

## Dialkyl(4,4'-di-*t*-butyl-2,2'-bipyridyl)ruthenium(II): A New Family of Organoruthenium Complexes; Molecular Structure of *cis*-RuEt<sub>2</sub>(Bu<sup>t</sup><sub>2</sub>bipy)<sub>2</sub>

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New dialkylruthenium complexes *cis*-RuR<sub>2</sub>(Bu<sup>t</sup><sub>2</sub>bipy)<sub>2</sub> (R = Me, Et, CH<sub>2</sub>-*cyclo*-C<sub>6</sub>H<sub>11</sub>, CH<sub>2</sub>SiMe<sub>2</sub>CH:CH<sub>2</sub>, CH<sub>2</sub>SiMe<sub>3</sub>, CH<sub>2</sub>SiMe<sub>2</sub>Ph; Bu<sup>t</sup><sub>2</sub>bipy = 4,4'-di-*t*-butyl-2,2'-bipyridyl) and *trans*-RuR<sub>2</sub>(Bu<sup>t</sup><sub>2</sub>bipy)<sub>2</sub> (R = CH<sub>2</sub>CMe<sub>2</sub>Ph), characterised by n.m.r. (<sup>1</sup>H and <sup>13</sup>C), mass spectrometry and, in the case of the diethyl derivative, X-ray diffractometry, display notable inertness (despite the availability, in most, of transferable hydrogens) due, proposedly, to their resistance to electron-transfer and their stereochemical rigidity.

Despite the expected inertness of diorganoruthenium(II) due to the high configurational stability of hexaco-ordinate d<sup>6</sup> complexes with strong-field ligands, the relatively few examples studied show remarkable lability, especially towards H-transfer. Ligands which lack readily transferable hydrogens, such as methyl and phenyl, have led to isolable complexes.<sup>1</sup> Attempts at alkylation of Ru<sup>II</sup> using other ligands with transferable, distal hydrogen, generally have yielded metallacycles,<sup>2</sup> proposedly *via* dialkylruthenium(II) precursors. This (unsubstantiated) mechanistic generalisation has been reinforced, in part, by parallel behaviour in (the more inert) dialkylplatinum(II), notably bis-neopentyl,<sup>3</sup> analogues. H-transfer lability, though, requires co-ordinative flexibility and it is therefore most curious that 18-electron, hexaco-ordinate d<sup>6</sup> systems, which enjoy maximal ligand-field stabilisation, should be so reactive compared with their d<sup>8</sup> cousins.

We suspect that some, at least, of this anomalous reactivity must be due to intervention by labile Ru<sup>III</sup> species; the chemistry of alkylruthenium(III) is notable for the absence of isolable mononuclear examples<sup>4</sup> and 17-electron species are generally highly reactive.<sup>5</sup> Traces of Ru<sup>III</sup> might be sufficient to catalyse such reactions *via* redox chain propagation.<sup>6</sup> Inert complexes RuR<sub>2</sub>(biL)<sub>2</sub> should be accessible, however (even if R has transferable H), by using ligands biL which: (a) allow

synthesis of an unequivocally Ru<sup>II</sup> precursor; (b) confer high stereochemical rigidity; (c) provide insulation from outer-sphere electron-transfer. Using this strategy, we have synthesised several of a new family of organoruthenium(II) complexes RuR<sub>2</sub>(Bu<sup>t</sup><sub>2</sub>bipy)<sub>2</sub> which are remarkably inert in spite of the availability in most of them of transferable hydrogens (Bu<sup>t</sup><sub>2</sub>bipy = 4,4'-di-*t*-butyl-2,2'-bipyridyl). Though polypyridyls are usually notable for facility of electron-transmission,<sup>7</sup> the bulky alkyl substituents here are an obstruction to close intermolecular approach and are orbitally unsuited to ready electron-transfer. These 4,4'-disubstituted bipyridyls have additional attractions of (i) inhibiting H-transfer *via* roll-over 3-metallation<sup>8</sup> and (ii) improving solubility. Related organoiron chemistry is well established<sup>9</sup> and two diethylruthenium analogues with bidentate phosphine ligands have been described briefly.<sup>10</sup>

The precursor, RuCl<sub>2</sub>(Bu<sup>t</sup><sub>2</sub>bipy)<sub>2</sub>, was prepared by modifications of published methods,<sup>11</sup> followed by Soxhlet extraction in toluene (under argon). An improved preparation has appeared recently.<sup>12</sup> Reaction of this complex with at least two equivalents of MgRX proceeds in diethyl ether or tetrahydrofuran (thf) at ambient temperature under argon. Reactions are slower in diethyl ether, owing to the low solubility of the dihalide. The facility of alkylation decreases

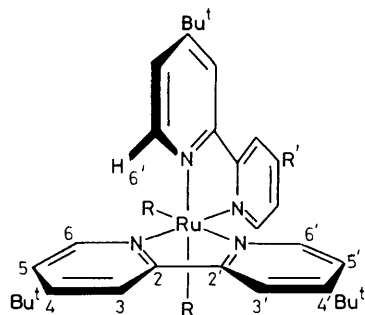


Figure 1. *cis*-RuR<sub>2</sub>(Bu<sup>t</sup>bipy)<sub>2</sub>, showing atom numbering.

with increasing bulk of the alkyl group, but most are complete in 2–6 h. The products can be obtained as green or brown crystals by extraction of evaporated reaction mixtures into (variously) hexane or toluene, concentration, and cooling. As solids, they appear to be fairly air-inert, though they react in solution. Products where R = Me, Et, CH<sub>2</sub>-*cyclo*-C<sub>6</sub>H<sub>11</sub>, CH<sub>2</sub>SiMe<sub>2</sub>CH:CH<sub>2</sub>, CH<sub>2</sub>SiMe<sub>3</sub>, CH<sub>2</sub>SiMe<sub>2</sub>Ph, and CH<sub>2</sub>CMe<sub>2</sub>Ph have been isolated and analysed by mass spectrometry, using fast-atom bombardment (FAB) ionisation. Each displays a characteristic fragment corresponding to [RuR(Bu<sup>t</sup>bipy)<sub>2</sub>]<sup>+</sup> as the most intense ion. Except where R has a β-hydrogen, [RuR<sub>2</sub>(Bu<sup>t</sup>bipy)<sub>2</sub>]<sup>+</sup> is also observed at highest *m/z*. Additionally, all but one of these new complexes have been identified, by <sup>1</sup>H and <sup>13</sup>C n.m.r. spectroscopy, as *cis*-dialkyl derivatives (Figure 1).<sup>†</sup> This configuration generates complex but characteristic spectra because (i) Ru is an asymmetric centre and (ii) the adjacent rings in each bipyridyl ligand are non-equivalent. The hydrogens on each metal-bound methylene unit are diastereotopic, as are the methyl groups of the CH<sub>2</sub>SiMe<sub>2</sub>R ligands (R = Ph, CH:CH<sub>2</sub>). Two distinct environments are apparent for the *t*-butyl groups as well as for the other bipyridyl sites. The close perpendicular approach of H-6' to the C<sub>5</sub>N ring of the neighbouring ligand (Figure 1) is another characteristic of the *cis*-configuration, and leads to a notable *upfield* co-ordination shift (δ 7.32–7.84; *cf.* δ 8.50 in free Bu<sup>t</sup>bipy) ascribable to the anisotropic magnetic influence of the ring.<sup>13</sup> H-6, on the other hand, exhibits a substantial downfield shift (δ 9.50–10.20).<sup>14</sup>

The molecular structure of RuEt<sub>2</sub>(Bu<sup>t</sup>bipy)<sub>2</sub> has been determined by X-ray diffractometry.<sup>‡</sup> This confirms the stereochemical assignments based on n.m.r. analysis, as

<sup>†</sup> Tables of <sup>1</sup>H and <sup>13</sup>C n.m.r. data are available from the authors on request.

<sup>‡</sup> Crystal data for C<sub>40</sub>H<sub>58</sub>N<sub>4</sub>Ru: *M* = 696.0, monoclinic, *a* = 28.398(7), *b* = 12.271(3), *c* = 26.874(6) Å, β = 102.95(2)°, *U* = 9126.6 Å<sup>3</sup> (at 20°C), space group *C2/c* and *Z* = 8. Intensity data were collected on a Nicolet R3m/Eclipse S140 diffractometer system using the ω scan technique with graphite-monochromated Cu-K<sub>α</sub> radiation. A total of 4692 independent reflections were measured (to θ = 50°), of which 875 were judged to be unobserved, *F* < 3σ(*F*). During data collection (*ca.* 2 days) the intensities of reference reflections dropped by *ca.* 5%. The structure was solved by Patterson and Fourier methods and block cascade refinement (SHELXTL) has now reached *R* = 0.057 and *R*<sub>w</sub> = 0.061. One *t*-butyl and one ethyl group show conformational disorder and no attempt has yet been made to localise the hydrogen atoms of these groups. (There is also some evidence for traces of disordered solvent, probably *n*-hexane, in the interstices of the structure). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See, Notice to Authors, Issue no. 1.

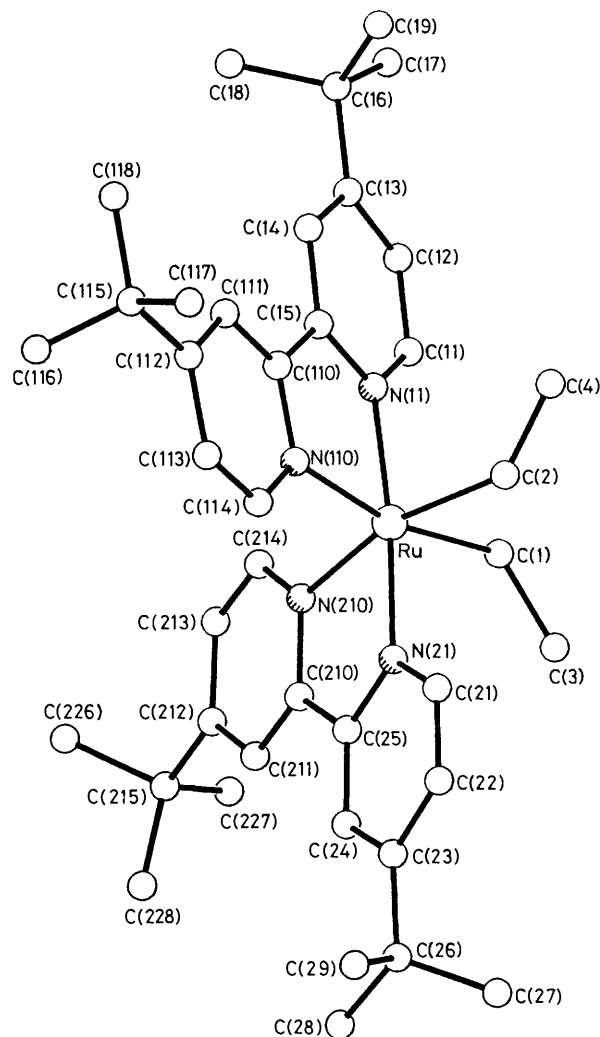


Figure 2. Molecular structure of RuEt<sub>2</sub>(Bu<sup>t</sup>bipy)<sub>2</sub>. Principal bond lengths (Å) are: Ru–N(11) 2.034(5); Ru–N(21) 2.042(5); Ru–N(110) 2.098(5); Ru–N(210) 2.094(6); Ru–C(1) 2.138(7); Ru–C(2) 2.142(8). Notable bond angles (°) are: N(110)–Ru–N(210) 104.3(2); C(1)–Ru–C(2) 85.2(3); N(11)–Ru–N(110) 77.3(2); N(21)–Ru–N(210) 77.3(2). For clarity, only one orientation of the two disordered groups is shown.

shown in Figure 2. The distorted octahedral co-ordination about ruthenium has a mean Ru–C of 2.140 Å and a mean Ru–N (*trans* to N) of 2.038 Å. The mean Ru–N (*trans* to C) of 2.096 Å reflects the greater *trans*-influence of the ethyl ligands.

In contrast, the <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra of Ru(CH<sub>2</sub>-CMe<sub>2</sub>Ph)<sub>2</sub>(Bu<sup>t</sup>bipy)<sub>2</sub> indicate a *trans*-configuration; only one environment is evident for each site in both the alkyl and the polypyridyl ligands. Greater steric encroachment by this ligand<sup>15</sup> near the metal apparently outweighs the unfavourability of two equatorial bipyridyls. The appreciable steric competition between the Bu<sup>t</sup>bipy and the alkyl ligands is reflected, presumably, in the large Ru–C–C angle [119.5(6)° in the non-disordered ethyl group] apparent in the structure of *cis*-RuEt<sub>2</sub>(Bu<sup>t</sup>bipy)<sub>2</sub>. We have, so far, been unable to recover pure diaryl complexes, or the neopentyl derivative. <sup>1</sup>H N.m.r. spectra of reaction mixtures indicate the presence of *trans*-products for these ligands also. We are continuing to explore this aspect. We are also currently investigating the thermo-

lytic, photolytic, and electrochemical reactivities of these compounds and their relatives, including osmium analogues.

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