

## A General Method of Promoting Agostic Interactions (Ru—H<sub>a</sub>—C) using Azine Phosphines

Sarath D. Perera and Bernard L. Shaw\*

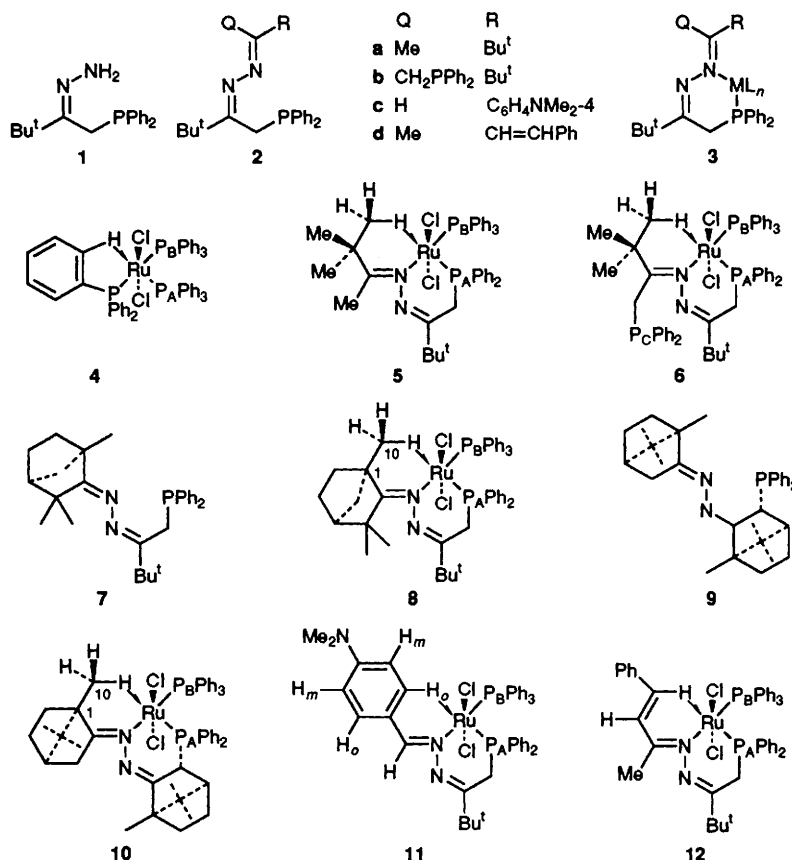
School of Chemistry, University of Leeds, Leeds, UK LS2 9JT

Treatment of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] with azine phosphines gives complexes showing strong agostic interactions between ruthenium and C—H bonds of *tert*-butyl, methyl, aryl or alkenyl groups in dynamic systems; for example, all nine hydrogens of a *tert*-butyl group are agostically interacting with ruthenium on the NMR timescale at 20 °C.

We report a new method of generating agostic C—H<sub>a</sub> interaction with a metal using the following synthetic strategy: the crystalline hydrazone phosphine (Z)-PPh<sub>2</sub>CH<sub>2</sub>C(Bu<sup>t</sup>)=NNH<sub>2</sub> **1** condenses easily with aldehydes and ketones, QC(=O)R, to give azines of type **2** with Q=H or Me and R more sterically demanding than Q, and we have shown this to be the case for Q = H and R = Ph,<sup>1,2</sup> and with other systems.<sup>3</sup> We expected that an azine of type **2** would form a six-membered ring chelate to a metal (M), as shown in **3**, in which the R group would be held close to the metal and in many cases compressed against it. We therefore thought that the overall strategy could be an effective general method either (i) of inducing a C—H bond in R to interact with the metal agostically, or (ii) of promoting oxidative addition of C—H to the metal. We report in this communication that the strategy works extremely well for inducing agostic interaction with ruthenium(II) and in the following communication that it works extremely well as a means of promoting oxidative addition of C—H to iridium(I).

The first suggestion of a C—H<sub>a</sub>→metal interaction followed from the crystal structure of the Wilkinson compound [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] determined by LaPlaca and Ibers<sup>4</sup> and shown diagrammatically in **4**, in which the agostic interaction is represented by a single headed arrow.<sup>5</sup> Since then many other examples of agostic interaction have been reported and the area has been reviewed.<sup>5–9</sup> [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] is labile and we

reasoned that, on treatment with an azine of type **2**, two molecules of PPh<sub>3</sub> might be displaced readily to give a chelate complex of type **3** showing agostic interaction with the R group. **1** was condensed with MeC(=O)Bu<sup>t</sup> to give the azine **2a** as a single isomer, which when treated with [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] at 50 °C for ca. 1 min in benzene solution displaced two PPh<sub>3</sub> ligands and gave a single complex **5** essentially quantitatively (<sup>31</sup>P-{<sup>1</sup>H} NMR evidence); **5** was isolated in 88% yield.† This δ-agostic *tert*-butyl complex **5** is remarkable in that in the <sup>1</sup>H NMR spectrum at 20 °C all nine hydrogens of the *tert*-butyl group are equally coupled to P<sub>A</sub>, δ{C(CH<sub>3</sub>)<sub>3</sub>} 1.17, <sup>2</sup>J<sub>P<sub>A</sub>H<sub>a</sub> 2.4 Hz, indicating an agostic interaction with rapid rotation of the *tert*-butyl group on the NMR timescale. Since the value 2.4 Hz will be an averaged value over the nine hydrogens it suggests that the agostic interaction is quite strong; in other metal complexes showing agostic interactions and where the metal carries a tertiary phosphine ligand <sup>2</sup>J<sub>P-M-H<sub>a</sub> is often too small to observe or is just a few Hz.<sup>5</sup> When the NMR sample was cooled to -50 °C, only three hydrogens (*i.e.* one methyl group) show coupling to P<sub>A</sub>, δ(CH<sub>3</sub>) 0.92, <sup>2</sup>J<sub>P<sub>A</sub>H<sub>a</sub> 7.3 Hz, and other two methyls appeared as singlets at δ 1.19 and 1.28; *i.e.* rotation around the Bu<sup>t</sup>—C bond has slowed down or stopped. We were unable to stop the rotation of the interacting methyl by cooling down the sample to -85 °C. The <sup>13</sup>C NMR data† also indicate agostic interaction. The far-IR band at 320 cm<sup>-1</sup> indicates a *trans* Cl—Ru—Cl moiety.<sup>10</sup> This is the first example</sub></sub></sub>



of a  $\delta$ -agostic *tert*-butyl complex showing spin-spin coupling of the *tert*-butyl hydrogens to a coordinated tertiary phosphine ligand. The azine phosphine derived from HC(=O)Bu<sup>t</sup> gave a complex analogous to **5** showing agostic *tert*-butyl-ruthenium interaction.

Other azine phosphine ligands analogous to **2a** readily displaced two molecules of PPh<sub>3</sub> from the labile [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>], with a reaction time of *ca.* 1 min at 50 °C, to give *mer*-, *trans*-agostic ruthenium(II) complexes as shown by their <sup>31</sup>P-{<sup>1</sup>H} NMR (<sup>2</sup>J<sub>P<sub>A</sub>P<sub>B</sub></sub> *ca.* 40 Hz), IR data [ $\nu$ /cm<sup>-1</sup> (Ru-Cl) *ca.* 320] and other data, as described below.

We have described the azine diphosphine, (*Z,Z*)-Ph<sub>2</sub>PCH<sub>2</sub>C(Bu<sup>t</sup>)=N-N=C(Bu<sup>t</sup>)CH<sub>2</sub>PPh<sub>2</sub> **2b**<sup>11</sup> and this when treated with [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] displaced only two PPh<sub>3</sub> to give the  $\delta$ -agostic *tert*-butyl complex **6**, *i.e.* the *tert*-butyl group again interacts agostically at ruthenium, showing coupling to P<sub>A</sub>, <sup>2</sup>J<sub>P<sub>A</sub>H<sub>a</sub></sub> 2.7 Hz, and one of the PPh<sub>2</sub> groups is uncoordinated with the resonance occurring as a singlet at  $\delta$ (P<sub>C</sub>) - 8.8; *i.e.* the ruthenium prefers the agostic interaction to a *tert*-butyl group rather than coordination to P<sub>C</sub>.

Treatment of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] with the phosphine **7**<sup>12</sup> derived from pinacolone-(1*R*)-(-)-fenchone mixed azine gave the  $\delta$ -agostic methyl complex **8**, in 61% yield, in which the methyl group (C<sup>10</sup>H<sub>3</sub>) in the 1-position of the fenchone residue interacts with ruthenium, and all three hydrogens are equally coupled to P<sub>A</sub>,  $\delta$ (Me) 0.99, <sup>2</sup>J<sub>P<sub>A</sub>H<sub>a</sub></sub> 7.1 Hz. Similarly, the azine phosphine **9**, prepared from (1*R*)-(+)-camphor azine,<sup>13</sup> by treatment with LiBu<sup>n</sup> (1 equiv.) at -15 °C followed by Ph<sub>2</sub>PCl, gave the  $\delta$ -agostic methyl complex **10**,  $\delta$ (Me) 0.94, <sup>2</sup>J<sub>P<sub>A</sub>H<sub>a</sub></sub> 3.8 Hz, in 69% yield.

We can similarly induce  $\delta$ -agostic interaction with aromatic C-H or alkenyl C-H bonds. The mixed azine phosphine **2c** from 4-dimethylaminobenzaldehyde reacts with [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] to give the  $\delta$ -agostic aryl complex **11** in which both *ortho*-hydrogens (*i.e.* the 2,6-positions of the C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub> ring) interact with ruthenium,  $\delta$ (H<sub>o</sub>) 6.57, <sup>2</sup>J<sub>P<sub>A</sub>H<sub>o</sub></sub> 2.1 and <sup>3</sup>J<sub>H<sub>o</sub>H<sub>m</sub></sub> 8.5 Hz. Similar results were obtained with the azines from 4-methoxybenzaldehyde and from 4-nitrobenzaldehyde. The mixed azine phosphine **2d** from benzylidene acetone reacted with [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] to give the  $\delta$ -agostic alkenyl complex **12** in 90% yield in which the alkenyl hydrogen (=CHPh) agostically interacted with ruthenium, and was coupled to P<sub>A</sub>,  $\delta$ (CH=) 6.88, J<sub>P<sub>A</sub>-M-HC=</sub> = 1.8 Hz and <sup>3</sup>J<sub>HC=CH</sub> 15.6 Hz.

Treatment of complex **5** with base *e.g.* Et<sub>3</sub>N or NaOAc does not lead to carbon-ruthenium bond formation and prolonged treatment of **5** with CO or H<sub>2</sub> at 1 atm/20°C caused no reaction. We are investigating other examples of agostic and related interaction with ruthenium and with other metals and are also studying types of mixed azine phosphines other than **2**.

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## Footnote

† New compounds were characterised by elemental analyses, and by IR, <sup>31</sup>P-{<sup>1</sup>H} NMR (36.2 MHz), <sup>1</sup>H NMR (100 MHz or 400 MHz) and mass spectrometry.

Selected spectral data for **2a**  $\delta$ <sub>P</sub>(CDCl<sub>3</sub>): -12.4; **2c**  $\delta$ <sub>P</sub>(CDCl<sub>3</sub>): -11.3; **2d**  $\delta$ <sub>P</sub>(CDCl<sub>3</sub>): -10.7.

**5**  $\delta$ <sub>P</sub>(CD<sub>2</sub>Cl<sub>2</sub>): 74.7 (d, P<sub>A</sub>), 44.0 (d, P<sub>B</sub>), <sup>2</sup>J<sub>PP</sub> 40 Hz; <sup>1</sup>H NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub> at 20 °C):  $\delta$  0.69 (9 H, s, Bu<sup>t</sup>) and 1.17 (9 H, d, <sup>2</sup>J<sub>P<sub>A</sub>H</sub> 2.4 Hz, agostic-Bu<sup>t</sup>); <sup>13</sup>C-{<sup>1</sup>H} NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -50 °C): 19.9 (1 C, d, <sup>3</sup>J<sub>PC</sub> 13.6 Hz, agostic-Me), 20.5 (1 C, s, MeC=), 26.7 (3 C, s, CMe<sub>3</sub>), 27.7 (1 C, s, CMe<sub>3</sub>) and 30.3 (1 C, s, CMe<sub>3</sub>),  $\nu$ /cm<sup>-1</sup> (Ru-Cl) 320; *m/z* (FAB, for <sup>102</sup>Ru and <sup>35</sup>Cl): 814 (M<sup>+</sup>), 779 (M - Cl) and 743 (M - Cl - HCl).

**6**  $\delta$ <sub>P</sub>(C<sub>6</sub>D<sub>6</sub>): 75.2 (d, P<sub>A</sub>), 43.9 (d, P<sub>B</sub>), -8.8 (s, P<sub>C</sub>), <sup>2</sup>J<sub>P<sub>A</sub>P<sub>B</sub></sub> 39 Hz; <sup>1</sup>H NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$  0.57 (9 H, s, Bu<sup>t</sup>) and 0.83 (9 H, d, <sup>2</sup>J<sub>P<sub>A</sub>H</sub> 2.7 Hz, agostic-Bu<sup>t</sup>).

**8**  $\delta$ <sub>P</sub>(CD<sub>2</sub>Cl<sub>2</sub>): 76.7 (d, P<sub>A</sub>), 43.1 (d, P<sub>B</sub>), <sup>2</sup>J<sub>PP</sub> 39 Hz; **9**  $\delta$ <sub>P</sub>(CDCl<sub>3</sub>): -0.3. **10**  $\delta$ <sub>P</sub>(C<sub>6</sub>D<sub>6</sub>): 81.4 (d, P<sub>A</sub>), 38.8 (d, P<sub>B</sub>), <sup>2</sup>J<sub>PP</sub> 41 Hz; **11**  $\delta$ <sub>P</sub>(CDCl<sub>3</sub>): 78.4 (d, P<sub>A</sub>), 45.8 (d, P<sub>B</sub>), <sup>2</sup>J<sub>PP</sub> 37 Hz; <sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  5.95 (2 H, d, <sup>3</sup>J<sub>H<sub>o</sub>H<sub>m</sub></sub> 8.5 Hz, 2 × H<sub>o</sub>), 6.57 (2 H, dd, <sup>2</sup>J<sub>P<sub>A</sub>H<sub>o</sub></sub> 2.1 Hz, <sup>3</sup>J<sub>H<sub>o</sub>H<sub>m</sub></sub> 8.5 Hz, 2 × H<sub>o</sub>) and 9.00 (1 H, d, <sup>4</sup>J<sub>P<sub>B</sub>H</sub> 6.6 Hz, CH=). <sup>13</sup>C-{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>, 20 °C): 27.3 (3 C, s, CMe<sub>3</sub>), 40.1 (2 C, s, NMe<sub>2</sub>), 111.9 (2 C, s, 2 × CH<sub>m</sub>) and 133.0 (2 C, d, <sup>3</sup>J<sub>PC</sub> 5.2 Hz, 2 × CH<sub>o</sub>).

**12**  $\delta$ <sub>P</sub>(CD<sub>2</sub>Cl<sub>2</sub>): 90.1 (d, P<sub>A</sub>), 47.0 (d, P<sub>B</sub>), <sup>2</sup>J<sub>PP</sub> 37 Hz; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$  6.88 (1 H, dd, <sup>2</sup>J<sub>P<sub>A</sub>H</sub> 1.8 Hz, <sup>3</sup>J<sub>CH=CH</sub> 15.6 Hz, =CHPh) and 7.34 [1 H, d, <sup>3</sup>J<sub>CH=CH</sub> 15.6 Hz, =C(Me)CH].

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