

# Ruthenium maltolato complexes

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**Two maltol molecules can be deprotonated and coordinated to Ru<sup>II</sup> to generate a series of octahedral complexes having the general formula Ru(ma)<sub>2</sub>L<sub>2</sub> (ma = C<sub>6</sub>H<sub>5</sub>O<sub>3</sub>; L = PPh<sub>3</sub>, Me<sub>2</sub>SO; L<sub>2</sub> = cycloocta-1,5-diene); when L = PPh<sub>3</sub>, a precursor for the dimerization of phenylacetylene is obtained.**

Maltol **1** is a naturally occurring, water-soluble, non-toxic food additive.<sup>1</sup> When deprotonated (pK<sub>a</sub> = 8.38),<sup>2</sup> it forms an anionic system capable of acting as a chelating, bidentate, O,O' ligand of the type shown as **2**.

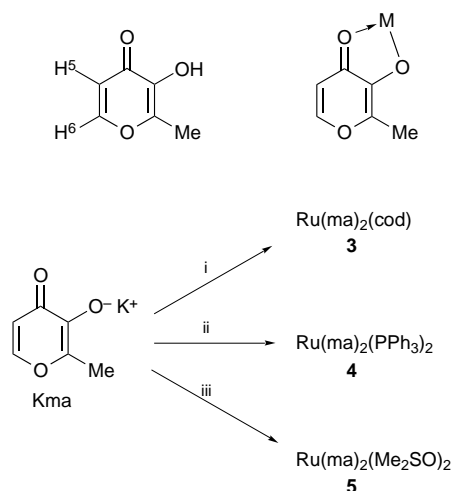
Because this ligand can confer water solubility on its metal complexes, even when the complexes are uncharged, there have been many reports on the use of this ligand in biological studies. For example, Al(ma)<sub>3</sub> has been used in studies related to Alzheimer's disease,<sup>3</sup> Fe(ma)<sub>3</sub> has been found to have potential as a treatment for iron-deficiency anaemia<sup>4</sup> and VO(ma)<sub>2</sub> has been tested as an insulin mimetic.<sup>5–7</sup> However, little work has been done on the use of this ligand in organometallic type complexes or in homogeneous catalysis.<sup>8–10</sup> Here we report the preparation and structure of a series of octahedral bis(maltolato) complexes of ruthenium<sup>11</sup> and show that one of these complexes shows activity for the dimerization of phenylacetylene.

The reaction of potassium maltolate, Kma (prepared by the addition of KOBu<sup>t</sup> to **1** in Et<sub>2</sub>O), with a variety of ruthenium(II) complexes in organic solvents proved to be successful as a preparative route for the incorporation of the maltolato ligand. Thus, reaction of Kma with [Ru(cod)Cl<sub>2</sub>]<sub>x</sub> in thf led to the formation of Ru(ma)<sub>2</sub>(cod) **3** as orange-red crystals in 95% yield; similarly, addition of Kma to RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> and RuCl<sub>2</sub>(Me<sub>2</sub>SO)<sub>4</sub> generated Ru(ma)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> **4** and Ru(ma)<sub>2</sub>(Me<sub>2</sub>SO)<sub>2</sub> **5**, respectively. These reactions are outlined in Scheme 1.

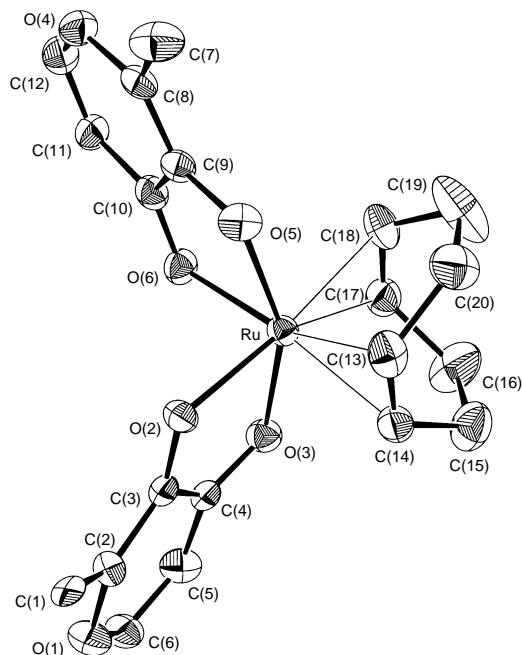
The solid-state structures of the cod complex **3** and the bis(dimethyl sulfoxide) derivative **5** were obtained and are shown in Figs. 1 and 2 respectively, along with selected bond lengths and angles.<sup>†</sup> Complex **3** is the first alkene complex of

ruthenium(II) having only oxygen donors as ancillary ligands to be structurally characterized. Both structures display similar *cis* octahedral geometries; in fact upon close examination of the two structures in the solid state, the same C<sub>1</sub> molecular symmetry is found for each derivative. Because the maltolato ligand has two different oxygen donors, it can be considered as an anionic AB bidentate ligand; for an octahedral molecule having the general formula M(AB)<sub>2</sub>L<sub>2</sub> (L = monodentate ligand), such a complex can exist in five stereoisomeric forms (*trans* and *cis* descriptors refer to disposition of L<sub>2</sub>): two *trans* stereoisomers with C<sub>2h</sub> and C<sub>2v</sub> symmetry, respectively and three *cis* stereoisomers two of which have C<sub>2</sub> symmetry while the last is completely asymmetric (C<sub>1</sub>). For the situation where L<sub>2</sub> is a symmetrical bidentate ligand, such as cod, only the three *cis* isomers are possible.

From the NMR spectroscopic data, the solid-state structure of **3** is maintained in solution such that only one species is observed and it displays peaks characteristic of a molecule with low symmetry. On the other hand, the bis(phosphine) complex **4** exists as a mixture of three of the possible five stereoisomers; one isomer shows two inequivalent phosphines by <sup>31</sup>P{<sup>1</sup>H}-NMR spectroscopy and resonances in the <sup>1</sup>H NMR spectrum that compare to the asymmetric *cis* isomer found for **3** above. The remaining two stereoisomers of **4** have equivalent phosphines and equivalent maltolato ligands and thus could either



**Scheme 1** Reagents and conditions: i, [Ru(cod)Cl<sub>2</sub>]<sub>x</sub>, thf, 65 °C, 16 h; ii, RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, thf, 22 °C, 16 h; iii, RuCl<sub>2</sub>(Me<sub>2</sub>SO)<sub>4</sub>, toluene, 90 °C, 16 h

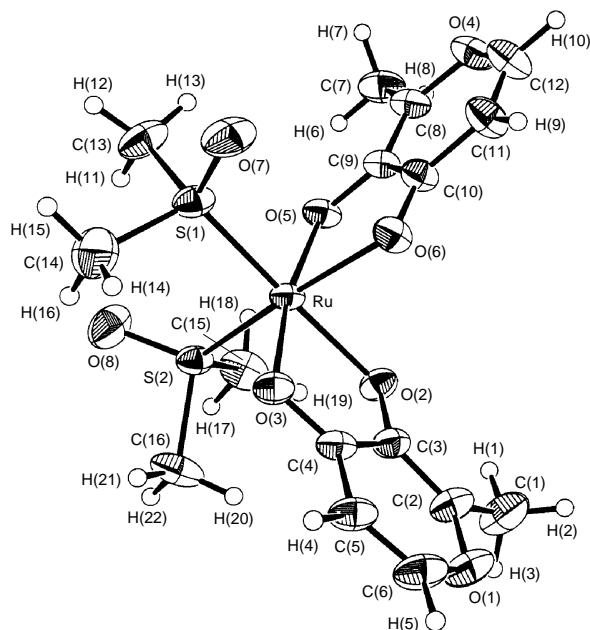


**Fig. 1** X-Ray crystal structure of Ru(ma)<sub>2</sub>(cod) (**3**) (ellipsoids drawn at the 33% probability level). Selected interatomic distances (Å) and bond angles (°): Ru–O(2) 2.126(4), Ru–O(3) 2.098(5), Ru–O(5) 2.072(4), Ru–O(6) 2.114(4), Ru–C(13) 2.138(5), Ru–C(14) 2.157(7), Ru–C(17) 2.153(7), Ru–C(18) 2.161(6), O(2)–C(3) 1.306(7), O(3)–C(4) 1.288(7), C(3)–C(4) 1.43(1), O(5)–C(9) 1.335(7), O(6)–C(10) 1.262(9), C(9)–C(10) 1.45(1), C(13)–C(14) 1.34(2), C(17)–C(18) 1.46(1); O(2)–Ru–O(3) 79.5(2), O(5)–Ru–O(6) 79.5(2), O(3)–Ru–O(5) 156.0(2), O(2)–Ru–O(6) 92.7(2).

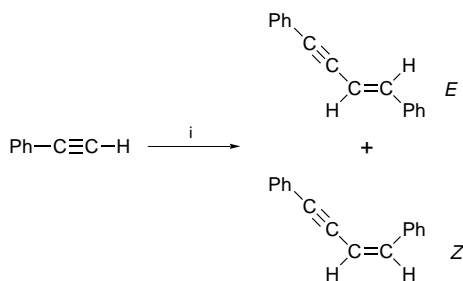
have *trans* or *cis* geometries. The situation for the Me<sub>2</sub>SO complex is more complex since isomers are also apparent in the crude reaction mixture but their <sup>1</sup>H NMR spectra overlap too much to be able to distinguish them.

While homoleptic maltolato complexes, M(ma)<sub>n</sub>, are generally water soluble we found that only the bis(dimethyl sulfoxide) complex **5** exhibited any water solubility;<sup>10</sup> both the cod derivative **3** and the bis(phosphine) **4** were insoluble in H<sub>2</sub>O. These complexes also displayed differences in their reactivity patterns. In this case, addition of phenylacetylene to either the cod complex **3** or the bis(dimethyl sulfoxide) **5** led to no reaction and recovery of starting materials. However, the bis(phosphine) derivative **4** was found to dimerize PhC≡CH to give the two possible linear isomers in a 1:1 ratio with turnover rates of ca. 20 h<sup>-1</sup> (Scheme 2).

Attempts to detect intermediates in this process by monitoring the reaction by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy were unsuccessful; however, when the dimerization was performed in the presence of excess PPh<sub>3</sub> the rate of the dimerization reaction was noticeably retarded. Thus, phosphine dissociation from **4** is



**Fig. 2** X-Ray crystal structure of Ru(ma)<sub>2</sub>(Me<sub>2</sub>SO)<sub>2</sub> **5** (ellipsoids drawn at the 33% probability level). Selected interatomic distances (Å) and bond angles (°): Ru–O(2) 2.106(2), Ru–O(3) 2.090(2), Ru–O(5) 2.078(2), Ru–O(6) 2.105(2), O(2)–C(3) 1.311(3), O(3)–C(4) 1.277(3), C(3)–C(4) 1.447(4), O(5)–C(9) 1.314(3), O(6)–C(10) 1.266(4), Ru–S(1) 2.2068(8), Ru–S(2) 2.1957(8), S(1)–O(7) 1.474(2), S(2)–O(8) 1.470(2); S(1)–Ru–S(2) 96.25(3), O(2)–Ru–O(3) 80.56(7), O(5)–Ru–O(6) 81.07(8), O(3)–Ru–O(5) 169.81(8), O(2)–Ru–O(6) 85.33(8).



**Scheme 2** Reagents and conditions: i, 1 mol% Ru(ma)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> **4**, 50 °C, toluene: E:Z ratio = 1:1

required for activity, and this is reasonable given that this 18-electron complex contains two rather large, monodentate ligands. One can speculate further that the mechanism of alkyne dimerization involves a vinylidene intermediate<sup>12,13</sup> as required for the production of both *E* and *Z* isomeric forms of the enyne product. Internal alkynes were generally found to be unreactive with all three of the bis(maltolato) complexes of Ru.

In this study we have demonstrated that organometallic type complexes and catalytic activity can be observed for Ru derivatives that are stabilized by the maltolato ancillary ligand. In addition, the cyclooctadiene complex **3** represents the first reported alkene-type complex of Ru stabilized by only oxygen donor ligands.

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## Footnote

† *Crystal data:* **3**, C<sub>20</sub>H<sub>22</sub>O<sub>6</sub>Ru, *M* = 459.46, orthorhombic, space group *Pna*2<sub>1</sub> (no. 33), *a* = 16.542(2), *b* = 9.684(2), *c* = 11.480(8) Å, *U* = 1839.2(6) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.659 g cm<sup>-3</sup>, μ(Mo-Kα) = 8.68 cm<sup>-1</sup>, *F*(000) = 936. An orange-red prism of dimensions 0.10 × 0.10 × 0.15 mm was used. 3755 reflections were measured on a Rigaku AFC6S with Mo-Kα radiation using ω–2θ scans. The structure was solved by Patterson methods using full-matrix least-squares on *F* for all non-hydrogen atoms using Lorentz polarization and absorption corrections to give *R* = 0.034 and *R*<sub>w</sub> = 0.029 for 1775 independent observed reflections with *I* > 3σ(*I*) and 244 variables for 2θ<sub>max</sub> = 65°.

**5**, C<sub>16</sub>H<sub>22</sub>O<sub>8</sub>RuS<sub>2</sub>·2.5C<sub>6</sub>H<sub>6</sub>, *M* = 702.82, triclinic, space group *P*1̄ (no. 2), *a* = 12.015(2), *b* = 16.509(2), *c* = 8.7933(8) Å, α = 99.853(9), β = 100.225(9), γ = 94.28(1)°, *U* = 1681.2(4) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.388 g cm<sup>-3</sup>, μ(Mo-Kα) = 6.19 cm<sup>-1</sup>, *F*(000) = 726. An orange prism of dimensions 0.30 × 0.35 × 0.45 mm was used. 8104 reflections were measured of which 7729 were unique using a Rigaku AFC6S with Mo-Kα radiation using ω–2θ scans. The structure was solved using direct methods using full-matrix least squares on *F* for all non-hydrogen atoms using Lorentz polarization and absorption corrections to give *R* = 0.038 and *R*<sub>w</sub> = 0.043 for 5946 independent observed reflections with *I* > 3σ(*I*) and 379 variables for 2θ<sub>max</sub> = 55°. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/293.

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