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 $[RuCl_2(PPh_3)_3]$ 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 phosphine crystalline hydrazone strategy: the (Z)-PPh₂CH₂C(Bu^t)=NNH₂ 1¹ 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(11) 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)But to give the azine 2a as a single isomer, which when treated with $[RuCl_2(PPh_3)_3]$ 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_{PAHa} 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 ${}^{2}J_{P-M-H_{a}}$ 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 , $\delta(CH_3)$ 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 But-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)But 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 { $^{2}J_{PAPB}$ ca. 40 Hz}, IR data {v/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 occuring as a singlet at $\delta(P_C) - 8.8$; *i.e.* the ruthenium prefers the agostic interaction to a *tert*-butyl group rather than coordination to P_C.

Treatment of $[RuCl_2(PPh_3)_3]$ with the phosphine 7^{12} derived from pinacolone–(1R)-(-)-fenchone mixed azine gave the δ -agostic methyl complex 8, in 61% yield, in which the methyl group $(C^{10}H_3)$ in the 1-position of the fenchone residue interacts with ruthenium, and all three hydrogens are equally coupled to P_A , $\delta(Me) 0.99$, ${}^2J_{P_AH_a}$ 7.1 Hz. Similarly, the azine phosphine 9, prepared from (1R)-(+)-camphor azine,13 by treatment with LiBun (1 equiv.) at -15 °C followed by Ph₂PCl, gave the δ -agostic methyl complex 10, $\delta(Me)$ 0.94,

 ${}^{2}J_{PAHa}$ 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 from 4-dimethylaminobenzaldehyde reacts with $[RuCl_2(PPh_3)_3]$ 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, $\delta(H_o)$ 6.57, ${}^2J_{P_AH_o}$ 2.1 and ${}^{3}J_{H_{0}H_{m}}$ 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 $[RuCl_2(PPh_3)_3]$ 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 ${}^{3}J_{HC=CH}$ 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 $\delta_P(CDCl_3)$: -12.4; 2c $\delta_P(CDCl_3)$:

betchet appendix data for 2a op(CDC₁₃). –12.4, 2c op(CDC₁₃). –11.3; 2d δ_P(CDC₁₃): –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, Bu⁴) and 1.17 (9 H, d, ²J_{PAH} 2.4 Hz, agostic-Bu⁴); 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), v/cm⁻¹ (Ru-Cl) 320; m/z (FAB, for 102Ru and 35Cl): 814 (M+), 779 (M - Cl) and 743 (M - Cl - HCl).

6 $\delta_P(C_6D_6)$: 75.2 (d, P_A), 43.9 (d, P_B), -8.8 (s, P_C), ²J_{PAPB} 39 Hz; ¹H NMR (100 MHz, CD₂Cl₂, 20 °C); δ 0.57 (9 H, s, Bu^t) and 0.83 (9

h H, d, ²*J*_{PAH} 2.7 Hz, agostic-Bu¹). **8** δ_P(CD₂Cl₂): 76.7 (d, P_A), 43.1 (d, P_B), ²*J*_{PP} 39 Hz; **9** δ_P(CDCl₃): -0.3. **10** δ_P(C₆D₆): 81.4 (d, P_A), 38.8 (d, P_B), ²*J*_{PP} 41 Hz; **11** δ_P(CDCl₃): 78.4 (d, P_A), 45.8 (d, P_B), ²*J*_{PP} 37 Hz; ¹H NMR (100) **b** function of the state of the stat MHz, CDCl₃, 20 °C): $\delta 5.95$ (2 H, d, ${}^{3}J_{H_{0}H_{m}}$ 8.5 Hz, 2 × H_m), 6.57 (2 H, dd, ${}^{2}J_{P_{A}H_{0}}$ 2.1 Hz, ${}^{3}J_{H_{0}H_{m}}$ 8.5 Hz, 2 × H_o) and 9.00 (1 H, d, ${}^{4}J_{P_{B}H}$ 6.6 Hz, CH=). ${}^{13}C$ -{ ${}^{1}H$ } 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, ${}^{3}J_{PC}$ 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): $\delta 6.88$ (1 H, dd, ²J_{PAH} 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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