

A General Method of Promoting Agostic Interactions (Ru—H_a—C) using Azine Phosphines

Sarath D. Perera and Bernard L. Shaw*

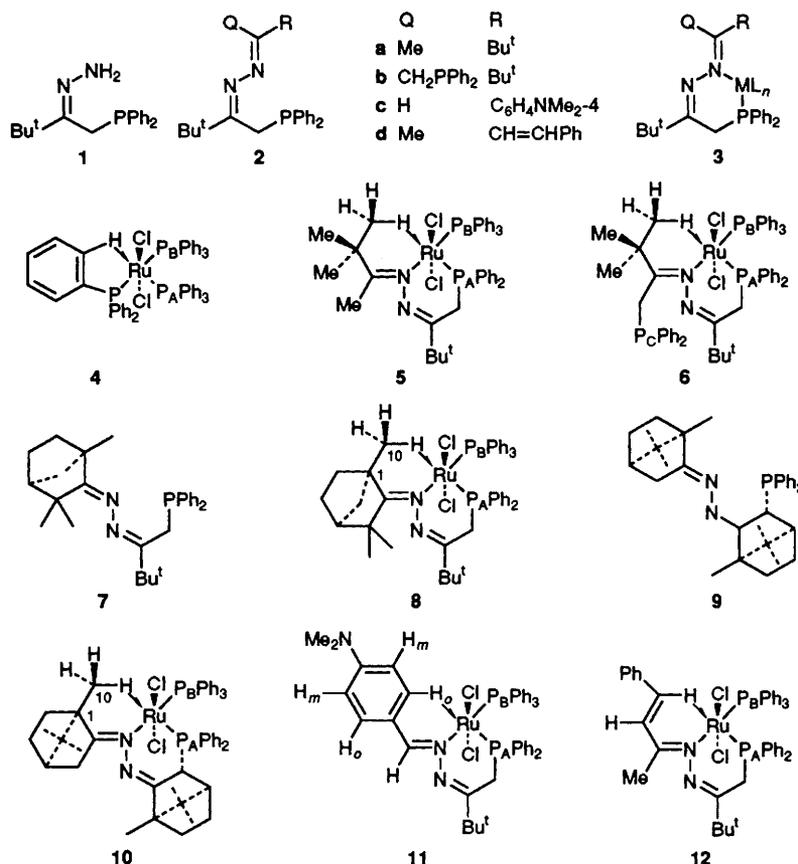
School of Chemistry, University of Leeds, Leeds, UK LS2 9JT

Treatment of [RuCl₂(PPh₃)₃] 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_a interaction with a metal using the following synthetic strategy: the crystalline hydrazone phosphine (Z)-PPh₂CH₂C(Bu^t)=NNH₂ **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,^{1,2} and with other systems.³ 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_a→metal interaction followed from the crystal structure of the Wilkinson compound [RuCl₂(PPh₃)₃] determined by LaPlaca and Ibers⁴ and shown diagrammatically in **4**, in which the agostic interaction is represented by a single headed arrow.⁵ Since then many other examples of agostic interaction have been reported and the area has been reviewed.^{5–9} [RuCl₂(PPh₃)₃] is labile and we

reasoned that, on treatment with an azine of type **2**, two molecules of PPh₃ 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^t to give the azine **2a** as a single isomer, which when treated with [RuCl₂(PPh₃)₃] at 50 °C for ca. 1 min in benzene solution displaced two PPh₃ ligands and gave a single complex **5** essentially quantitatively (³¹P-{¹H} NMR evidence); **5** was isolated in 88% yield.† This δ-agostic *tert*-butyl complex **5** is remarkable in that in the ¹H NMR spectrum at 20 °C all nine hydrogens of the *tert*-butyl group are equally coupled to P_A, δ{C(CH₃)₃} 1.17, ²J_{P_AH_a}} 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 ²J_{P-M-H_a}} is often too small to observe or is just a few Hz.⁵ When the NMR sample was cooled to -50 °C, only three hydrogens (*i.e.* one methyl group) show coupling to P_A, δ(CH₃) 0.92, ²J_{P_AH_a}} 7.3 Hz, and other two methyls appeared as singlets at δ 1.19 and 1.28; *i.e.* rotation around the Bu^t-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 ¹³C NMR data† also indicate agostic interaction. The far-IR band at 320 cm⁻¹ indicates a *trans* Cl—Ru—Cl moiety.¹⁰ This is the first example



of a δ -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^t gave a complex analogous to **5** showing agostic *tert*-butyl-ruthenium interaction.

Other azine phosphine ligands analogous to **2a** readily displaced two molecules of PPh₃ from the labile [RuCl₂(PPh₃)₃], with a reaction time of *ca.* 1 min at 50 °C, to give *mer*-, *trans*-agostic ruthenium(II) complexes as shown by their ³¹P-{¹H} NMR (²J_{PAPB} *ca.* 40 Hz), IR data [ν /cm⁻¹ (Ru-Cl) *ca.* 320] and other data, as described below.

We have described the azine diphosphine, (*Z,Z*)-Ph₂PCH₂C(Bu^t)=N-N=C(Bu^t)CH₂PPh₂ **2b**¹¹ and this when treated with [RuCl₂(PPh₃)₃] displaced only two PPh₃ to give the δ -agostic *tert*-butyl complex **6**, *i.e.* the *tert*-butyl group again interacts agostically at ruthenium, showing coupling to P_A, ²J_{P_AH_a} 2.7 Hz, and one of the PPh₂ groups is uncoordinated with the resonance occurring as a singlet at δ (P_C) - 8.8; *i.e.* the ruthenium prefers the agostic interaction to a *tert*-butyl group rather than coordination to P_C.

Treatment of [RuCl₂(PPh₃)₃] with the phosphine **7**¹² derived from pinacolone-(1*R*)-(-)-fenchone mixed azine gave the δ -agostic methyl complex **8**, in 61% yield, in which the methyl group (C¹⁰H₃) in the 1-position of the fenchone residue interacts with ruthenium, and all three hydrogens are equally coupled to P_A, δ (Me) 0.99, ²J_{P_AH_a} 7.1 Hz. Similarly, the azine phosphine **9**, prepared from (1*R*)-(+)-camphor azine,¹³ by treatment with LiBuⁿ (1 equiv.) at -15 °C followed by Ph₂PCl, gave the δ -agostic methyl complex **10**, δ (Me) 0.94, ²J_{P_AH_a} 3.8 Hz, in 69% yield.

We can similarly induce δ -agostic interaction with aromatic C-H or alkenyl C-H bonds. The mixed azine phosphine **2c** from 4-dimethylaminobenzaldehyde reacts with [RuCl₂(PPh₃)₃] to give the δ -agostic aryl complex **11** in which both *ortho*-hydrogens (*i.e.* the 2,6-positions of the C₆H₄NMe₂ ring) interact with ruthenium, δ (H_o) 6.57, ²J_{P_AH_o} 2.1 and ³J_{H_oH_m} 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 [RuCl₂(PPh₃)₃] to give the δ -agostic alkenyl complex **12** in 90% yield in which the alkenyl hydrogen (=CHPh) agostically interacted with ruthenium, and was coupled to P_A, δ (CH=) 6.88, J_{P_A-M-HC=} = 1.8 Hz and ³J_{HC=CH} 15.6 Hz.

Treatment of complex **5** with base *e.g.* Et₃N or NaOAc does not lead to carbon-ruthenium bond formation and prolonged treatment of **5** with CO or H₂ 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, ³¹P-{¹H} NMR (36.2 MHz), ¹H NMR (100 MHz or 400 MHz) and mass spectrometry.

Selected spectral data for **2a** δ _P(CDCl₃): -12.4; **2c** δ _P(CDCl₃): -11.3; **2d** δ _P(CDCl₃): -10.7.

5 δ _P(CD₂Cl₂): 74.7 (d, P_A), 44.0 (d, P_B), ²J_{PP} 40 Hz; ¹H NMR (100 MHz, CD₂Cl₂ at 20 °C): δ 0.69 (9 H, s, Bu^t) and 1.17 (9 H, d, ²J_{P_AH} 2.4 Hz, agostic-Bu^t); ¹³C-{¹H} NMR (100.6 MHz, CD₂Cl₂, -50 °C): 19.9 (1 C, d, ³J_{PC} 13.6 Hz, agostic-Me), 20.5 (1 C, s, MeC=), 26.7 (3 C, s, CMe₃), 27.7 (1 C, s, CMe₃) and 30.3 (1 C, s, CMe₃), ν /cm⁻¹ (Ru-Cl) 320; *m/z* (FAB, for ¹⁰²Ru and ³⁵Cl): 814 (M⁺), 779 (M - Cl) and 743 (M - Cl - HCl).

6 δ _P(C₆D₆): 75.2 (d, P_A), 43.9 (d, P_B), -8.8 (s, P_C), ²J_{P_AP_B} 39 Hz; ¹H NMR (100 MHz, CD₂Cl₂, 20 °C): δ 0.57 (9 H, s, Bu^t) and 0.83 (9 H, d, ²J_{P_AH} 2.7 Hz, agostic-Bu^t).

8 δ _P(CD₂Cl₂): 76.7 (d, P_A), 43.1 (d, P_B), ²J_{PP} 39 Hz; **9** δ _P(CDCl₃): -0.3. **10** δ _P(C₆D₆): 81.4 (d, P_A), 38.8 (d, P_B), ²J_{PP} 41 Hz; **11** δ _P(CDCl₃): 78.4 (d, P_A), 45.8 (d, P_B), ²J_{PP} 37 Hz; ¹H NMR (100 MHz, CDCl₃, 20 °C): δ 5.95 (2 H, d, ³J_{H_oH_m} 8.5 Hz, 2 × H_o), 6.57 (2 H, dd, ²J_{P_AH_o} 2.1 Hz, ³J_{H_oH_m} 8.5 Hz, 2 × H_o) and 9.00 (1 H, d, ⁴J_{P_BH} 6.6 Hz, CH=). ¹³C-{¹H} NMR (100.6 MHz, CDCl₃, 20 °C): 27.3 (3 C, s, CMe₃), 40.1 (2 C, s, NMe₂), 111.9 (2 C, s, 2 × CH_m) and 133.0 (2 C, d, ³J_{PC} 5.2 Hz, 2 × CH_o).

12 δ _P(CD₂Cl₂): 90.1 (d, P_A), 47.0 (d, P_B), ²J_{PP} 37 Hz; ¹H NMR (400 MHz, CD₂Cl₂, 20 °C): δ 6.88 (1 H, dd, ²J_{P_AH} 1.8 Hz, ³J_{CH=CH} 15.6 Hz, =CHPh) and 7.34 [1 H, d, ³J_{CH=CH} 15.6 Hz, =C(Me)CH].

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