Two-electron, Three-centre Carbon–Hydrogen–Cobalt Bonds in the Compounds [Co(η-C5Me4R)(η-C2H4)(η-C2H4-μ-H)]BF4, R = Me and Et

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Protonation of Co(η-C5H4R)(η-C2H4)2, R = Me or Et with tetrafluoroboric acid gives the compounds [Co(η-C5Me4R)(η-C2H4)Et]BF4, R = Me (**1**) or Et (**2**), in which a β-hydrogen of the Co–ethyl group forms a C–H→Co bridge *via* a two-electron, three-centre bond.

Recently it has been shown that there can be an equilibrium between transition metal–diene–hydrides and isomers in which the hydrogen has formed a covalent, two-electron, three-centre bond between the metal centre and a terminal carbon of the diene ligand. Moreover, the isomer with the C–H→M bridge can be the ground state structure of the compound,[1–4] [equation (1)]. In a current review the term agostic is proposed to describe the C–H→M system.[5]

It has been reported that the bis-ethylene derivative Co-(η-C5Me4Et)(η-C2H4)2 can be protonated by tetrafluoroboric acid forming a cation [Co(η-C5Me4Et)(C4H9)]+ (**2**). On the basis of variable temperature [1]H n.m.r. studies it was proposed that at low temperatures (−85 °C) the spectrum was most consistent with the bis-ethylene–hydride structure A, R = Et (Figure 1).[6]
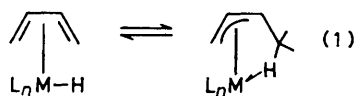
L = ligand

Several unusual features were noted in the [1]H n.m.r. spectrum of the presumed bis-ethylene–hydride cation (**2**). These included: (a) substantial coupling (*ca.* 9.3 Hz) between the Co-hydrogen H_e and H_c,H_d but *no* coupling between H_e and H_a,H_b, (b) appearance of H_a and H_b as *symmetrical* triplets implying the *cis* olefinic couplings J_{ac} and J_{bd} were approximately equal in magnitude to the *trans* olefinic couplings J_{ad} and J_{bc}, and (c) remarkably high field shifts for the olefinic hydrogens $H_d(\delta 1.48)$ and H_c ($\delta 0.46$).

Agostic alkyl C–H→M systems are now well established including the ethyl derivative $\overline{Ti(CH_2CH_2}$–H)Cl3(Me2PCH2-$\overline{CH_2PMe_2)}$[7] and the methyl analogue $\overline{Ti(CH_2}$–H)Cl3(Me2PCH2-CH2PMe2)[8] and rapid equilibrium between the bridged and terminal hydrogens of agostic alkyl systems can occur.[1–4,7,8] Here we propose an alternative and more satisfactory interpretation of the [1]H n.m.r. spectrum of cation (**2**) which incorporates a C–H→Co bond. The new structure proposed for (**2**) is shown as B in Figure 1. The observed [1]H n.m.r. spectrum at −85 °C requires a rapid degenerate equilibration between B and B' *via* transfer of the bridging H_e from one ethylene unit to the other. The transfer may proceed *via* the bis-ethylene–hydride A, as shown, or possibly directly. The new assignment of the [1]H n.m.r. spectrum of (**2**) at −85 °C is:
$\delta 2.74\{2H, t, H_a,H_{a'}$ (av.), J_{obs} (av.) 11 Hz $[(J_{ad} + J_{a'd'})/2$
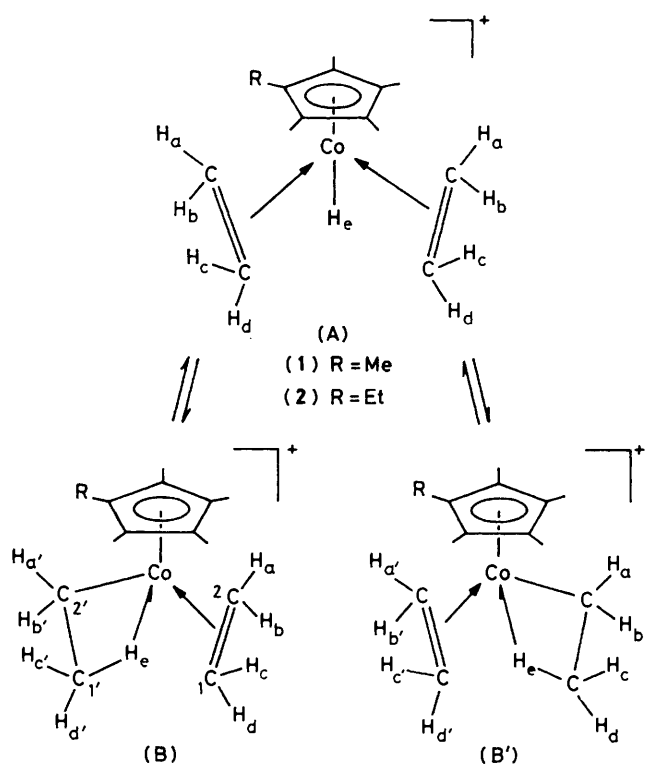
Figure 1. The structure B proposed for (1) and (2) and the equilibrium between B and B' *via* A.
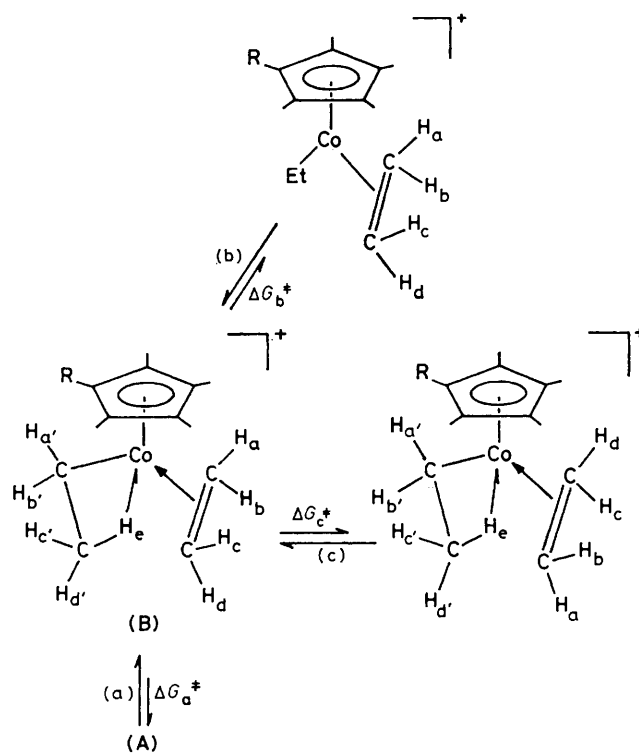

Figure 2. Proposed dynamic behaviour of (1) and (2). B indicates (1) and (2). The equilibrium (c) represents the rotation of the ethylene ligand about the cobalt–ethylene axis.

and $(J_{ac} + J_{a\cdot c\cdot})/2$]}, 2.22{2H, t, $H_b,H_{b'}$ (av.), J_{obs} (av.) 11 Hz [$(J_{bc} + J_{b\cdot c\cdot})/2$ and $(J_{bd} + J_{b\cdot d\cdot})/2$]}, 1.48[2H, m, $H_c,H_{c'}$ (av.)], 0.46[2H, m, $H_d,H_{d'}$ (av.)], −12.1{1H, q, H_e, J_{obs} 9.3 Hz [$(J_{c\cdot e}$ 0 + $J_{c'\cdot e}$ 18 Hz)/2 and $(J_{d\cdot e}$ 0 + $J_{d'\cdot e}$ 18 Hz)/2]}. Ring resonances are as previously assigned: δ 2.11(2H, quart., CH_2, J 7.4 Hz), 1.57(6-, s, Me_a), 1.48(6H, s, Me_b), 0.88(3H, t, CH_3 of Et, J 7.4 Hz).

The spectral features of (2) are now accounted for completely by the agostic structure B. Substantial coupling (up to 22 Hz) between bridged hydrogens and the hydrogens attached to the bridged carbon has been previously verified.[1,9] The H_a,H_b resonances would be expected at high fields based on similar agostic systems,[1-5,9] and the near equivalence of J_{bd} with J_{bc} and J_{ac} with J_{ad} represents an *averaged* coupling involving one ethylene unit and one agostic ethyl moiety. Furthermore, the high field shift of the bridged hydrogen H_e (δ −12.1) is in the region expected for bridged hydrogens.[5]

In order to verify these assignments, the pentamethylcyclo-pentadienylanalogueof(2),namely[Co(CH_2CH_2–H)(η-C_5Me_5)-(C_2H_4)]BF_4, (1), was prepared in a manner analogous to that for (2)[6] as red crystals.

The [1]H n.m.r. (200 MHz) of (1) at −90 °C closely resembles that of (2) including the shifts and splittings of the olefin and alkyl hydrogens. The [1]H-coupled [13]C n.m.r. spectrum (50 MHz, CH_2Cl_2) of (1) at −90 °C shows four resonances assigned as follows: δ 98.7(s, C_5Me_5), 51.3[t, C-2,C-2' (av.), J 160.7 Hz], 26.6 [td, C-1,C-1' (av.), J 155 (t) and 33.5 Hz (d)], 7.9 p.p.m. (quart., C_5Me_5, J 129.1 Hz). These data provide additional strong support for the structure B for compound (1) where rapid degenerate equilibrium occurs between B and B' at −90 °C. In particular, the observed coupling of H_e with C-1,C-1' of 33.5 Hz is inconsistent with the terminal hydride structure A, but is as expected for B ⇌ B'. Thus, with reference to the enantiomer B, the value of J_{obs} 33.5 Hz represents an

averaged value for J(C-1'–H) 67 and J(C-1–H) 0 Hz. The value of 67 Hz lies in the region characteristic for C–H→M systems.[1-5,8] The high values of J(C-1–H) and J(C-2–H) (ca. 150—160 Hz) for the agostic ethyl group are atypical of normal transition metal–ethyl groups. The resonance at δ 26.6 p.p.m. must represent an average shift of C-1 and C-1'. Estimating the olefinic C-1 shift as δ ca. 50 p.p.m., the agostic C-1' must lie at ca. 0 p.p.m. which is in accord with high field shifts for related C–H→M systems.[1-5]

The hydrogen scrambling processes observed by Pardy *et al.*[6] using deuterium labelling, n.m.r. line-broadening, and spin-saturation transfer experiments can be understood on the basis of the isomerisation reactions shown in Figure 2.

Both the ^{1}H and [13]C n.m.r. spectra are in accord with the equilibrium (a) shown in Figure 2, which is fast on the n.m.r. time-scale at −85 °C, as earlier noted. $\Delta G_a^{\ddagger}$ must be less than 30 kJ/mol. Reaction (b), the agostic methyl rotation, when coupled with the much faster reaction (a) serves to scramble H_a, H_b, $H_{a'}$, $H_{b'}$, and H_e with $\Delta G_b^{\ddagger} = 43$ kJ/mol.‡ Reaction (c), involving olefin rotation, when coupled with the more rapid reactions (a) and (b) serves to scramble $H_{c'}$, $H_{d'}$, H_c, and H_d with H_a, H_b, $H_{a'}$, $H_{b'}$, and H_e, $\Delta G_c^{\ddagger} = 51$ kJ/mol.‡

It is interesting to note that for B, $\Delta G_a^{\ddagger} < \Delta G_b^{\ddagger}$, whereas for the analogous processes in the bridged diene complex studies thus far $\Delta G_a^{\ddagger} > \Delta G_b^{\ddagger}$.[1-5]

The compounds (1) and (2) provide the second example(s) of agostic ethyl groups with a cyclic M–CH_2CH_2–H system.

The first example namely Ti(CH_2CH_2–H)Cl_3($Me_2PCH_2CH_2$-PMe_2) might have been thought to be unusual since it has an unusually low electron number (formally 14 electrons if the

bridging hydrogen is allowed to contribute two electrons to the titanium, see ref. 5) for a transition metal alkyl compound.[10] However, the compounds (1) and (2) are normal 18-electron compounds and are typical organometallic systems. Thus the occurrence of the agostic bonds in (1) and (2) provides strong support for our proposal[5,7,8] that bridging C–H→M systems can occur widely as ground state structures of transition metal–alkyl derivatives.

This work also emphasises that agostic hydrogens attached to d^n transition metal centres, where $n > 0$, can have chemical shifts in the same high field region in the ^1H n.m.r. spectrum which is commonly associated with terminal M–H groups.

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