The Synthesis and Structure of $[Co(\eta\text{-}C_5Me_5)Et\{P(p\text{-tolyl})_3\}]$ Cation: a Model for the β-Elimination Transition State

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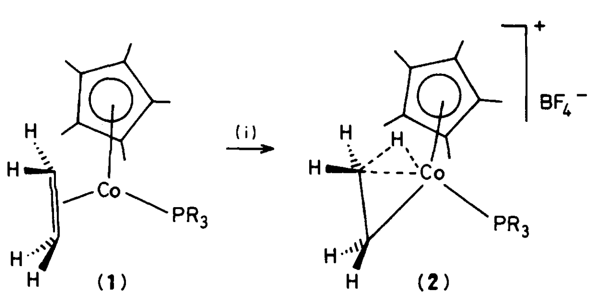
Protonation of $[Co(\eta\text{-}C_5Me_5)(C_2H_4)\{P(p\text{-tolyl})_3\}]$ affords the ethyl cation $[Co(\eta\text{-}C_5Me_5)Et\{P(p\text{-tolyl})_3\}]^+$ in which there is a strong three-centre interaction between the metal and a β-C–H, as indicated by ^1H and ^{13}C n.m.r. and by a single crystal *X*-ray diffraction study of the tetrafluoroborate salt.

It has become clear that a C–H bond may act as a ligand to an otherwise co-ordinatively unsaturated transition metal atom. Thus a number of complexes have been characterised in which a C–H bond of a ligand is close to the metal.[1] A particularly striking example is $[TiCl_3(Et)(Me_2PCH_2CH_2PMe_2)]$[2] where the Ti–C–C angle is markedly distorted in order to allow one of the β-C–H bonds of the ethyl group to interact with the metal. An intermediate with a similarly distorted ethyl group has been identified in the β-elimination rearrangement of $[WEt(\eta\text{-}C_5H_5)(CO)_2]$ (produced by photolysis) to *trans*-$[W(H)(C_2H_4)(\eta\text{-}C_5H_5)(CO)_2]$,[3] and the dynamic ^1H and ^{13}C n.m.r. spectra of $[Co(C_5Me_4R)Et(C_2H_4)]^+$ (R = Me, Et) have been reinterpreted in terms of a ground state with an 'agostic' ethyl group.[4]

In the course of exploring the chemistry of the group of compounds $[Co(C_5Me_5)(C_2H_4)(PR_3)]$[5] we have synthesised complexes which contain ethyl ligands with β-C–H bonds strongly co-ordinated to cobalt. Protonation of $[Co(\eta\text{-}C_5Me_5)(C_2H_4)(PR_3)]$ [R = *p*-tolyl, (**1a**); Ph, (**1b**); Me, (**1c**)] with $HBF_4{\cdot}OEt_2$ affords the dark red crystalline compounds $[Co(\eta\text{-}C_5Me_5)Et(PR_3)][BF_4]$ (**2a—c**). The attachment of the proton to a carbon atom of what was formerly the ethylene



a; R = *p*-tolyl
b; R = Ph
c; R = Me
Reagent: (i) $HBF_4{\cdot}OEt_2$

ligand is demonstrated by the proton-coupled ^{13}C n.m.r. spectrum of (**2a**) (−80 °C) in which one carbon resonance (δ −5.92 p.p.m.) appears as a triplet† of doublets [^1J(C–H) 146 and 66 Hz respectively]. The latter coupling constant is too large to result from two-bond coupling ^1H–Co–$^{13}C^1$ {for example ^2J(C–H) in [Nb(η-C_5Me_5)$_2$H(C_2H_4)] is 6 Hz[6]} and must therefore indicate direct, albeit weakened, C–H bonding. The methylene carbon atom gives rise to a triplet at δ 25.90 p.p.m. [^1J(C–H) 163 Hz]. In the ^1H n.m.r. spectrum of (**2a**) (−80 °C) the unique hydrogen resonates at δ −12.67, in the region normally associated with hydridic hydrogen atoms. There are, in addition, four broad resonances associated with the other ethyl group hydrogens (δ −1.78, −0.44, 1.65, and 2.86).‡ These features are consistent with the presence of an ethyl group in which one β-C–H bond is substantially weakened by interaction with the cobalt atom. In contrast, n.m.r. data on related rhodium and ruthenium systems have been interpreted in terms of the hydrido olefin complexes [Rh(η-C_5H_5)H(C_2H_4)(PMe_3)]$^+$ and [Ru(η-C_6H_6)H(C_2H_4)(PMe_3)]$^+$.[7]

In order to characterize further this interaction we have carried out a low-temperature *X*-ray diffraction study of (**2a**) as the toluene solvate. *Crystal data* for (**2a**)·C_7H_8: $C_{33}H_{41}BCoF_4P{\cdot}C_7H_8$, M = 706.5, monoclinic, space group $P2_1/c$, a = 11.949(8), b = 16.326(9), c = 20.382(16) Å, β = 113.50(8)°, U = 3628(4) Å^3, Z = 4, D_c = 1.29 g cm^{-3}, F(000) = 1488, λ = 0.710 69 Å, μ(Mo-K_α) = 5.6 cm^{-1}. Data were collected on a Nicolet P3m diffractometer at *ca.* 200 K for a quadrant of reciprocal space with $4 < 2\theta < 50°$; current residual R 0.047 for 4515 unique, observed [$I > 2.5\sigma(I)$], absorption-corrected data. All hydrogen atoms were located directly in difference electron density syntheses, and those of the ethyl group allowed to refine without positional constraints.§

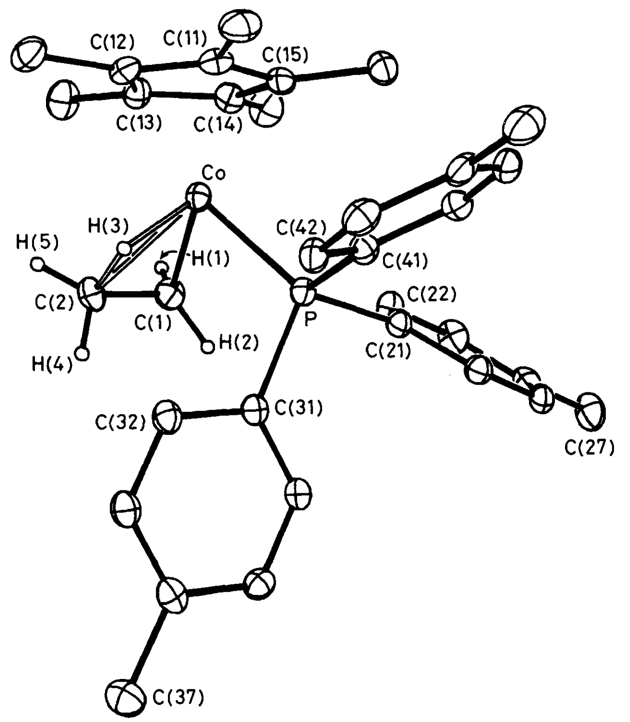


Figure 1. Molecular structure of (**2a**). Important molecular parameters: distances: Co–C(1) 1.974(4), Co–C(2) 2.128(4), Co–H(3) 1.46(4), C(2)–H(3) 1.31(4), other C–H 0.92(4)—0.98(4) Å, Co–C (C_5Me_5) av. 2.089 Å; angles: P–Co–C(1) 90.6(1), P–Co–C(2) 99.4(1), P–Co–H(3) 88(2), C(1)–Co–H(3) 77(2), Co–C(2)–C(1) 63.4(2)°.

The structure of (**2a**) in the solid state (Figure 1) is consistent with the solution n.m.r. data. The geometry of the ethyl group resembles the transition state often postulated[8] for the β-elimination reaction. Thus not only is the Co–C_α–C_β angle acute [74.5(2)°] and the β-carbon attached to cobalt *via* a hydrogen bridge, but the C–C distance is substantially reduced relative to an ordinary C(sp^3)–C(sp^3) single bond distance [1.480(5) *vs.* 1.54 Å]. A consequence of this is that the conformation about the C–C bond is eclipsed rather than staggered as is usually found in unconstrained ethyl groups.[9] Thus the β-C–H interaction with the unsaturated cobalt atom forces an unusual and rigid (on the n.m.r. time-scale at −80 °C) conformation on the ethyl group. The rigidity of the conformation with respect to methyl group rotation is presumably a consequence of the partial double bond character of the C_α–C_β bond. The implication is therefore that the cation contains an ethyl moiety considerably distorted towards the ethylene and hydride extreme of the β-elimination reaction. That such a geometry can represent the ground state and not merely the transition state has been noted elsewhere.[1]

The ethyl group is therefore capable of acting as an anionic, two-electron, σ ligand in the accepted manner, or as an anionic four-electron ligand with both σ-donor and 'agostic' (C–H) interactions. Such behaviour has been the focus of attention in, for example, the chemistry of the nitrosyl ligand, since it might permit complexes of such ligands to act as catalysts by allowing facile co-ordination of substrate molecules. In this way the 'agostic' interaction in (**2**) may serve to store the co-ordinative unsaturation of the otherwise 16-electron Co^{III} centre, prior to reaction with donor substrates. Consistent with this proposal, we note that solutions of (**2**) polymerize ethylene under mild conditions of temperature and pressure.

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† Although all three C–H bonds must be inequivalent, ^1J(C–H) for the two not involved in 'agostic' interaction with the metal are apparently identical within the precision of the experiment.

‡ ^1H N.m.r. at 20 °C (CD_2Cl_2, 200 MHz): δ −4.94 (br., 3 H, $CoCH_2CH_3$), 1.44 (s, 15 H, C_5Me_5), 1.65 (br., 1H, $CoCH_2CH_3$), 2.40 (s, 9 H, C_6H_4Me), 2.84 (br., 1 H, $CoCH_2CH_3$), and 7.20—7.46 (m, 12 H, C_6H_4Me).

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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9 For a recent organometallic example see M. L. H. Green, N. J. Hazel, P. D. Grebenik, V. S. B. Mtetwa, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1983, 356.