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Preliminary communication

Tris(η^4-1-oxa-1,3-diene)molybdenum and -tungsten: Preparation and properties of new homoleptic enone complexes

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Abstract

Homoleptic tris(η^4-1-oxa-1,3-diene)complexes of tungsten and molybdenum have been prepared in moderate to high yields starting from the α,β-unsaturated ketones **1–3** and tricarbonyltris(propionitrile)tungsten(0) or from **1** and η^6-benzenetricarbonylmolybdenum(0), respectively. The method is limited to enone ligands without substituents in the β-position. The new crystalline and air-stable yellow complexes have been characterized, and preliminary reactivity studies carried out. Their NMR-spectra show the compounds to have three-fold symmetry.

There have been only a few reports of organometallic compounds of chromium group metals containing η^4-bonded 1-oxa-1,3-dienes as ligands. The only homoleptic complexes of this type were prepared by King more than two decades ago [1]. Tris(but-3-en-2-one)tungsten was obtained in 60% yield and characterized by X-ray crystallography [2]. The corresponding molybdenum compound was formed in only 1.9% yield, the major product being a polymeric complex. A presumably polymeric carbonyl complex with propenal (acrolein) ligands has also been described [3] but monomeric complexes of the type $L_2M(CO)_2$ (M = Mo, W), for example with the chiral α,β-unsaturated ketone ligand (L) *R*-(+)-pulegone, became available only recently [4].

As a part of our research on the chemistry of enone complexes, we discovered that various α,β-unsaturated ketones without substituents in the β-position smoothly form homoleptic tris(enone)complexes with molybdenum and tungsten in yields of 42–80%. To produce the title complexes, a hexane suspension of η^6-benzenetricarbonylmolybdenum(0) or tricarbonyltris(propionitrile)tungsten(0) is heated to reflux with the appropriate α,β-unsaturated ketone in a molar ratio of about 1 : 3 (eqs. 1 and 2). The tris(enone)complexes are generated with liberation

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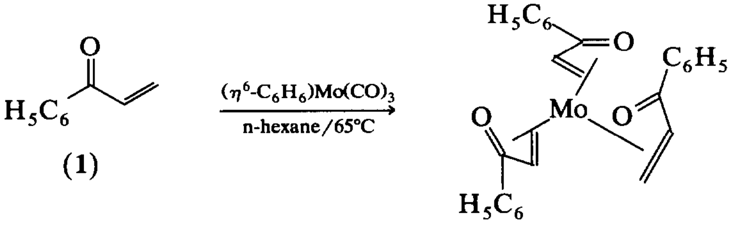
Table 1

Preparation and properties of tris(enone)complexes

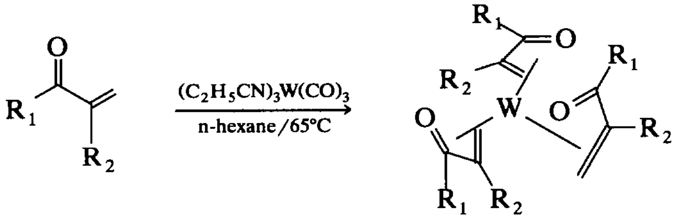
Metal	Enone	Complex	Scale (mmol)	Yield (%)	M.p. (°C)
Mo	1	**4**	3	64	160 (dec.)
			10	42	
W	1	**5**	3	80	160 (dec.)
			10	51	
W	3	**6**	3	62	165 (dec.)
W	4	**7**	3	57	190 (dec.)

of carbon monoxide. The reaction is thus one of the few examples in which all the carbon monoxide ligands are displaced from a chromium group metal by organic molecules to give an organometallic compound. As in the case of the but-3-en-2-one complexes [1], in all the complexation reactions described here the yields decrease with increased scale, as shown for complexes **4** and **5** in Table 1.



(4)

(1)



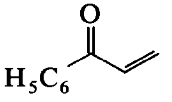
(2)

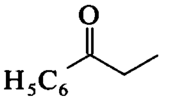
Enone	R_1	R_2	Complex
1	C_6H_5	H	5
2	C_6H_5	CH_3	6
3	CH_3	C_6H_5	7

It is especially remarkable that in the preparation of complex **4** even in the absence of an excess of the enone the benzene-complex is totally consumed during the reaction, reflecting the strong preference for formation of the homoleptic complex. Unfortunately, with enones **2** or **3** and benzenetricarbonylmolybdenum, mixtures of complexes are obtained, and these have not yet been separated and identified. Complexes **4–7** can be isolated as yellow, air-stable crystals, readily soluble in benzene, THF and CH_2Cl_2 but only slightly soluble in diethyl ether, hexane and ethanol. Whereas the tungsten complexes are stable in solution even under air, the solution of the molybdenum compound undergoes slow decomposition to give polymeric material. The phenyl-substituted ketones **1**–**3** were chosen as substrates for this preliminary investigation, because they are easily made by vacuum pyrolysis of Mannich base hydrochlorides [5]. The complexation reaction can, nevertheless, be extended to other ketones as long as they are not substituted in the β-position. In many of these cases, however, mixtures of products are formed, and these are currently under investigation [6].

From spectroscopic data the ligand arrangement in the new complexes appears to be similar to that in the crystallographically characterized tris(but-3-en-2-one)tungsten(0) [2]. In the ^{13}C NMR spectra, only one set of signals appears for all three enone ligands, which is consistent with the threefold symmetry of the complexes. The resonances of both the olefinic and the carbonyl carbon atoms undergo a large upfield complexation shift ($\Delta\delta$: 22–32 (C=O); 48–50 (C_α); 57–74 ppm (C_β)) that can be taken as indicating η^4-coordination of the unsaturated ketone [4]. Further evidence for this comes from the IR spectra, which show no absorptions between 1700 and 1620 cm^{-1}, strongly favouring a π-type complexation of the ketocarbonyl group. η^1-Bonded ketones, on the other hand, usually show only small shifts of the carbonyl stretching vibration [7].

With gram quantities of compounds **4**–**7** available, preliminary studies of their reactivity were undertaken. Reaction of **4** with carbon monoxide (60 bar, 85°C, 48 h) in a stainless steel autoclave in diethyl ether cleanly liberates the enone (94% purity), as shown by ^{1}H NMR-spectroscopic studies and GLC-analysis. Hexacarbonylmolybdenum is also formed, and was isolated in 90% yield (equation 3). Complexes of the type $L_2M(CO)_2$ (L = 1-oxa-1,3-diene) were not detected as intermediates in these reactions. In contrast to the behaviour of tris(η^4-1,3-butadien)molybdenum(0) [8], under similar conditions no coupling of the ligands was observed, a result again illustrating the different reactivities of diene and enone complexes. This may be due to the greater polarity of enones than of hydrocarbon 1,3-dienes. Reaction of the tungsten complex **5** with carbon monoxide under the same conditions gave a mixture of polymeric enone, hexacarbonyltungsten and insoluble tungsten compounds which were not characterized. When a solution of **4** or **5** in diethyl ether is stirred under hydrogen pressure (60 bar, 85°C, 48 h), reduction of the olefinic double bond of the enone occurs, to give the saturated ketone (equation 4).

4 $\xrightarrow[85°C,\ Et_2O]{CO(60\ bar)}$  + $Mo(CO)_6$ (3)

4 or **5** $\xrightarrow[85°C,\ Et_2O]{H_2(60\ bar)}$  (4)

Attempts to reduce the complexes with alkali metals in THF gave air-sensitive, deeply coloured ionic species, which have not yet been isolated or trapped. Cyclic voltammetry studies of **5** at room temperature revealed complex electrochemical behaviour partly due to the phenyl substituents, and showed that the reduction of the tris(enone)complex is not reversible under the conditions employed.

Experimental

All manipulations were carried out under argon by standard techniques. All solvents were distilled from $Na[Al(C_2H_5)_4]$ before use. η^6-Benzenetricarbonylmolybdenum(0) [9] and tricarbonyltris(propionitrile)tungsten(0) [10] were prepared by modifications of published methods. ^1H NMR spectra were recorded at 200.1 MHz, ^{13}C NMR spectra at 50.3 MHz on Bruker AC 200 instruments. The multiplicities of the ^{13}C NMR signals as derived from DEPT experiments are shown in brackets after the shift-values. Mass spectra were recorded on a Varian 311A, IR spectra on a Nicolet 7199 FT-IR instrument. Melting points were determined in closed capillary tubes under argon and are uncorrected. Microanalysis were performed by Dornis and Kolbe, Microanalytical Laboratory, Mülheim an der Ruhr.

Synthesis of tris(1-oxo-1-phenylprop-2-ene)molybdenum(0) (4)

A suspension of 2.58 g (10 mmol) of $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ and 3.96 g (30 mmol) of **1** in 120 ml of n-hexane was refluxed for 18 h. The solvent was then removed under reduced pressure and finally under high vacuum (10^{-4} mbar). The residue was washed with diethyl ether (100 ml) to leave a brown-yellow solid, which was further purified by continuous extraction with boiling diethyl ether through a bed of silica gel. The solvent was removed under reduced pressure to yield analytically pure **4**. Yield: 2.05 g (42%); M.p. 160°C (dec.); Anal. Found: C, 65.69; H, 4.96; Mo, 19.34%; $C_{27}H_{24}MoO_3$ calcd.: C, 65.86; H, 4.91; Mo, 19.48%. IR (KBr pellet): ν 1620, 1600, 1470, 1450 cm^{-1} (phenyl); 1505 cm^{-1} (C=C); ^1H NMR (benzene-d_6): δ 7.96 (m, C_6H_5-*o*, 6H), 7.12 (m, C_6H_5-*m,p*, 9H), 4.67 (m, α-vinyl, 3H), 2.29 (m, β-vinyl, 6H); ^{13}C NMR (benzene-d_6): δ 169.37 (s, CO), 135.39 (s), 131.65 (d, C_6H_5-*p*), 129.33 (d), 128.26 (d), 82.64 (d, C_α), 59.10 (t, C_β); MS (EI, 70 eV): *m/z* (rel. int.) 494 (9, M^+), 362 (25, $M^+ - C_9H_8O$), 105 (100, $C_6H_5CO^+$).

Synthesis of tris(1-oxo-1-phenylprop-2-ene)tungsten(0) (5)

To a suspension of 1.30 g (3.0 mmol) of $(CO)_3W(EtCN)_3$ in 50 ml of n-hexane was added 1.32 g (10 mmol) of **1**, and the mixture was stirred under reflux for 16 h, during which carbon monoxide was continuously liberated. The resulting dark red to brown suspension was evaporated to dryness and the residue washed with 20 ml of cold ether to give a dark yellow solid. Further purification was carried out by continuous extraction through silica gel with boiling diethyl ether. From the pale yellow extracts the analytically pure product was obtained by evaporation of the solvent under reduced pressure. Yield: 1.39 g (80%); M.p. 160°C (dec.); Anal. Found: C, 55.94; H, 4.21; W, 31.75%; $C_{27}H_{24}O_3W$ calcd.: C, 55.88; H, 4.17; W, 31.68%. IR (KBr pellet): ν 1600, 1580, 1477, 1447 cm^{-1} (phenyl); 1520 cm^{-1} (C=C); ^1H NMR (benzene-d_6); δ 7.96 (m, C_6H_5-*o*, 6H), 7.18 (m, C_6H_5-*m,p*, 9H), 5.01 (m, α-vinyl, 3H), 2.19 (m, β-vinyl, 3H), 1.90 (m, β-vinyl, 3H); ^{13}C NMR (benzene-d_6): δ 164.02 (s, CO), 134.80 (s), 131.41 (d, C_6H_5-*p*), 129.29 (d), 128.24 (d), 83.00 (d, C_α), 55.10 (t, C_β); MS (EI, 70 eV): *m/z* (rel. int.) 580 (18, M^+), 448 (30, $M^+ - C_9H_8O$), 105 (100, $C_6H_5CO^+$).

Synthesis of tris(1-oxo-2-methyl-1-phenylprop-2-ene)tungsten(0) (6)

This was prepared as described for **5** but with dichloromethane as the solvent for the extraction. Yield: 62%; M.p. 165°C (dec.); Anal. Found: C, 57.75; H, 4.89;

W, 29.66%; $C_{30}H_{30}O_3W$ calcd.: C, 57.89; H, 4.86; W, 29.54%. IR (KBr pellet): ν 2950 cm^{-1} (CH_3), 1600, 1560, 1483, 1439 cm^{-1} (phenyl), 1520 cm^{-1} (C=C); ^1H NMR ($CDCl_3$): δ 7.85 (m, C_6H_5-*o*, 6H), 7.39 (m, C_6H_5-*m,p*, 9H), 2.20 (s, CH_3, 9H), 1.91 (d, =CH_2, 3H), 1.69 (d, =CH_2, 3H), $^2J(HH) = 4.9$ Hz; ^{13}C NMR ($CDCl_3$): δ 158.68 (s, CO), 134.58 (s), 130.67 (d), 130.22 (d, C_6H_5-*p*), 127.77 (d), 95.49 (s, C_α), 68.99 (t, C_β), 19.59 (q, CH_3); MS (EI, 70 eV): m/z (rel. int.) 622 (7, M^+), 476 (15, $M^+ - C_{10}H_{10}O$), 105 (100, $C_6H_5CO^+$).

Synthesis of tris(3-phenylbut-3-en-2-one)tungsten(0) (7)

This was prepared as described for **6**. Yield: 57%; M.p. 190°C (dec.); Anal. Found: C, 58.06; H, 4.93; W, 29.62%; $C_{30}H_{30}O_3W$ calcd.: C, 57.89; H, 4.86; W, 29.54%. IR (KBr pellet): ν 2970 cm^{-1} (CH_3), 1600, 1575, 1480 cm^{-1} (phenyl), 1515 cm^{-1} (C=C); ^1H NMR ($CDCl_3$): δ 7.22 (m, C_6H_5, 15H), 2.40 (s, CH_3, 9H), 1.80 (d, =CH_2, 3H), 1.52 (d, =CH_2, 3H), $^2J(HH) = 5.5$ Hz; ^{13}C NMR ($CDCl_3$): δ 167.64 (s, CO), 138.52 (s), 130.67 (d), 127.90 (d), 127.23 (d, C_6H_5-*p*), 96.65 (s, C_α), 68.19 (t, C_β), 20.81 (q, CH_3); MS (EI, 70 eV): m/z (rel. int.) 622 (8, M^+), 476 (45, $M^+ - C_{10}H_{10}O$), 91 (100, $C_7H_7^+$).

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