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# Spontaneous disproportionation of rhodium(I) bisoxazolinates to rhodium(II)†

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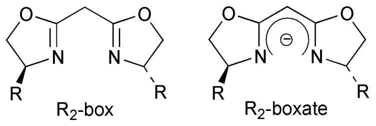
**[Rh$^{I}$(*t*-Bu$_2$-boxate)(C$_2$H$_4$)$_2$] spontaneously disproportionates to the mononuclear [Rh$^{II}$(*t*-Bu$_2$-boxate)$_2$], whereas [Rh$^{I}$(Ph$_2$-boxate)(C$_2$H$_4$)$_2$] is stable against disproportionation.**

Over the last decade chiral $C_2$-symmetric bisoxazoline (box) ligands have been established as valuable ligands for a range of catalytic enantioselective reactions, including cyclopropanation and aziridination of olefins and imines, oxidation, and allylic substitution.[1] Although most attention has been dedicated to the neutral bisoxazoline ligands, encouraging results were also obtained with the anionic bisoxazolinates (boxates) (Scheme 1).[2,3]

In this communication we report on two bisoxazolinate rhodium bis(ethene) complexes [Rh(Ph$_2$-boxate)(ethene)$_2$] **1** (R = phenyl) and [Rh(*t*-Bu$_2$-boxate)(ethene)$_2$] **2** (R = *t*-butyl). These were obtained as part of an ongoing study into the reactivity of rhodium diiminate complexes.[4]

The bis(ethene) complexes were readily obtained in high yield by conversion of the neutral ligands into their lithium salts with LDA in THF, followed by reaction of the obtained lithium salts with [Rh(μ-Cl)(C$_2$H$_4$)$_2$]$_2$ in THF.†[5] Complex **1** proved stable in THF. Its crystal structure is shown in Fig. 1.

The structure shows that both ethenes are displaced from the ideal perpendicular geometry in a rotatory or 'rolling' fashion.[6] The dark brown solution of **2** gradually turned to deep purple upon standing in [D$_8$]THF at −20 °C for several weeks. After two months a few deep purple crystals were obtained. X-ray analysis (Fig. 2) revealed them to be [Rh$^{II}$(*t*-Bu$_2$-boxate)$_2$], **3**.‡ Complex **3** was easily prepared in moderate yield (59% isolated) by heating a solution of **2** in THF at 40 °C for 45 min. The same behaviour was observed in benzene.



**Scheme 1**

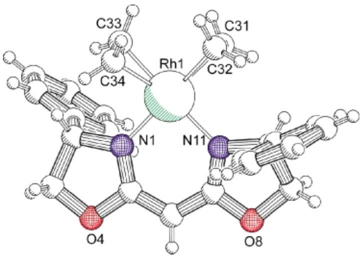


**Fig. 1** X-Ray structure of **1**. Selected bond lengths (Å) and angles (°): Rh1–N11 2.056(7), Rh1–N1 2.070(8), Rh1–C33 2.108(10), Rh1–C31 2.127(9), Rh1–C34 2.136(9), Rh1–C32 2.137(9), C31–C32 1.396(15), C33–C34 1.390(15); N11–Rh1–N1 88.5(3), N1–Rh1–C31 151.6(4), N11–Rh1–C34 149.6(4), N1–Rh1-C(32) 170.1(3), N11–Rh1–C(33) 172.1(4).

Rhodium is usually associated with the Rh$^{I}$ and Rh$^{III}$ oxidation states; rhodium(II) complexes are rare. Isolated *mononuclear* rhodium(II) complexes are especially scarce, owing to the relative instability of the +2 oxidation state.[7,8] The formation of compound **3** was accompanied by precipitation of an 'equimolar' amount of rhodium(0) as a black powder. The black powder was identified as rhodium(0) by elemental analysis. Thus, complex **3** constitutes the first example of a fully characterised mononuclear rhodium(II) complex obtained through disproportionation of a rhodium(I) species to Rh$^{0}$ and Rh$^{II}$.[9] The mechanism of this disproportionation is still under investigation.

Complex **3** is stable at room temperature under inert gas but slowly decomposes in air over months. In THF no apparent reaction is observed either with hydrogen or carbon monoxide, and reaction with oxygen is slow (hours). The low reactivity of **3** can probably be ascribed to shielding of the Rh$^{II}$ centre by the ligand *t*-butyl groups.

As can be seen from the 'stripped' sideview of **3** (Fig. 2, right) the coordination geometry of the rhodium(II) centre is approximately halfway between square planar and tetrahedral. The observed twist is intriguing, since most other four-coordinate, structurally characterized Rh$^{II}$-compounds are square planar.[10] DFT calculations[11] on the model compound [Rh$^{II}$(H$_2$-boxate)$_2$] (R = H), which lacks the bulky *t*-Bu substituents of **3**, indicate that the preferred geometry for rhodium(II) in an unhindered bis(boxate) ligand environment is actually the one observed in the crystal structure of **3**. The optimized geometry for the rhodium(I) model compound [Rh$^{I}$(H$_2$-boxate)$_2$]$^{-}$ was calculated to be nearly ideally square planar. Apparently the unusual twisted geometry of **3** stems from electronic effects. The HOMO of [Rh$^{I}$(H$_2$-boxate)$_2$]$^{-}$ consists of an anti-bonding molecular orbital resulting from overlap of the metal d$_{xz}$ orbital with filled ligand π-orbitals (π$_B$, see Fig. 3). Since this orbital is doubly occupied, there is no net

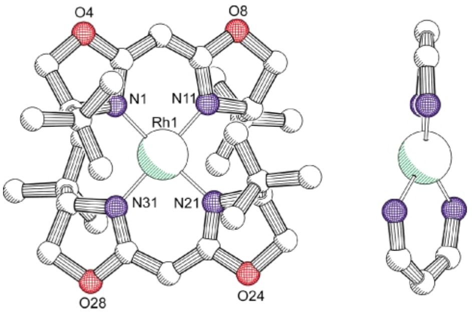


**Fig. 2** X-Ray structure of [Rh$^{II}$(*t*-Bu$_2$-boxate)$_2$] **3.** Front view (left) and side view (right) of the rhodium diiminate core. All hydrogens have been omitted. Selected bond lengths (Å) and angles (°): Rh1–N31 2.037(2), Rh1–N1 2.041(2), Rh1–N21 2.049(2), Rh1–N11 2.0511(18), N31–Rh1–N1 94.75(9), N31–Rh1–N21 89.80(10), N1–Rh1–N21 154.44(9), N31–Rh1–N11 153.84(8), N1–Rh1–N11 90.14(10), N21–Rh1–N11 96.78(10). The angle between the least-squares planes of the ligands (*t*-Bu subst., Rh and hydrogens not included) is 35.89(0.06)°.

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† Electronic supplementary information (ESI) available: synthetic procedures (including $^{1}$H NMR, $^{13}$C NMR and elemental analysis data), EPR spectrum and cyclic voltammogram. See http://www.rsc.org/suppdata/cc/b1/b110183h/

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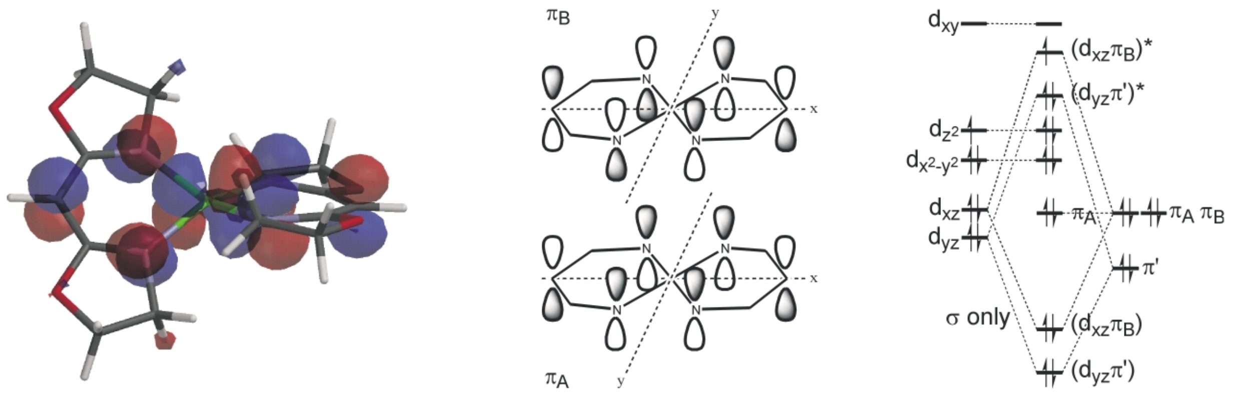

**Fig. 3** $[Rh^{II}(H_2\text{-boxate})_2]$ (R = H): SOMO of the non-planar optimised structure (left); schematic electron configuration of the planar structure (right).

π-bond with $\pi_B$. Apparently the ligands are strong enough π-donors to lift $(d_{xz}\pi_B)^*$ above $d_{z^2}$.[12] The DFT calculations further suggest that the HOMO for $[Rh^I(H_2\text{-boxate})_2]^-$ is nearly identical to the SOMO of $[Rh^{II}(H_2\text{-boxate})_2]$. Since the latter orbital is only half-filled, a net π-bondorder of ½ results. Twisting of the structure allows for an additional π-donation from the filled $\pi_A$ to the empty $d_{xy}$.[13] The rhombic EPR spectrum of **3** in a frozen solution of acetone–methanol (2 : 3) at 20 K could be satisfactorily simulated with the *g*-values $g_1$ = 1.947, $g_2$ = 2.016, and $g_3$ = 2.794.[14] The cyclic voltammogram of **3** shows an oxidation wave (probably $Rh^{II}/Rh^{III}$) at $E^p_{\text{anode}}$ = 0.48 V and a reduction wave (probably $Rh^{II}/Rh^I$) at $E^p_{\text{cathode}}$ = −1.32 V. Thus **3** is thermodynamically stable to disproportionation to $[Rh^I(t\text{-Bu}_2\text{-boxate})_2]^-$ and $[Rh^{III}(t\text{-Bu}_2\text{-boxate})_2]^+$. None of the observed redox waves is entirely reversible.

The present study provides a new example of a stable mononuclear rhodium(II) complex, surprisingly formed by disproportionation of the corresponding rhodium(I) bis(ethene) complex. The unusual, distorted orientation of the ligands around $Rh^{II}$ apparently stems from an electronic preference, rather than steric influences.

We thank Johnson Matthey for a generous loan of rhodium, and Dr F. Neese (Abteilung Biologie der Universität Konstanz) for a copy of his EPR simulation program. X-Ray data for **3** were collected on the CCD diffractometer of the national NWO-CW facility in Utrecht.

## Notes and references

‡ *Crystal data*: **1**: $C_{23}H_{25}N_2O_2Rh$, *M* = 464.36, orthorhombic, space group $P2_12_12_1$, *a* = 8.9724(7), *b* = 11.7974(9), *c* = 19.1120(19) Å, *U* = 2023.0(3) Å³, *T* = 293(2) K, *Z* = 4, $\mu$(Mo-Kα) = 0.865 mm⁻¹, 2635 reflections measured on an Enraf-Nonius CAD4 diffractometer, 2635 unique, which were used in all calculations. The final $wR(F^2)$ was 0.1609 (all data). CCDC 174014. **3**: $C_{30}H_{50}N_4O_4Rh$, *M* = 633.65, monoclinic, space group $P2_1$, *a* = 16.5080(4), *b* = 10.9760(2), *c* = 17.9908(3) Å, $\beta$ = 107.2252(9)°, *U* = 3113.58(11) Å³, *T* = 153(2) K, *Z* = 4, $\mu$(Mo-Kα) = 0.588 mm⁻¹, 17110 reflections measured on a Nonius KappaCCD diffractometer with area detector, 10938 unique ($R_{\text{int}}$ = 0.0421) which were used in all calculations. The final $wR(F^2)$ was 0.0792 (all data). CCDC 174015. Structure **1** was solved using the PATTY option (P. T. Beurskens *et al.*, in *Patterson and Pattersons*, Clarendon, Oxford, 1987, p. 356) of the DIRDIF-96 program system (P. T. Beurskens *et al.*, University of Nijmegen, The Netherlands, 1996). Structure **3** was solved using the SIR97 program (A. Altomare *et al.*, *J. Appl. Crystallogr.*, 1999, **32**, 115–119). Refinements (full-matrix least-squares on $F^2$) were carried out with the SHELXL-97 package (G. M. Sheldrick, University of Göttingen, Germany, 1997). Geometry calculations were performed with the PLATON-93 program (A. L. Spek, University of Utrecht, The Netherlands, 1995). See http://www.rsc.org/suppdata/cc/b1/b110183h/ for crystallographic data in CIF or other electronic format.

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6 This type of deviation can be quantified taking the difference between the angles subtended at rhodium by each of the carbons of one ethene and its *trans* substituent; D. W. Price, M. G. B. Drew, K. K. Hii and J. M. Brown, *Chem. Eur. J.*, 2000, **6**, 4587–4596. The rather large values 18.7° and 22.6° found for **1** correlate well with the values (19.8° and 21.4°) found for $[Rh(Me_2\text{-boxate})(\text{ethene})_2]$ (R = methyl); see ref. 5.

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11 Spartan v5.1.3, pBP functional, DN basis.

12 In related rhodium(II) complexes the single electron is generally associated with the $d_{z^2}$ orbital, see *e.g.*; (*a*) Y. P. Ni, J. P. Fitzgerald, P. Caroll and B. B. Wayland, *Inorg. Chem.*, 1994, **33**, 2029–2035; (*b*) M. P. Garcia, M. V. Jimenez, F. J. Lahoz, J. A. Lopez and L. A. Oro, *J. Chem. Soc., Dalton Trans.*, 1998, 4211–4214; (*c*) A. H. Maki, N. Edelstein, A. Davison and R. H. Holm, *J. Am. Chem. Soc.*, 1964, **86**, 4580–4587.

13 At the same time, on going from square planar $Rh^I$ to twisted $Rh^{II}$, some of the Rh–N σ* character is transferred from $d_{xy}$ to the $(d_{xz}\pi_B)^*$ SOMO. Since this orbital is only singly occupied, the cost of this σ-transfer is apparently not too high and the improved π-bonding prevails.

14 The spectrum reveals no resolved (super)hyperfine coupling with either rhodium or nitrogen. The signals, however, are rather broad which might originate from underlying hyperfine coupling patterns. Assuming a superhyperfine coupling with four equivalent nitrogen donor atoms, we estimate maximum superhyperfine coupling constants of 30 MHz for $g_1$, 20 MHz for $g_2$ and 75 MHz for $g_3$.