.03 (s)	1	H(aldehyde) (sal)

[a] Relative to $SiMe_4$. [b] In CD_2Cl_2. [c] In CD_3CN. [d] Partially obscured by the Me resonance; showed a slight temperature shift and was completely resolved at 60 °C. [e] In $CDCl_3$.

In view of the known crystal structures of both neutral and charged complexes referred to earlier, the most likely stereochemistries for (V) are (C) and (D). The n.m.r. spectra of complexes (V: A = pd, Me_2NCS_2, and sal; L = py) (Table 4) show the equivalence (in pairs) of the


(C)


(D)

A = pd, $MeNCS_2$, Et_2NCS_2, or sal

syn and *anti* protons of the allyl group as expected for structure (D) in which both donor centres of the chelating anionic ligand are equivalent or nearly so.* Further splitting of the allyl proton signals into five separate bands is expected for structure (C), as recently show in complexes of the type $[Pd(\eta\text{-}C_3H_5)(N\text{-}R\text{-}sal)]$.[24,†] Consequently, it is likely that the final products containing charged chelating ligands have structures closely analogous to the reactants containing uncharged bidentates (*i.e.* the chelate ligand *trans* to the carbonyl groups and *cis* to the η-allyl ligand), despite the initial replacement of halide ion *cis* to the carbonyl groups.

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* Although the two donor centres of sal are not completely equivalent, no splitting of individual *syn* and *anti* protons in the n.m.r. spectrum of $[Pd(\eta\text{-}C_3H_5)(sal)]$ was observed.[24]

† *N*-R-sal = *N*-Alkylsalicylideneiminato.

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