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Novel (η^4-1-oxa-1,3-diene) complexes of molybdenum(0) and tungsten(0): compounds with *R*-(+)-pulegone ligands

Thomas Schmidt *, Carl Krüger and Peter Betz
Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, W-4330 Mülheim a.d. Ruhr 1 (Germany)

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Abstract

Starting from the chiral enone *R*-(+)-pulegone (**1**) the yellow, crystalline dicarbonylbis(η^4-1-oxa-1,3-diene) complexes $(pulegone)_2M(CO)_2$ (**2a**: M = Mo, **2b**: M = W) have been prepared by treatment with $(THF)_3Mo(CO)_3$ and $(C_2H_5CN)_3W(CO)_3$, respectively. The α,β-unsaturated ketone is η^4-bonded, as shown by X-ray crystallographic investigation of the tungsten complex **2b** and ^{13}C NMR spectroscopic data. Only one stereoisomer of the complex is formed. Both the enone ligands in **2b** can readily be substituted by trimethylphosphane in a photoinduced reaction, producing the known complex *cis*-$(OC)_2W(P(CH_3)_3)_4$ (**3**).

Introduction

Carbonyl transition metal complexes of η^4-bonded hetero-1,3-dienes, in particular α,β-unsaturated ketones and imines, have been known for a long time for iron as the coordinating metal [1]. They have been used to transfer tricarbonyliron groups to other η^4-diene ligands [2], and they readily react with carbon nucleophiles to form 1,4-diketones with carbon monoxide insertion, as recently demonstrated by Thomas [3]. For metals of the chromium group only very few complexes of this kind are known so far, e.g. the homoleptic complexes of but-3-en-2-one (methyl vinyl ketone) with molybdenum(0) and tungsten(0) [4a] and some polymeric complexes of unsaturated aldehydes [4b].

In the course of our research directed towards the reactivity of metal-coordinated heterodienes we have been interested in new model complexes suitable for intramolecular carbon–carbon coupling reactions of the metal-bound ligands. In this connection we have found a promising type of complex $L_2M(CO)_2$ (L = 1-oxa-1,3-diene, M = Mo, W). Only a few similar complexes derived from conjugated and nonconjugated hydrocarbon diene ligands have been reported previously, e.g. the compounds with cyclohexa-1,3-diene, butadiene, and norbornadiene [5]. In the following we report on the synthesis and characterization of such compounds derived from the chiral 1-oxa-1,3-diene *R*-(+)-pulegone (**1**) [6*,7*].

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* Reference number with asterisk indicates a note in the list of references.

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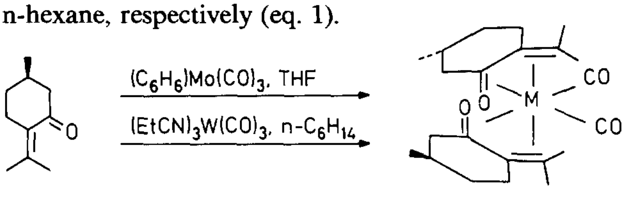
Results and discussion

Complexes **2a** and **2b** were prepared in high yields starting from **1** by treatment with the solvent complex tricarbonyltris(tetrahydrofuran)molybdenum(0) [8] that can be obtained *in situ* from η^6-benzenetricarbonylmolybdenum(0) and tetrahydrofuran (THF) at 5 ° C or with tricarbonyltris(propionitrile)tungsten(0) [9] in refluxing n-hexane, respectively (eq. 1).



1 **2a**, M = Mo; **2b**, M = W (1)

Both compounds form yellow crystals which are very soluble in many polar and non-polar organic solvents, but are reasonably stable only in hydrocarbons under inert atmosphere. The products obtained are homogeneous, and of the several theoretically possible coordination isomers only one has been observed so far. A by-product of the complexation reaction is the corresponding metalhexacarbonyl as would be predicted from the stoichiometry of the reaction, which can be idealized as shown in eq. 2, where L_3M means $(\eta^6\text{-}C_6H_6)Mo$ or $(C_2H_5CN)_3W$, and P is *R*-(+)-pulegone (**1**). No gaseous carbon monoxide is liberated during complexation.

$$4\ L_3M(CO)_3 + 6\ P \rightarrow 3\ P_2M(CO)_2 + M(CO)_6 + 12\ L \qquad (2)$$

The presence of a dicarbonylmetal sub-unit in the pulegone complexes becomes evident from the IR spectra showing two strong bands at ν(CO) 1936 and 1850 cm^{-1} (M = Mo) and ν(CO) 1935 and 1840 cm^{-1} (M = W). The ^{13}C NMR spectra data give some support for the η^4-coordination of the enone ligands. All the sp^2 carbon resonances are shifted markedly towards higher field compared to those for the free ligand [10*]. The resonances of the ketone carbons are found at δ 180.54 (M = Mo) and δ 175.45 (M = W). The signal positions for the olefinic carbons are influenced even more drastically by complexation. These shifts have average values [11*] of $\Delta\delta = 51.5$ for the molybdenum and $\Delta\delta = 57.9$ for the tungsten compound. Proton and carbon NMR spectra demonstrate the symmetry of both complexes in solution at room temperature; only one set of ligand signals being observed in each case. ^1H and ^{13}C NMR spectra remain unchanged at temperatures as low as −80 ° C in THF-d_8 solution. Mass spectra and elemental analyses of **2a** and **2b** are consistent with the formulation of the compounds as $(pulegone)_2M(CO)_2$.

Crystals suitable for an X-ray diffraction study were obtained from the tungsten compound **2b** by slowly evaporating a concentrated solution in n-pentane under reduced pressure at room temperature. The molecular structure is depicted in Fig. 1. The coordination geometry of the tungsten atom can best be described as distorted trigonal prismatic. This is illustrated in Fig. 2. The basis planes of the coordination polyhedron are defined by the carbon atoms of the CO ligands and the midpoints of the ketone- and ene-functions of both pulegone ligands [12*]. The molecule contains a noncrystallographically-caused twofold rotational axis along the bisector of the angle C21–W–C22.

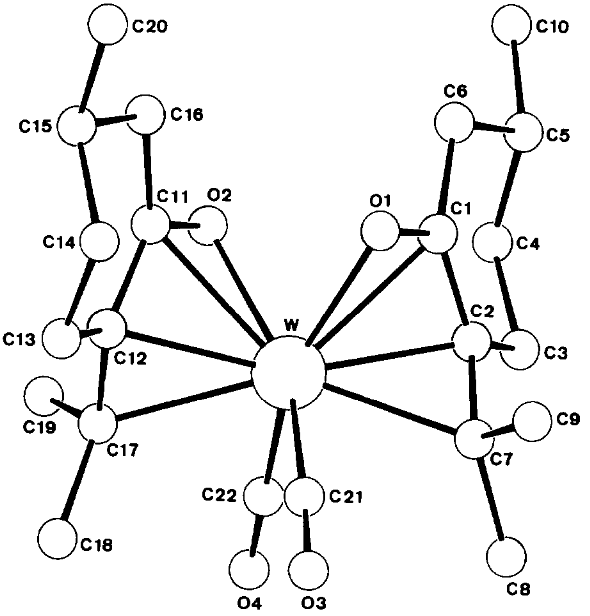


Fig. 1. Structure of (η^4-*R*-(+)-pulegone)$_2$W(CO)$_2$ (**2b**).

The distances of the O=C–C=C units from the central tungsten atom vary between 2.19(1) or 2.18(1) Å (W–O1, W–O2) and 2.386(8) or 2.376(8) Å (W–C1, W–C11). The coordination geometry is more distorted in the region of the C=O groups than at the olefinic C=C bonds. Bond distances within the O=C–C=C unit (see Table 2 for details) are markedly different from those for a known tungsten enone complex, i.e. tris(but-3-en-2-one)tungsten(0) [13]. Whereas complex **2b** exhibits a moderately shortened single bond (1.42(1) and 1.41(1) Å) and a relatively long coordinated C=C bond (1.47(1), 1.47(1) Å), the trisbutenone complex is characterized by a very short C–C bond (1.32(4) Å), which has previously [13] been taken as indication of a 1,4-σ/2,3-π type coordination, and a C=C bond length (1.45(4) Å) similar to that observed in **2b**. Another obvious difference from the above complex is a clear bending of the enone system in the pulegone tungsten compound **2b**, which gives rise to a torsional angle (O=C–C=C) of 18.7°. This can be taken as additional support for the more pronounced single bond character of

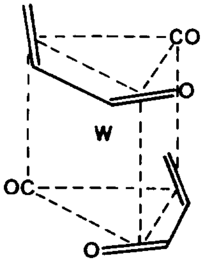


Fig. 2. Coordination scheme of **2b**.

Table 1

Specific rotation values [a] for **2a** and **2b** at various wavelengths in cyclohexane

	c [mg/l]	$[\alpha]^{20}_{\lambda}$					
		λ [nm]	589	578	546	436	365
2a	415		+400	+370	+205	–	–
	285		–	–	–	+5950	+10900
2b	400		+130	+80	−150	+7200	+12900

[a] $[\alpha]^{20}_{\lambda}$ in $[10^{-2}$ deg m^2 $kg^{-1}]$.

the central C–C bond in **2b**. The compound gives monoclinic crystals, with space group $P2_1$. The absolute structure was determined by refining the κ-parameter as described by Flack [14].

Polarimetric measurements on both of the pulegone complexes show relatively large values for the specific rotation although, due to the intense absorbance of the solutions, measurements had to be performed at high dilution and therefore may be less exact. Results for cyclohexane solutions are summarized in Table 1. The analogous optical behaviour of **2a** and **2b** presents further evidence for their structural similarity. The complexation reaction is found to be highly diastereoselective. By assuming a stepwise mechanism, this can be understood in terms of a strong stereodirecting influence of the initially coordinated pulegone ligand.

Table 2

Selected bond distances (Å) and angles (°) in **2b**

W–O(1)	2.19(1)	C(22)–W–C(21)	86.2(4)
W–O(2)	2.18(1)	C(17)–W–C(12)	37.1(3)
W–C(1)	2.386(8)	C(17)–W–O(1)	135.3(3)
W–C(2)	2.274(8)	C(17)–W–C(7)	146.7(3)
W–C(7)	2.317(9)	C(12)–W–C(11)	35.1(3)
W–C(11)	2.376(8)	C(11)–W–O(2)	34.0(3)
W–C(12)	2.299(8)	C(7)–W–C(2)	37.2(3)
W–C(17)	2.339(8)	C(7)–W–O(2)	135.7(3)
W–C(21)	1.960(9)	C(2)–W–C(1)	35.3(3)
W–C(22)	1.964(9)	C(1)–W–O(1)	33.9(3)
O(1)–C(1)	1.35(1)	O(2)–W–O(1)	79.3(4)
O(2)–C(11)	1.34(1)	C(6)–C(1)–C(2)	124.3(7)
O(3)–C(21)	1.17(1)	C(6)–C(1)–O(1)	118.0(8)
O(4)–C(22)	1.16(1)	C(2)–C(1)–O(1)	117.6(8)
C(1)–C(2)	1.42(1)	C(7)–C(2)–C(3)	123.5(7)
C(1)–C(6)	1.48(1)	C(7)–C(2)–C(1)	116.9(7)
C(2)–C(3)	1.51(1)	C(3)–C(2)–C(1)	118.8(7)
C(2)–C(7)	1.47(1)	C(9)–C(7)–C(2)	119.0(8)
C(11)–C(12)	1.41(1)	C(8)–C(7)–C(2)	116.3(7)
C(11)–C(16)	1.51(1)	C(16)–C(11)–C(12)	121.6(8)
C(12)–C(13)	1.48(1)	C(16)–C(11)–O(2)	119.9(8)
C(12)–C(17)	1.47(1)	C(12)–C(11)–O(2)	118.1(8)
		C(17)–C(12)–C(13)	123.0(7)
		C(17)–C(12)–C(11)	115.5(8)
		C(13)–C(12)–C(11)	121.0(7)
		C(19)–C(17)–C(12)	118.7(7)
		C(18)–C(17)–C(12)	116.2(7)

Table 3

Details of the crystal structure investigation of **2b**

Formula	$C_{22}H_{32}O_4W$
Mw	544.3
Space group	$P2_1$
a (Å)	9.799(2)
b (Å)	10.459(1)
c (Å)	11.579(3)
β (°)	111.23(1)
V (Å^3)	1106.0
d_{calc} (g cm^{-3})	1.63
μ (cm^{-1})	53.53
Z	2
λ (Å)	0.71069
Measured reflections	3520 ($\pm h$, $+k$, $+l$)
Sin θ/λ_{max}	0.70
Empirical abs. corr. (min–max)	0.889–1.000
Independent reflections	3379
Observed reflections	3090
Refined parameters	244
R	0.029
R_w	0.029
ρ_{max} (e Å^{-3})	2.98

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 54064, the name of the authors, and the journal citation.

In a photoinduced process the tungsten complex **2b** can be converted into a phosphane complex with octahedral coordinated tungsten. On irradiation of a dilute etheral solution of **2b** (Sunlamp Osram 250W, DURAN-filtered, −30 °C) in the presence of an excess of trimethylphosphane both the pulegone ligands are replaced by phosphane, to give a microcrystalline product with a high melting point (Eq. 3). From its analytical data it can be identified as the known *cis*-dicarbonyltetrakis(trimethylphosphane)tungsten(0) [15].

$$\mathbf{2b} \xrightarrow{PMe_3,\ Et_2O,\ -30\,°C,\ h\nu} \underset{\mathbf{3}}{cis\text{-}(OC)_2W(PMe_3)_4} \qquad (3)$$

The ^{31}P NMR spectum of **3** shows an A_2B_2 system for the four phosphane ligands, two of which are coordinated to the tungsten atom in axial and equatorial positions, respectively. No formation of the isomeric *trans* complex was observed in the above reaction.

Further investigations of the reactions of the new pulegone complexes are in progress.

Experimental

All manipulations were carried out under argon by standard techniques. All solvents were distilled from $NaAl(C_2H_5)_4$ before use. η^6-Benzenetricarbonylmo-

Table 4

Atomic fractional coordinates and equivalent isotropic thermal parameters (Å^2) for **2b** [a]

Atom	x	y	z	U_{eq}
W	0.8393(1)	0.7529	0.6942(1)	0.035(1)
O(1)	0.647(1)	0.877(1)	0.6256(9)	0.050(6)
O(2)	0.665(1)	0.6117(9)	0.6471(9)	0.046(5)
O(3)	1.0748(7)	0.9342(7)	0.8735(6)	0.059(5)
O(4)	1.1035(7)	0.5960(7)	0.6800(6)	0.063(5)
C(1)	0.6518(8)	0.8390(9)	0.5163(7)	0.042(5)
C(2)	0.7899(8)	0.8394(9)	0.5031(7)	0.047(5)
C(3)	0.8033(8)	0.779(1)	0.3896(7)	0.048(7)
C(4)	0.6743(9)	0.6928(9)	0.3236(8)	0.054(6)
C(5)	0.5291(8)	0.756(2)	0.2981(6)	0.054(5)
C(6)	0.5153(7)	0.7911(8)	0.4212(7)	0.049(6)
C(7)	0.9050(9)	0.9177(8)	0.5912(8)	0.044(5)
C(8)	1.0561(9)	0.9139(9)	0.5784(9)	0.052(6)
C(9)	0.871(1)	1.0552(9)	0.6137(9)	0.059(7)
C(10)	0.401(1)	0.678(1)	0.2180(9)	0.075(8)
C(11)	0.6612(8)	0.6503(9)	0.7568(8)	0.045(5)
C(12)	0.7954(8)	0.6610(9)	0.8577(7)	0.044(5)
C(13)	0.8028(9)	0.7229(9)	0.9750(7)	0.050(7)
C(14)	0.6699(9)	0.8056(9)	0.9584(8)	0.057(6)
C(15)	0.5303(9)	0.732(1)	0.8955(9)	0.055(8)
C(16)	0.5184(9)	0.694(1)	0.7661(9)	0.060(7)
C(17)	0.9197(9)	0.5919(8)	0.8439(7)	0.043(5)
C(18)	1.0670(9)	0.6089(9)	0.9480(9)	0.049(6)
C(19)	0.898(1)	0.4543(9)	0.8008(9)	0.062(7)
C(20)	0.395(1)	0.812(1)	0.888(1)	0.09(1)
C(21)	0.9874(9)	0.8684(9)	0.8038(8)	0.048(6)
C(22)	1.0044(9)	0.6530(9)	0.6843(8)	0.047(6)

[a] $U_{eq} = 1/3\, \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

lybdenum [8] and tricarbonyltris(propionitrile)tungsten(0) [9] were prepared by modifications of published methods. ^{1}H NMR spectra were recorded at 200.1 MHz, ^{13}C NMR spectra at 50.3 MHz, and ^{31}P NMR spectra at 81.0 MHz, all on Bruker AC 200 instruments. The multiplicities of the ^{13}C NMR signals as obtained from DEPT experiments are given in brackets after the shift values. Mass spectra were recorded on a Varian 311 A, IR spectra on a Nicolet 7199 FT-IR instrument and polarimetric measurements were performed on a Perkin Elmer Polarimeter 241. Melting points were determined in closed capillary tubes under argon and are uncorrected. Microanalyses were performed by Dornis and Kolbe, Microanalytical Laboratory, Mülheim a.d. Ruhr.

*Synthesis of dicarbonylbis(η^4-pulegone)molybdenum(0) (**2a**)*

258 mg (1.0 mmol) of (η^6-C_6H_6)Mo(CO)$_3$ were dissolved in 3 ml of THF to give a pale yellow solution. Cooling to 5 °C gave a pale yellow to greenish precipitate of the solvent complex. After dropwise addition of 304 mg (2.0 mmol) of *R*-(+)-pulegone the solution immediately turned clear and dark red. After 6 h stirring at room temperature, the mixture was evaporated to dryness under reduced pressure. The yellow to brown solid residue was recrystallized from a small amount of n-pentane to yield yellow, analytically pure, crystals of **2a** (340 mg, 75%). M.p. 56–58 °C

(dec.); Anal. Found: C, 57.56; H, 7.06%; $C_{22}H_{32}O_4Mo$ calcd.: C, 57.89; H, 7.07%. IR (KBr pellet): ν 1936, 1850 cm^{-1} (CO); ^1H NMR (benzene-d_6): δ 2.64–2.30 (m, 3H), 2.15–2.00 (m, 1H), 1.88, 1.63 (s, $=C(CH_3)_2$, 6H) 1.70–1.55 (m, 3H) 0.85 (d, ^3J(HH) 5.5 Hz, CH_3, 3H); ^{13}C NMR (benzene-d_6) δ 232.69 (s, CO), 180.54 (s, CO ketone), 87.39 (s), 82.37 (s), 42.45 (t), 31.50 (t), 30.08 (d), 29.07 (t), 27.02 (q), 22.26 (q), 21.69 (q); MS (EI, 70 eV): m/z (rel. int.) 458 (4, M^+), 430 (5, $M^+ - CO$), 152 (89, $C_{10}H_{16}O^+$), 81 (100).

*Synthesis of dicarbonylbis(η^4-pulegone)tungsten(0) (**2b**)*

1.824 g (12 mmol) of *R*-(+)-pulegone were added dropwise to a stirred yellow suspension of 2.165 g (5 mmol) $(C_2H_5CN)_3W(CO)_3$ in 40 ml n-hexane. The mixture was heated under reflux, gradually turning red. After 72 h the hot suspension was filtered through a plug of glass wool. The filtrate was evaporated to dryness under reduced pressure to remove the solvent and liberated propionitrile. Remaining traces of volatile compounds ($W(CO)_6$ and propionitrile) were removed under high vacuum (10^{-4} mbar) at 60 ° C. The yellow to brown, solid residue was recrystallized from n-pentane. Cooling to −78 ° C gave yellow crystals of **2b** in analytically pure form (1.52 g, 56%). M.p. 95–96 ° C; Anal. Found: C, 48.66; H, 6.11%; $C_{22}H_{32}O_4W$ calcd.: C, 48.54; H, 5.93%. IR (KBr pellet): ν 1935, 1840 cm^{-1} (CO); ^1H NMR (benzene-d_6): δ 2.60–2.05 (m, 4H), 2.03, 1.76 (s, $=C(CH_3)_2$, 6H), 1.65–1.43 (m, 3H), 0.84 (d, ^3J(HH) 5.3 Hz, CH_3, 3H); ^{13}C NMR (benzene-d_6) δ 224.80 (s, CO), 175.45 (s, CO ketone), 85.88 (s), 71.00 (s), 41.64 (t), 31.31 (t), 29.97 (d), 28.40 (t), 27.00 (q), 21.58 (q), 21.14 (q); MS (EI, 70 eV): m/z (rel. int.) 544 (22, M^+), 486 (51, $M^+ - 2$ CO), 152 (52, $C_{10}H_{16}O^+$), 81 (100).

*Structure determination of **2b***

A single crystal was mounted in a capillary under argon. Unit cell parameters were determined and intensity data collected on an Enraf–Nonius CAD 4 diffractometer using Mo-K_α radiation. Crystallographic data are summarized in Table 3, selected bond distances and angles in Table 2, atomic coordinates and thermal parameters in Table 4.

*Structure solution and refinement of **2b***

The structure of **2b** was solved by the heavy atom method. Hydrogen atom positions were calculated and kept fixed during final refinement.

*Reaction of **2b** with $P(CH_3)_3$ under irradiation*

A solution of 136 mg (0.25 mmol) **2b** in 40 ml diethyl ether was cooled to −30 ° C in a 100 ml DURAN round bottom flask. 200 mg (2.55 mmol) of trimethylphosphane were added and the stirred yellow solution was irradiated with light from two 250W Sunlamps (OSRAM) at a distance of about 20 cm. The solution was kept at between −20 ° C and −30 ° C by means of a methanol/dry-ice bath. After 60 min of irradiation, none of the starting material **2b** could be detected by TLC (pentane/ether 9 : 1). The slightly cloudy solution was warmed to room temperature, filtered through a plug of glass wool, and evaporated. The oily orange brown residue was dissolved in 10 ml of benzene and the solution filtered through 2 cm of neutral alumina. The filtrate was evaporated and the residue once washed with n-pentane, to yield a pale brown powder of pure *cis*-$(OC)_2W(P(CH_3)_3)_4$ (**3**)

(100 mg, 73%); m.p. ≈ 280 °C; ^{1}H NMR (benzene-d_6): δ 1.51 (m, 18H), 1.17 (m, 18H); ^{13}C NMR (benzene-d_6): δ 216.78, 25.88, 24.95 (complex spin system); ^{31}P NMR (benzene-d_6, 85% H_3PO_4 as reference): δ -36.6, -38.8 (A_2B_2 system, ^2J(PP) 19.7 Hz); MS (EI, 70 eV): m/z (rel. int.) 544 (18, M^+), 468 (18, M^+- $P(CH_3)_3$), 61 (100, $P(CH_3)_2^+$).

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