A General Method of generating Agostic Interaction between Ru^{II} and C–H Bonds of *tert*-Butyl, Methyl, Aryl, Heterocyclic or Alkenyl Groups using Azine Phosphines

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Treatment of $[RuCl_2(PPh_3)_3]$ **2** with the azine phosphine *Z,E*-$PPh_2CH_2C(Bu^t)$=N–N=C(Me)Bu^t **3a**, derived from MeC(=O)Bu^t, gave the δ-agostic *tert*-butyl complex *mer,trans*-$[RuCl_2(PPh_3)\{PPh_2CH_2C(Bu^t)$=N–N=C(Me)$Bu^t\}]$ **4a**, in which all nine hydrogens of the *tert*-butyl group are agostically interacting with ruthenium on the NMR time-scale at 20 °C. The analogous δ-agostic *tert*-butyl complex *mer,trans*-$[RuCl_2(PPh_3)\{PPh_2CH_2C(Bu^t)$=N–N=C(H)$Bu^t\}]$ **4b** was also prepared. Treatment of **2** with the symmetrical azine diphosphine *Z,Z*-$PPh_2CH_2C(Bu^t)$=N–N=$C(Bu^t)CH_2PPh_2$ **5** gave the δ-agostic *tert*-butyl complex *mer,trans*-$[RuCl_2(PPh_3)\{PPh_2CH_2C(Bu^t)$=N–N=$C(Bu^t)CH_2PPh_2\}]$ **6**, in which one of the PPh_2 groups is unco-ordinated. Treatment of **2** with the azine phosphine *Z,E*-$PPh_2CH_2C(Bu^t)$=N–N=$C_{10}H_{16}$ **7**, derived from pinacolone–fenchone mixed azine, gave the δ-agostic methyl complex *mer,trans*-$[RuCl_2(PPh_3)\{PPh_2CH_2C(Bu^t)$=N–N=$C_{10}H_{16}\}]$ **8**, in which the methyl group ($C^{10}H_3$) in the 1-position of the fenchone residue interacts with ruthenium (fenchone = 1,3,3-trimethylbicyclo[2.2.1]heptan-2-one). The unsymmetrical camphor azine monophosphine *Z,Z*-PPh_2-$C_{10}H_{15}$=N–N=$C_{10}H_{16}$ **9** also gave a similar δ-agostic methyl complex *mer,trans*-$[RuCl_2(PPh_3)\{PPh_2$-$C_{10}H_{15}$=N–N=$C_{10}H_{16}\}]$ **10** (camphor = 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one). Treatment of **2** with the azine *Z,E*-$PPh_2CH_2C(Bu^t)$=N–N=$CH(C_6H_4NMe_2$-4) **11a**, derived from 4-dimethylaminobenzaldehyde, gave the δ-agostic complex *mer,trans*-$[RuCl_2(PPh_3)\{PPh_2CH_2C(Bu^t)$=N–N=$CH(C_6H_4NMe_2$-4)$\}]$ **12a**, in which the hydrogens in the 2 and 6 positions of the aryl group are agostically interacting with ruthenium. Similarly, the azines **11b** and **11c**, derived from 4-methoxybenzaldehyde or 4-nitrobenzaldehyde, gave the δ-agostic complexes **12b** and **12c**, respectively. Treatment of **2** with the azine **13**, derived from 1-methylpyrrole-2-carbaldehyde, gave the δ-agostic complex **14**, in which the hydrogen in the 3-position of the heterocyclic group is agostically interacting with ruthenium. Treatment of **2** with the azine **15**, derived from benzylideneacetone, gave the δ-agostic alkenyl complex **16**. Proton, ^{31}P-$\{^1H\}$ and some ^{13}C-$\{^1H\}$ NMR data are given.

In a previous paper[1] we have described the synthesis of a very reactive phosphino hydrazone *Z*-$PPh_2CH_2C(Bu^t)$=NNH_2 **1** from the corresponding phosphino *N,N*-dimethylhydrazone *Z*-$PPh_2CH_2C(Bu^t)$=$NNMe_2$ by a hydrazine exchange reaction. We have shown that **1** is a convenient reagent for converting aldehydes or ketones QC(=O)R into azines of type *Z,E*-$PPh_2CH_2C(Bu^t)$=N–N=C(Q)R [1–11] (Q = H or Me; R = an aryl, heterocyclic or alkyl group) which were then cyclometallated using transition metal centres such as Ir^I,[2–5] W^0[6] or Pt^{II}.[2,7] We have also promoted co-ordination of an aryl fluoride to ruthenium(II).[10] In this paper we have used the strategy to promote C–H (agostic) interactions with ruthenium(II). The first suggestion of a C–H ··· metal interaction came from the crystal structure of $[RuCl_2(PPh_3)_3]$[12] as determined by LaPlaca and Ibers[13] and shown diagrammatically in **2**; the agostic interaction is represented by a single headed arrow.[14] Since then many other examples of agostic interaction have been reported and the area has been reviewed.[14–18] We anticipated that an azine phosphine of type *Z,E*-$PPh_2CH_2C(Bu^t)$=N–N=C(Q)R would displace two PPh_3 ligands from the labile ruthenium(II) complex $[RuCl_2(PPh_3)_3]$ **2** to give a six-membered (P–N) chelate, through P and N=C(Q)R nitrogen. This would force the R group to be in close proximity to the metal and induce interaction, *i.e.* agostic interaction, between a C–H bond in the R group and the ruthenium. We found this to be the case and report examples of agostic interactions with *tert*-butyl, methyl, aryl, heterocyclic and alkenyl groups. A preliminary account of some of this work has been published.[19]

Results and Discussion

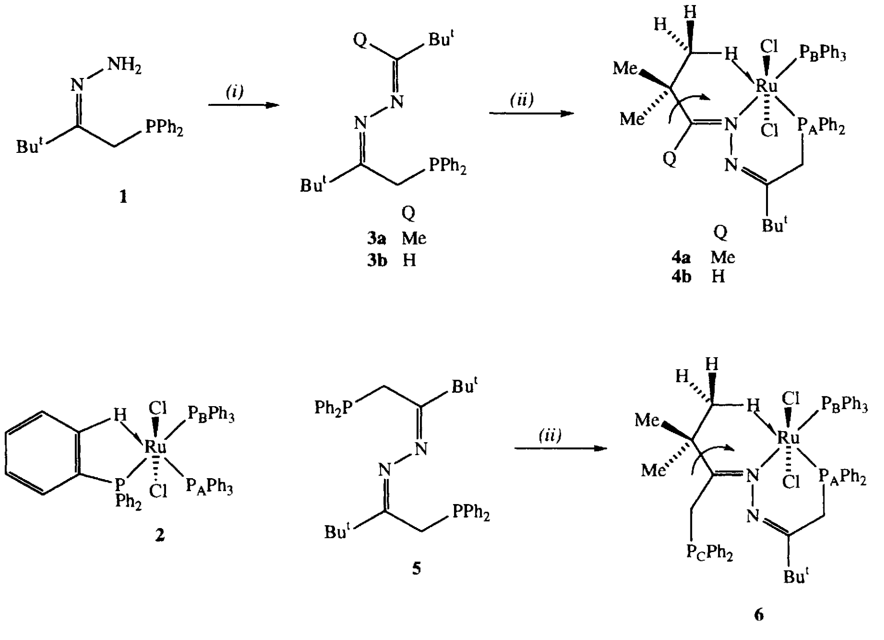
For the convenience of the reader the various reactions are shown in Schemes 1–3. Elemental analytical, IR, mass spectral and some selected carbon-13 NMR data are in the Experimental section, and phosphorus-31 and proton NMR data in Tables 1 and 2, respectively. Carbon-13 spectra were assigned using Attached Proton Tests (APT) and by comparison with published data.[11,20,21]

We first attempted to generate agostic interactions with a C–H of a *tert*-butyl group. We have shown that treatment of the phosphino hydrazone *Z*-$PPh_2CH_2C(Bu^t)$=NNH_2 **1** with pinacolone, MeC(=O)Bu^t, gives the azine *Z,E*-$PPh_2CH_2C(Bu^t)$=N–N=C(Me)Bu^t **3a**;[5] **1** when treated with $[RuCl_2(PPh_3)_3]$ **2** in benzene at *ca.* 50 °C for 1 min displaced two triphenylphosphine ligands and gave the hoped for δ-agostic *tert*-butyl complex *mer,trans*-$[RuCl_2(PPh_3)\{PPh_2CH_2C(Bu^t)$=N–N=C(Me)$Bu^t\}]$ **4a** (Scheme 1) essentially quantitatively (^{31}P-$\{^1H\}$ NMR evidence). This complex was isolated in 88% yield as brick-red microcrystals. The ^{31}P-$\{^1H\}$ NMR spectrum of the complex showed two doublets [$\delta(P_A)$ 74.7 (d) and $\delta(P_B)$ 44.0 (d)] with $^2J(PP)$ = 40 Hz, typical of *cis*-phosphine ligands.[19] The occurrence of an infrared band at 320s cm^{-1} for ν(Ru–Cl) indicates a *trans* Cl–Ru–Cl moiety,[22] therefore, this complex must have the *mer,trans*-geometry at the metal centre. At 20 °C the proton NMR spectrum of this remarkable ruthenium(II) complex **4a** showed a doublet for one of the *tert*-butyl protons at δ 1.17 with coupling only to P_A [$^2J(P_AH)$ = 2.4 Hz] as shown by selective decoupling of P_A, indicating the presence of

Table 1 ^{31}P-{^{1}H} NMR data[a]

Compound	δ(P_A)	δ(P_B)	^2J(PP)	Compound	δ(P_A)	δ(P_B)	^2J(PP)
3a	−12.4 (s)			**11a**	−11.3 (s)		
3b	−10.5 (s)			**11b**	−10.0 (s)		
4a[b]	74.7 (d)	44.0 (d)	40	**11c**	−10.4 (s)		
4b[b]	73.7 (d)	43.3 (d)	37	**12a**	78.4 (d)	45.8 (d)	37
5	−14.4 (s)			**12b**	78.6 (d)	45.9 (d)	37
6[c,d]	75.2 (d)	43.9 (d)	39	**12c**[b]	81.3 (d)	45.7 (d)	38
7	−12.4 (s)			**13**	−10.9 (s)		
8[b]	76.7 (d)	43.1 (d)	39	**14**	78.2 (d)	44.0 (d)	37
9	−0.3 (s)			**15**	−10.7 (s)		
10[c]	81.4 (d)	38.8 (d)	41	**16**[b]	90.1 (d)	47.0 (d)	37

[a] Recorded at 36.2 MHz, chemical shifts δ(P) are in ppm relative to 85% H_3PO_4, ^2J(PP) values are in Hz, solvent $CDCl_3$ unless otherwise stated, s = singlet and d = doublet. [b] In CD_2Cl_2. [c] In C_6D_6. [d] Unco-ordinated PPh_2 at δ −8.8.



Scheme 1 (*i*) QC(=O)Bu^t; (*ii*) [$RuCl_2(PPh_3)_3$] **2**

δ-agostic interactions between ruthenium and all nine hydrogens of the *tert*-butyl group. The appearance of this *tert*-butyl resonance as a doublet suggests that all nine hydrogens of the *tert*-butyl group are chemically equivalent and equally coupled to P_A due to the rapid rotation around the C–Bu^t bond on the NMR time-scale. Since the observed $^2J(P_AH)$ value (2.4 Hz) is an averaged value over the nine hydrogens we infer that the agostic interaction is quite strong. When the NMR sample was cooled to −50 °C, only three hydrogens (*i.e.* one methyl group) showed coupling to P_A, δ(Me–agostic) 0.92 [$^2J(P_AH)$ = 7.3 Hz], and the other two methyl resonances appeared as singlets at δ 1.19 and 1.28 (see Fig. 1); *i.e.* rotation around the Bu^t–C bond has slowed down or stopped. At −50 °C, the ^{1}H-{^{31}P} NMR spectrum showed an AB-pattern with ^2J(HH) ≈ 12 Hz for the CH_2 protons (Fig. 1) as previously observed for methylene protons in similar six-membered chelate rings.[6,8] We were unable to stop the rotation of the interacting methyl group by cooling the NMR solution to −85 °C. The ^{13}C-{^{1}H} NMR data (Experimental section) also support the fluxional behaviour referred above; at room temperature, the resonance for the three agostic methyl carbons was a very broad peak at δ ≈ 29, but at −50 °C, three separate signals were observed at δ 19.9 [d, ^3J(PC) = 13.6 Hz], 27.7 (s) and 30.3 (s) for these methyl carbons of which the doublet resonance with coupling to phosphorus was assigned to the agostic methyl carbon. This is the first example of a δ-agostic *tert*-butyl complex showing spin–spin coupling of the *tert*-butyl hydrogens through the metal atom to a co-ordinated tertiary phosphine ligand, *i.e.* a ^2J(PH) coupling. The azine phosphine **3b**, derived from HC(=O)Bu^t, gave the analogous δ-agostic *tert*-butyl complex [$RuCl_2(PPh_3)${$PPh_2CH_2C(Bu^t)$=N–N=C(H)Bu^t}] **4b** in excellent (92%) yield. In the proton NMR spectrum, the resonance due to the agostic *tert*-butyl group was a doublet at δ 1.12 with $^2J(P_AH)$ = 2.0 Hz whilst the imine proton (HC=N) resonance gave a doublet of doublets at 8.24 [dd, $^4J(P_BH)$ = 6.1, $^4J(P_AH)$ = 0.6 Hz]; *i.e.* the imine proton is strongly coupled to P_B (which is *trans* to the imine nitrogen HC=N) as reported for similar complexes *e.g.* [$RuCl_2(PPh_3)${$PPh_2CH_2C(Bu^t)$=N–N=C(H)$C_6H_{4-n}F_n$}] (*n* = 1 or 2).[10]

Similarly, other azine phosphine ligands discussed below readily displaced two PPh_3 ligands from [$RuCl_2(PPh_3)_3$] **2** to give *mer,trans*-ruthenium(II) complexes as shown by their ^{31}P-{^{1}H} NMR [^2J(PP) ≈ 40 Hz] and IR data [ν(Ru–Cl) ≈ 320 cm^{-1}].

We have described the azine diphosphine, *Z,Z*-$Ph_2PCH_2C(Bu^t)$=N–N=$C(Bu^t)CH_2PPh_2$ **5**[23] and this when treated with [$RuCl_2(PPh_3)_3$] displaced only two PPh_3 to give the δ-agostic *tert*-butyl complex **6** *i.e.* the *tert*-butyl groups again interacts agostically on to ruthenium, showing coupling to P_A [$^2J(P_AH)$ = 2.7 Hz] and one of the PPh_2 groups is unco-ordinated with the resonance occurring as a singlet at δ(P_C) −8.8; *i.e.* the ruthenium prefers the agostic interaction to the *tert*-butyl group rather than co-ordination to P_C.

Treatment of [$RuCl_2(PPh_3)_3$] with the phosphine **7**,[24]

Table 2 Proton NMR data[a]

Compound	δ(Bu^t)	δ(CH_2P)	Others
3a	0.99 (9 H, s) 1.02 (9 H, s)	3.23 [2 H, d, ^{2}J(PH) 4.4]	1.83 (3 H, s, =CMe)
3b	0.98 (9 H, s) 1.06 (9 H, s)	3.41 [2 H, d, ^{2}J(PH) 4.0]	—
4a[b,c]	0.64 (9 H, s) 1.17 [9 H, d, $^{2}J(P_AH)$ 2.4]	3.23 (1 H, br) 3.92 (1 H, br)	2.27 (3 H, s, =CMe)
4b[b,d]	0.66 (9 H, s) 1.12 [9 H, d, $^{2}J(P_AH)$ 2.0]	3.55 (2 H, br)	8.24 [1 H, dd, $^{4}J(P_BH)$ 6.1, $^{4}J(P_AH)$ 0.6, =CH]
5	0.90 (18 H, s)	3.26 [4 H, d, ^{2}J(PH) 3.9]	—
6[b,e]	0.57 (9 H, s) 0.83 [9 H, d, $^{2}J(P_AH)$ 2.7]	3.62 (4 H, m, br)	—
7	1.05 (9 H, s)	3.31 [1 H, dd, ^{2}J(HH) 12.7, ^{2}J(PH) 4.4] 3.43 [1 H, dd, ^{2}J(HH) 12.7, ^{2}J(PH) 4.4]	1.08 (3 H, s, H^{10}) 1.24 (3 H, s, H^8 or H^9) 1.25 (3 H, s, H^8 or H^9)
8[b]	0.69 (9 H, s)	3.19 [1 H, dd, ^{2}J(HH) 11.7, $^{2}J(P_AH)$ 12.0] 3.83 [1 H, dd, ^{2}J(HH) 11.7, $^{2}J(P_AH)$ 12.2]	0.99 [3 H, d, $^{2}J(P_AH)$ 7.1, agostic Me] 1.26 (3 H, s, H^8 or H^9) 1.57 (3 H, s, H^8 or H^9)
9	—	—	0.13s, 0.68s, 0.74s, 0.76s, 0.96s and 1.04s (camphor methyls) 3.28 [1 H, d, ^{2}J(PH) 2.7, C*H*P]
10	—	—	−0.20s, 0.51s, 0.59s, 0.96s and 1.12s (camphor methyls) 0.94 [3 H, d, $^{2}J(P_AH)$ 3.8, agostic Me] 4.45 [1 H, d, $^{2}J(P_AH)$ 18.8, C*H*P]
11a	1.19 (9 H, s)	3.54 [2 H, d, ^{2}J(PH) 2.9]	2.99 (6 H, s, NMe_2) 6.57 [2 H, d, ^{3}J(HH) 9.0, H_m] 8.05 (1 H, s, CH=)
11b	1.22 (9 H, s)	3.52 [2 H, d, ^{2}J(PH) 3.2]	3.81 (3 H, s, OMe) 8.04 (1 H, s, CH=)
11c	1.25 (9 H, s)	3.50 [2 H, d, ^{2}J(PH) 2.9]	8.03 [2 H, d, ^{3}J(HH) 8.6, H_m] 8.14 (1 H, s, CH=)
12a	0.72 (9 H, s)	3.44 [2 H, d, $^{2}J(P_AH)$ 15.2]	2.85 (6 H, s, NMe_2) 5.95 [2 H, d, ^{3}J(HH) 8.5, H_m] 6.57 [2 H, dd, ^{3}J(HH) 8.5, $^{2}J(P_AH)$ 2.1, H_o] 9.00 [1 H, d, $^{4}J(P_BH)$ 6.4, CH=]
12b	0.73 (9 H, s)	3.42 [2 H, d, $^{2}J(P_AH)$ 15.1]	3.62 (3 H, s, OMe) 6.18 [2 H, d, ^{3}J(HH) 8.6, H_m] 6.83 [2 H, dd, ^{3}J(HH) 8.6, $^{2}J(P_AH)$ 2.0, H_o] 9.10 [1 H, d, $^{4}J(P_BH)$ 6.4, CH=]
12c[b,f]	0.75 (9 H, s)	3.41 [2 H, d, $^{2}J(P_AH)$ 14.3]	7.36 [2 H, dd, ^{3}J(HH) 8.6, $^{2}J(P_AH)$ 1.8, H_o] 7.50 [2 H, d, ^{3}J(HH) 8.6, H_m] 8.91 [1 H, d, $^{4}J(P_BH)$ 6.4, CH=]
13[g]	1.15 (9 H, s)	3.49 [2 H, d, ^{2}J(PH) 3.4]	3.56 (3 H, s, NMe) 6.09 [1 H, dd, J(HH) 2.6, 3.8, H^4] 6.41 [1 H, dd, J(HH) 1.8, 3.8, H^3] 6.62 [1 H, t, J(HH) 2.2, H^5] 8.07 [1 H, s, CH=]
14[g]	0.77 (9 H, s)	3.54 [2 H, d, ^{2}J(PH) 15.0]	3.76 (3 H, s, NMe) 5.74 [1 H, m, J(HH) 0.5, 2.4, 3.8, H^4] 6.67 [1 H, m, J(HH) 1.6, 3.8, $^{2}J(P_AH)$ 3.8, H^3] 6.86 [1 H, dd, J(HH) 1.6, 2.4, H^5] 9.22 [1 H, dd, $^{4}J(P_BH)$ 5.8, ^{5}J(HH) 0.5, CH=]
15	1.20 (9 H, s)	3.31 [2 H, d, ^{2}J(PH) 3.4]	1.93 (3 H, s, Me) 6.51 [1 H, d, ^{3}J(HH) 16.4, =CH] 6.80 [1 H, d, ^{3}J(HH) 16.4, =CH]
16[b,f]	0.74 (9 H, s)	3.47 [2 H, d, $^{2}J(P_AH)$ 14.5]	2.71 (3 H, s, Me) 6.88 [1 H, dd, ^{3}J(HH) 15.6, $^{2}J(P_AH)$ 1.8, agostic H] 7.34 [1 H, d, ^{3}J(HH) 15.6, =CH]

[a] Recorded at 100 MHz, unless stated otherwise; chemical shifts are in ppm relative to $SiMe_4$, J values are in Hz; solvent $CDCl_3$ unless otherwise stated; s = singlet, d = doublet, t = triplet, dd = doublet of doublets. Multiplicities refer to ^1H spectra although $^1H-\{^{31}P\}$ spectra were also measured and $^1H-\{^{31}P_A\}$ and $^1H-\{^{31}P_B\}$ spectra, when necessary. [b] In CD_2Cl_2. [c] At −50 °C, δ 0.62 (9 H, s, Bu^t), 0.92 [3 H, d, $^{2}J(P_AH)$ 7.3, agostic Me], 1.19 (3 H, s, Me of Bu^t), 1.28 (3 H, s, Me of Bu^t), 3.2 [1 H, dd, br, ^{2}J(HH) 12, $^{2}J(P_AH)$ 13, CH_2] and 3.7 [1 H, dd, br, ^{2}J(HH) 12, $^{2}J(P_AH)$ 13, CH_2]. [d] At −50 °C, δ 3.1 [1 H, dd, br, ^{2}J(HH) 12, $^{2}J(P_AH)$ 13, CH_2], 3.8 [1 H, dd, br, ^{2}J(HH) 12, $^{2}J(P_AH)$ 13, CH_2] and the resonance due to the agostic Bu^t group is broad even at −70 °C. [e] At −40 °C, δ 1.0 (br, agostic Bu^t), 3.1 [1 H, m, ^{2}J(HH) 12, CH_2], 3.3 [1 H, m, ^{2}J(HH) 13, CH_2], 4.0 [1 H, m, ^{2}J(HH) 12, CH_2] and 4.3 [1 H, m, ^{2}J(HH) 13, CH_2]. [f] At 400 MHz. [g] At 250 MHz.

derived from pinacolone fenchone mixed azine (fenchone = 1,3,3-trimethylbicyclo[2.2.1]heptan-2-one), gave the δ-agostic methyl complex **8** in which the methyl group in the 10-position of the fenchone residue interacts with ruthenium, and all three hydrogens are equally coupled to P_A, δ(Me) 0.99, $^{2}J(P_AH)$ = 7.1 Hz (Scheme 2).

We anticipated that a similar agostic interaction of a methyl group in the 10-position of camphor (1,7,7-trimethylbicyclo-

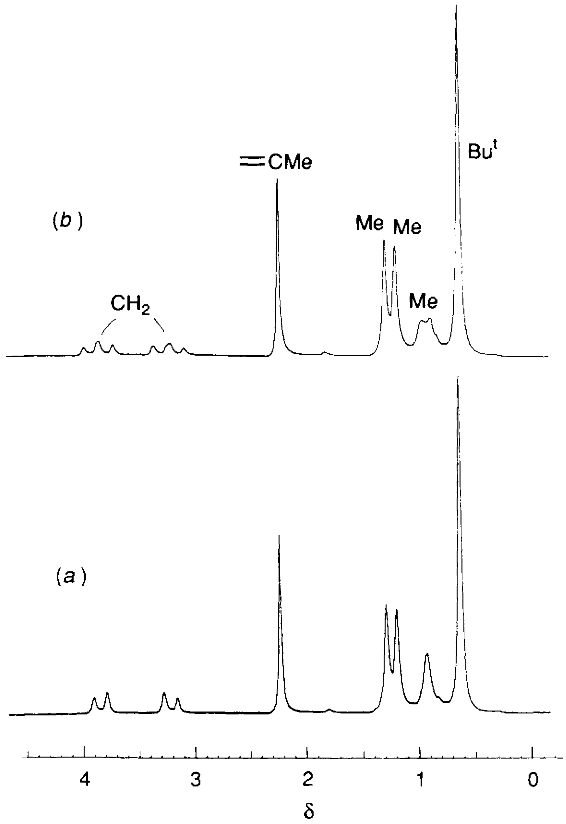
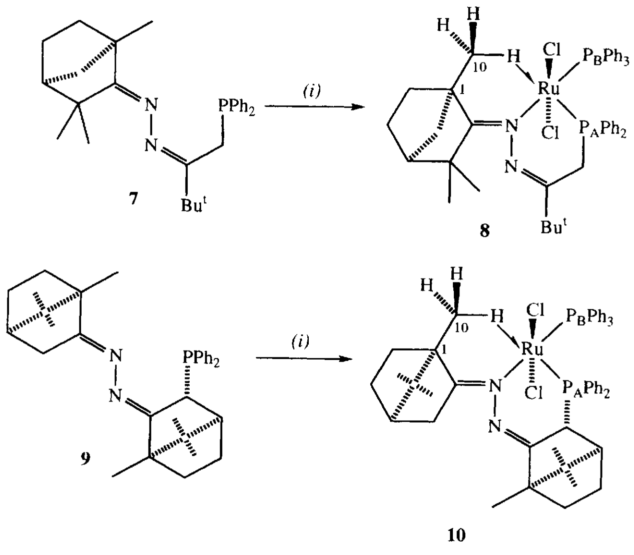


Fig. 1 Part of the proton NMR spectra of **4a** at −50 °C in $CDCl_3$. (*a*) $^1H-\{^{31}P\}$ spectrum (*b*) ^1H spectrum. The spectra show that, for the *tert*-butyl group which interacts agostically and dynamically with Ru at 20 °C, only one of its methyls is agostically interacting at −50 °C (see Discussion and Table 2 for data)



Scheme 2 (*i*) $[RuCl_2(PPh_3)_3]$

[2.2.1]heptan-2-one) would be induced by complexing the phosphine generated from camphor azine to ruthenium. Treatment of (1*R*)-(+)-camphor azine[25] with 1 mol of $LiBu^n$, followed by addition of PPh_2Cl introduced a PPh_2 group into the *exo*-3-position of one of the camphor residues *i.e.* giving the camphor azine phosphine **9**. Preparative details are in the Experimental section and characterizing data are in Tables 1 and 2 (we are very grateful to Dr. N. Iranpoor, who was the first to make **9** and to characterize it). Treatment of $[RuCl_2(PPh_3)_3]$ with **9** for *ca.* 1 min gave the hoped for derivative **10** in 69% yield; characterizing data are in the Experimental section and in the Tables; in particular the δ-agostic methyl showed coupling to the phosphorus in *trans*-position, δ(Me) 0.94, $^2J(P_AH)$ = 3.8 Hz.

We can similarly induce δ-agostic interaction with aromatic C–H bonds (Scheme 3). The mixed azine phosphine **11a** from 4-dimethylaminobenzaldehyde reacted with $[RuCl_2(PPh_3)_3]$ to give the δ-agostic aryl complex **12a** in which both *ortho* hydrogens (*i.e.* at the 2,6-positions of the $C_6H_4NMe_2$ ring) interact with ruthenium, $\delta(H_o)$ 6.57, $^2J(P_AH_o) = 2.1$, $^3J(H_oH_m) = 8.5$ Hz. Similar results were obtained with the azine phosphine **11b**,[7] derived from 4-methoxybenzaldehyde; and **11c**,[5] from 4-nitrobenzaldehyde. In each case agostic interaction with both *ortho*-hydrogens occurred *i.e.* for **12b** $^2J(P_AH_o) = 2.0$ Hz and for **12c** $^2J(P_AH_o) = 1.8$ Hz. Thus an electron-releasing group (NMe_2) or electron-withdrawing group (NO_2) in the 4-position had essentially no substantial effect on the agostic interaction of the two hydrogens in the 2,6-positions with the ruthenium; similarly for a 4-methoxy group.

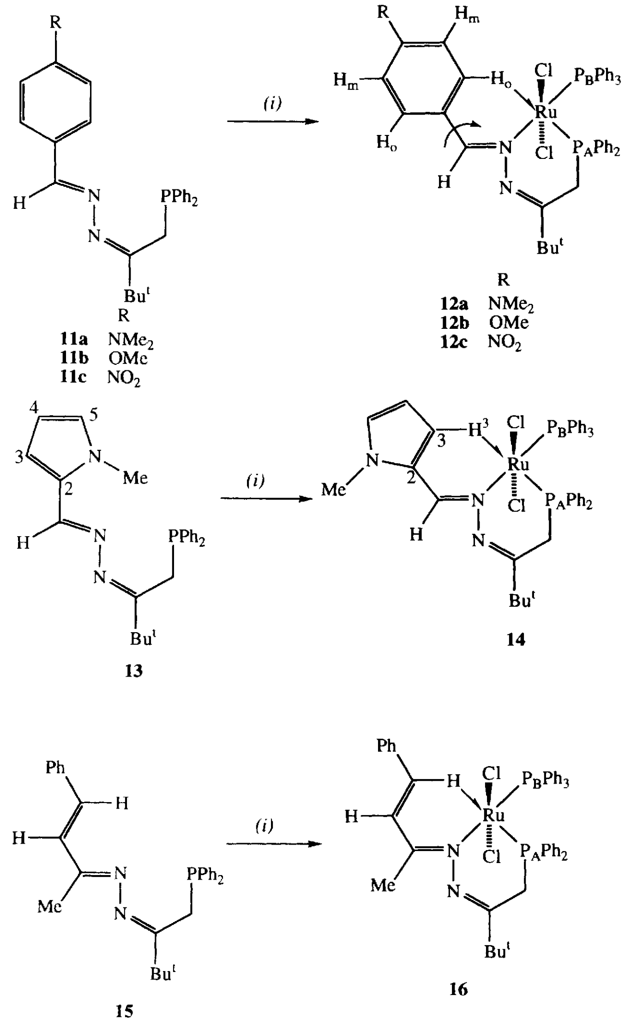
We have described the mixed azine phosphine **13** made by condensing the hydrazone phosphine **1** with *N*-methylpyrrole-2-carbaldehyde[5] and have shown that, when treated with $[IrCl(CO)_2(MeC_6H_4NH_2\text{-}p)]$, cyclometallation occurs at the carbon in the 3-position of the pyrrole residue. We therefore hoped that treatment with $[RuCl_2(PPh_3)_3]$ would give a product which would show agostic interaction of the C^3–H on the pyrrole residue and the ruthenium. This we have found to be the case and **14** was isolated in 85% yield with the agostic hydrogen showing a coupling to P_A of 3.8 Hz (see Table 2). The coupling constants within the pyrrole residue were assigned using selective decoupling experiments *i.e.* for both H–H and P–H couplings.

The mixed azine phosphine **15** from benzylideneacetone reacted with $[RuCl_2(PPh_3)_3]$ to give an agostic alkenyl complex in which one of the alkenyl hydrogens was agostically interacting with the ruthenium, and was coupled to P_A, δ(CH=) 6.88, $^2J(P_ACH{=}) = 1.8$, $^3J(HC{=}CH) = 15.6$ Hz. We tentatively suggest that it has the structure **16** having δ-agostic interaction with the =C*H*Ph alkenyl hydrogen, however, we cannot rule out a γ-agostic interaction with the C*H*=CPh hydrogen.

We found no evidence of carbon metallation by ruthenium in any of these reactions. For example, prolonged treatment of the agostic *tert*-butyl complex **5** with a base, *e.g.* NEt_3 or NaO_2CMe did not lead to ruthenium–carbon bond formation nor did prolonged exposure of a solution of **5** to CO or H_2 at 20 °C lead to any reaction. The failure of agostic interactions with these ruthenium complexes, of the types shown in the Schemes, to lead to metal–carbon bond formation is probably because the chlorides in the *trans*-Cl–Ru–Cl moiety are very poor leaving groups. In our previously reported work on the reactions of mixed azines of type *Z*,*E*-$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Q)R$ with iridium(I)[2,5] cyclometallation occurred, accompanied by oxidative addition with four-co-ordinate iridium(I) going to six-co-ordinate iridium(III); and treatment of $[PtMe_2(cod)]$ (cod = cycloocta-1,5-diene) with the mixed azines, a methyl group was lost as methane and cyclometallation of the R group occurred.[2,7]

Experimental

All the reactions were carried out in an inert atmosphere of dry nitrogen or dry argon. Infrared spectra were recorded using a Perkin-Elmer model 457 grating spectrometer. The NMR spectra were recorded using a JEOL FX-90Q spectrometer (operating frequencies for ^1H and ^{31}P of 89.5 and 36.2 MHz respectively), a JEOL FX-100 spectrometer (operating frequencies for ^1H and ^{31}P of 99.5 and 40.25 MHz respectively), a Bruker ARX-250 spectrometer (operating frequencies for ^1H, ^{31}P and ^{13}C of 250.1, 101.3 and 62.9 MHz respectively) or a Bruker AM-400 spectrometer (operating frequencies for ^1H, ^{31}P and ^{13}C of 400.13, 161.9 and 100.6 MHz respectively). The



Scheme 3 (*i*) $[\mathrm{RuCl_2(PPh_3)_3}]$

^{1}H and ^{13}C chemical shifts are relative to tetramethylsilane and ^{31}P shifts are relative to 85% phosphoric acids, and all coupling constants are in Hz. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded using a VG Autospec spectrometer with 8 kV acceleration, and for metal complexes the *m*/*z* values are quoted for ^{102}Ru.

Preparation of Phosphine Ligands.—The phosphines **1**,[1] **3a**,[5] **5**,[23] **7**,[24] **11b**,[7] **11c**[7] and **13**[5] were prepared according to our published procedures.

The following three azine phosphines, **3b**, **11a** and **15**, were prepared and isolated as crystalline solids in a similar manner to that described for **11b**.[7] *Z,E*-$\mathrm{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(H)Bu^t}$ **3b**. Yield 81% (Found: C, 74.9; H, 8.4; N, 7.35. $C_{23}H_{31}N_2P$ requires C, 75.35; H, 8.5; N, 7.65%). *m*/*z* (EI) 309 (*M* − Bu^t). *Z,E*-$\mathrm{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_6H_4NMe_2\text{-}4)}$ **11a**. Yield 78% (Found: C, 75.45; H, 7.8; N, 9.85. $C_{27}H_{32}N_3P$ requires C, 75.5; H, 7.5; N, 9.8%). *m*/*z* (EI): 372 (*M* − Bu^t). *Z,E*-$\mathrm{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Me)CH{=}CHPh}$ **15**. Yield 79% (Found: C, 78.9; H, 7.45; N, 6.7. $C_{28}H_{31}N_2P$ requires C, 78.85; H, 7.35; N, 6.55%). *m*/*z* (EI); 426 (M^+) and 369 (*M* − Bu^t).

$\mathrm{PPh_2C_{10}H_{15}{=}N{-}N{=}C_{10}H_{16}}$ **9** (with Dr. N. Iranpoor). A solution of lithium diisopropylamide (0.05 mol) was prepared by treating a solution of LiBu^n (0.05 mol) in hexane (3.4 cm^3) with diisopropylamine (5.1 g, 0.05 mol) in tetrahydrofuran (thf) (7 cm^3). A solution of (1*R*)-(+)-camphor azine (15.0 g, 0.05 mol) in thf (70 cm^3) was then added to the lithium diisopropylamide solution at −20 °C, with stirring. After a further 30 min a solution of $\mathrm{PPh_2Cl}$ (11.1 g, 0.05 mol) in thf (150 cm^3) was added dropwise with stirring at −15 °C; the solution was then stirred for a further 30 min and then allowed to warm to room temperature. The resultant mixture was evaporated to low bulk on a Rotavap; ethanol was added to the residue, which was then cooled to *ca.* +5 °C. The required product crystallized as microcrystals which were filtered off, washed with ethanol and dried. Yield 9.8 g, 67% (Found: C, 77.85; H, 8.45; N, 5.6. $C_{32}H_{41}N_2P{\cdot}0.2EtOH$ requires C, 77.8; H, 8.35; N, 5.65%).

Preparation of Ruthenium(II) *Complexes.*—*mer,trans*-$[\mathrm{RuCl_2(PPh_3)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Me)Bu^t\}}]$ **4a**. The complex $[\mathrm{RuCl_2(PPh_3)_3}]$ (80 mg, 0.083 mmol) and the azine phosphine **3a** (33 mg, 0.083 mmol) were warmed (*ca.* 60 °C) in benzene (*ca.* 2 cm^3) for 1 min. The resulting cherry red solution was concentrated to a low volume (*ca.* 0.5 cm^3). Addition of hexane (*ca.* 1.5 cm^3) to the residue gave the *mer,trans*-ruthenium(II) complex **4a** as brick-red microcrystals (60 mg, 88%) (Found: C, 63.0; H, 6.25; Cl, 8.2; N, 3.05. $C_{42}H_{48}Cl_2N_2P_2Ru{\cdot}0.5C_6H_6$ requires C, 63.3; H, 6.0; Cl, 8.3; N, 3.3%). *m*/*z* (FAB): 814 (M^+), 779 (*M* − Cl) and 743 (*M* − Cl − HCl). ν(Ru–Cl) 320 cm^{-1}. ^{13}C-{^{1}H} NMR (100.6 MHz, CD_2Cl_2, −50 °C): δ_C 19.9 [1 C, d, ^3J(PC) 13.6, agostic Me], 20.5 (1 C, s, *Me*C=), 26.7 (3 C, s, C*Me*$_3$), 27.7 (1 C, s, C*Me*$_3$ of agostic Bu^t), 30.3 (1 C, s, C*Me*$_3$ of agostic Bu^t), 30.8 [1 C, d, $^1J(P_AC)$ 29.2, CH$_2$], 40.7 (1 C, s, *C*Me$_3$), 42.0 (1 C, s, *C*Me$_3$), 170.4 (1 C, s, C=N) and 185.2 (1 C, s, C=N). The ^{13}C-{^{1}H} NMR spectrum, recorded at room temperature (20 °C), showed a very broad peak at δ ≈ 29 for the three methyl carbons of the agostic *tert*-butyl group.

The following *mer,trans*-ruthenium(II) complexes were prepared similarly. *mer,trans*-$[\mathrm{RuCl_2(PPh_3)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(H)Bu^t\}}]$ **4b**. Yield 92% (Found: C, 61.6; H, 5.6; Cl, 8.45; N, 2.8. $C_{41}H_{46}Cl_2N_2P_2Ru$ requires C, 61.5; H, 5.8; Cl, 8.85; N, 2.5%). *m*/*z* (FAB): 800 (M^+), 765 (*M* − Cl) and 729 (*M* − Cl − HCl). ν(Ru–Cl) 315 cm^{-1}. *mer,trans*-$[\mathrm{RuCl_2(PPh_3)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2\}}]$ **6**. Yield 72% (Found: C, 64.8; H, 5.55; Cl, 6.8; N, 2.8. $C_{54}H_{57}Cl_2N_2P_3Ru$ requires C, 64.9; H, 5.75; Cl, 7.1; N, 2.8%). *m*/*z* (FAB): 998 (M^+), 963 (*M* − Cl) and 927 (*M* − Cl − HCl). ν(Ru–Cl) 320 cm^{-1}. *mer,trans*-$[\mathrm{RuCl_2(PPh_3)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C_{10}H_{16}\}}]$ **8**. Yield 61% (Found: C, 65.4; H, 5.85; Cl, 7.6; N, 2.8. $C_{46}H_{52}Cl_2N_2P_2Ru{\cdot}0.6C_6H_6$ requires C, 65.2; H, 6.15; Cl, 7.7; N, 3.05%). *m*/*z* (FAB): 866 (M^+), 831 (*M* − Cl) and 795 (*M* − Cl − HCl). ν(Ru–Cl) 320 cm^{-1}. *mer,trans*-$[\mathrm{RuCl_2(PPh_3)\{PPh_2C_{10}H_{15}{=}N{-}N{=}C_{10}H_{16}\}}]$ **10**. Yield 69%. *m*/*z* (FAB): 918 (M^+), 883 (*M* − Cl) and 847 (*M* − Cl − HCl). ν(Ru–Cl) 315 cm^{-1}. *mer,trans*-$[\mathrm{RuCl_2(PPh_3)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_6H_4NMe_2\text{-}4)\}}]$ **12a**. Yield 83% (Found: C, 62.4; H, 5.4; Cl, 8.15; N, 4.6. $C_{45}H_{47}Cl_2N_3P_2Ru$ requires C, 62.55; H, 5.5; Cl, 8.2; N, 4.85%). *m*/*z* (FAB): 863 (M^+), 828 (*M* − Cl) and 792 (*M* − Cl − HCl). ν(Ru–Cl) 320 cm^{-1}. ^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 27.3 (3 C, s, C*Me*$_3$), 31.3 [1 C, d, $^1J(P_AC)$ 28.2, CH$_2$], 39.8 [1 C, d, $^3J(P_AC)$ 2.6, *C*Me$_3$], 40.1 (2 C, s, NMe$_2$), 111.9 (2 C, s, C_{meta} of $C_6H_4NMe_2$), 120.8 (1 C, s, C_{ipso} or C_{para} of $C_6H_4NMe_2$], 133.0 [2 C, d, $^3J(P_AC)$ 5.2, C_{ortho} of $C_6H_4NMe_2$], 151.7 (1 C, s, C_{ipso} or C_{para} of $C_6H_4NMe_2$), 168.2 (1 C, s, HC=N) and 170.8 (1 C, s, Bu^t*C*=N). *mer,-trans*-$[\mathrm{RuCl_2(PPh_3)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_6H_4OMe\text{-}4)\}}]$ **12b**. Yield 81% (Found: C, 62.35; H, 5.35; Cl, 8.25; N, 3.05. $C_{44}H_{44}Cl_2N_2OP_2Ru$ requires C, 62.1; H, 5.2; Cl, 8.35; N, 3.3%). *m*/*z* (FAB): 850 (M^+), 815 (*M* − Cl) and 779 (*M* − Cl − HCl). ν(Ru–Cl) 320 cm^{-1}. *mer,trans*-$[\mathrm{RuCl_2(PPh_3)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_6H_4NO_2\text{-}4)\}}]$ **12c**. Yield 97% (Found: C, 61.6; H, 4.65; Cl, 7.25; N, 4.5. $C_{43}H_{41}Cl_2N_3O_2P_2Ru{\cdot}0.6C_6H_6$ requires C, 61.35; H, 4.95; Cl, 7.75; N, 4.6%). *m*/*z* (FAB): 865 (M^+), 829 (*M* − HCl) and 794 (*M* − Cl − HCl). ν(Ru–Cl) 320 cm^{-1}. *mer,trans*-$[\mathrm{RuCl_2(PPh_3)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH(C_4H_3NMe)\}}]$ **14**. Yield 85% (Found: C, 63.45; H, 5.35; Cl, 8.35; N, 4.65. $C_{42}H_{43}Cl_2N_3P_2Ru{\cdot}0.75C_6H_6$ requires C, 63.3; H, 5.45; Cl, 8.05; N, 4.75%). *m*/*z* (FAB): 823 (M^+) and 788 (*M* − Cl). ν(Ru–Cl) 320 cm^{-1}. *mer,trans*-

$[RuCl_2(PPh_3)\{PPh_2CH_2C(Bu^t)=N-N=C(Me)CH=CHPh)\}]$ **16**. Yield 90% (Found: C, 64.0; H, 5.25; Cl, 8.1; N, 3.15. $C_{46}H_{46}Cl_2N_2P_2Ru$ requires C, 64.2; H, 5.4; Cl, 8.25; N, 3.25%). *m*/*z* (FAB): 860 (M^+), 825 (M − Cl) and 789 (M − Cl − HCl). ν(Ru–Cl) 320 cm^{-1}.

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