Synthesis of Coordinatively Unsaturated Diphosphine Nickel(II) and Palladium(II) β-Agostic Ethyl Cations: X-Ray Crystal Structure of $[Ni\{Bu^t_2P(CH_2)_2PBu^t_2\}(C_2H_5)][BF_4]$

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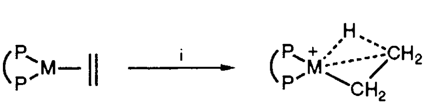
Protonation of $[M(L_2)(\eta^2\text{-}C_2H_4)]$ (L_2 = chelating diphosphine; M = Ni, Pd) with HBF_4 affords a series of cations $[M(L_2)(C_2H_5)]^+$ characterized as β-agostic ethyl complexes by NMR spectroscopy and X-ray structure analysis.

Complexes with three-centre, two-electron $M\cdots H\cdots C_\beta$ (β-agostic) interactions may be considered as intermediates in industrially important processes, such as alkene polymerisation.[1] With the exception of the recently reported norbornyl[2] and ethyl[3] ligands in $[Pt(L_2)(C_7H_{11})]^+$ and $[Pt(L_2)(C_2H_5)]^+$ (L_2 = tetraalkyldiphosphine) respectively, there are no examples of β-agostic bonding involving the metals of the nickel sub-group, although more remote interactions have been reported including δ-agostic interactions in *trans*-$[PdBr\{C_4(CO_2Me)_4H\}(PPh_3)_2]$[4] and $[NiCl(\eta\text{-}C_3H_5)\{P(menthyl)(Me)Bu^t\}]$.[5] We now report the preparation of the first β-agostic ethyl cations of nickel and palladium from the protonation of neutral ethene precursors.



	P–P	M	
1a	$Bu^t_2P(CH_2)_2PBu^t_2$	Ni	**3a**
1b	$Bu^t_2P(CH_2)_3PBu^t_2$	Ni	**3b**
1c	*o*-$(Bu^t_2PCH_2)_2C_6H_4$	Ni	**3c**
2a	$Bu^t_2P(CH_2)_2PBu^t_2$	Pd	**4a**
2b	$Bu^t_2P(CH_2)_3PBu^t_2$	Pd	**4b**
2c	*o*-$(Bu^t_2PCH_2)_2C_6H_4$	Pd	**4c**

Scheme 1 *Reagents and conditions*: i, $HBF_4{\cdot}OEt_2$, Et_2O, 273 K

A series of compounds $[M(L_2)(\eta\text{-}C_2H_4)]$ [M = Ni, L_2 = $Bu^t_2P(CH_2)_2PBu^t_2$ **1a**, $Bu^t_2P(CH_2)_3PBu^t_2$ **1b** and *o*-$(Bu^t_2PCH_2)_2C_6H_4$ **1c**; M = Pd, L_2 = $Bu^t_2P(CH_2)_2PBu^t_2$ **2a**, $Bu^t_2P(CH_2)_3PBu^t_2$ **2b** and *o*-$(Bu^t_2PCH_2)_2C_6H_4$ **2c**] have been prepared and characterised by elemental analyses and NMR spectroscopy.†

Protonation of the complexes **1a–1c** and **2a–2c** with $HBF_4{\cdot}OEt_2$ in diethyl ether at 273 K (Scheme 1) caused an immediate precipitation of the complexes $[M(L_2)(C_2H_5)]$-

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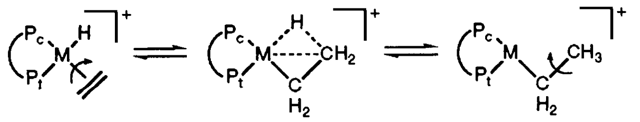
† Complexes **1a**, the C_2D_4 analogue of **1a**, and **1b** were prepared by the reaction of $[Ni(L_2)Cl_2]$ with zinc powder under ethene (1 atm) as yellow crystals in *ca.* 75% yield,[6] whereas **1c** was synthesized by the treatment of $[Ni(cycloocta\text{-}1,5\text{-}diene)_2]$ with *o*-$(Bu^t_2PCH_2)_2C_6H_4$ under ethene (1 atm). The analogous palladium complexes **2a–2c** were prepared by the reaction of the diphosphine with $[Pd(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)]$[7] in hexane at 273 K under ethene as orange crystals in 85% yield. ^1H NMR data for the $(\eta^2\text{-}C_2H_4)$ ligand in **1a–1c** and **2a–2c** in C_6D_6: δ 2.43 for **1a**; 2.26 **1b**; 2.20 **1c**; 3.04 **2a**, 2.85 **2b** and 2.86 **2c**; ^{31}P NMR data in C_6D_6: δ 90.6 for **1a**; 46.0 **1b**; 49.7 **1c**; 82.7 **2a**; 46.9 **2b** and 50.0 **2c**.



Scheme 2

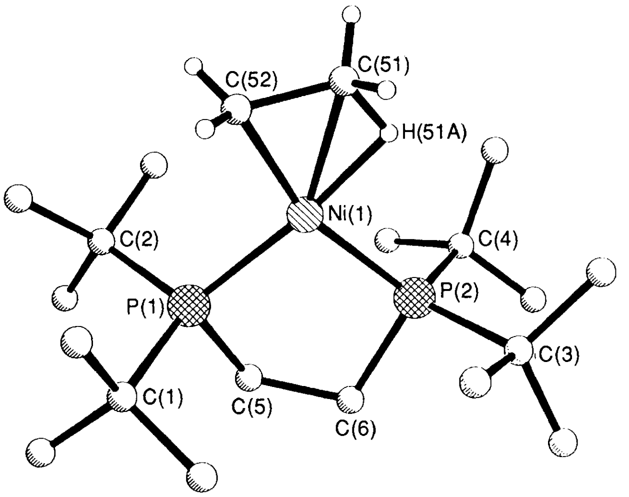


Fig. 1 Molecular structure of the cation in **3a** with all hydrogens omitted except those on C(51) and C(52). Selected bond lengths (Å): Ni(1)–P(1) 2.181(1), Ni(1)–P(2) 2.214(1), Ni(1)–C(51) 2.081(5), Ni(1)–C(52) 1.940(5), C(51)–C(52) 1.433(8), C(51)–H(51A) 1.015(18), Ni(1)–H(51A) 1.644(19); bond angles (°): Ni(1)–H(51A)–C(51) 100.7(15), C(51)–Ni(1)–C(52) 41.6(2), P(1)–Ni(1)–P(2) 93.2(1), C(52)–Ni(1)–P(1) 104.4(2), P(1)–Ni(1)–H(51A) 174.5(6), P(2)–Ni(1)–H(51A) 92.2(6), Ni(1)–C(52)–C(51) 74.5(3), Ni(1)–C(51)–C(52) 63.9(3); torsion angle (°) H(51A)–C(51)–C(52)–Ni(1) −1.5(1).

[BF_4] (**3a–3c**: M = Ni and **4a–4c**: M = Pd) in yields of >90% as pale yellow and orange microcrystals respectively.

The new cations were characterized by NMR spectroscopy‡ which indicated the presence of β-agostic bonding. For **3a** at 293 K a multiplet is observed at δ −1.24 (J_{PH} 12 Hz) in the ^1H NMR spectrum (CD_2Cl_2) which was assigned to the protons of the β-carbon of the ethyl group; the protons on the α-carbon are obscured in the ^1H NMR spectrum but appear in the corresponding ^2H spectrum of the [$^2H_4$] analogue at δ 1.6. At 173 K the ^1H NMR spectrum of **3a** in CD_2Cl_2–Me_2O showed a broad signal at δ −5.8 assigned to the agostic hydrogen; the other four ethyl protons were obscured by the *tert*-butyl signals of the diphosphine. At the same temperature in the ^2H NMR spectrum of the [$^2H_4$] analogue, the agostic deuteron appears at δ −6.2 whereas the signal for the other two deuterons on the β-carbon is coincident with the signal for those on the α-carbon at δ 1.1.

The ^{13}C NMR spectra of **3a–3c** showed separate signals for the two carbon atoms of the ethyl group at temperatures below 300 K; thus for **3a** signals at δ −0.5 and 25.1 were assigned to the CH_3 and CH_2 groups respectively. At 180 K, the signal at δ −0.5 shows a gross triplet of doublets structure with $^1J(CH)$ = 151 and 68 Hz typical of an agostic alkyl group.[1] At all temperatures recorded the $^{31}P\{^1H\}$ NMR spectra of **3a–3c** show two separate signals (for example, δ 93.7 and 99.2, J_{PP} 13 Hz in complex **3a**) indicating the inequivalence of the two phosphorus nuclei.

The ^1H NMR spectra of the palladium complex **4b** showed a single multiplet signal at δ 1.6 (J_{PH} 16 Hz) for all five protons of the ethyl group at room temperature and the ^{13}C NMR spectrum at the same temperature revealed one signal for both carbon atoms at δ 18.0. As in the case of the Pt analogues[3] this behaviour can be rationalized by consideration of two distinct fluxional processes (Scheme 2), a combination of which scrambles all five ethyl protons and both carbon atoms. In contrast it is apparent that for the Ni compounds **3a–3c** β-elimination and alkene rotation do not occur rapidly on the NMR timescale at temperatures below 300 K.

A ^{13}C NMR spectrum of a dichloromethane sample of **4b** recorded at 195 K showed the ethyl carbon atoms as two separate signals at δ 6.1 and 28.3 (C_α and C_β). However, only average values of $^1J(CH)$ could be obtained for the methyl group (124 Hz). At *ca.* 155 K in the ^1H NMR spectrum of **4b**, there is a very broad high field signal at δ −2.6 due to the agostic hydrogen; the signals for the other four protons are obscured by the broadened *tert*-butyl signals.

The structure§ of **3a** was determined at 203 K by single crystal X-ray diffraction to confirm the bonding mode of the ethyl group and is shown in Fig. 1 together with selected bond lengths and bond angles. The coordination geometry around the nickel atom can be described as distorted square planar with a dihedral angle of 2.9° between the planes P(1)–Ni(1)–P(2) and C(51)–Ni(1)–C(52). The cation consists of the bidentate ditertiary phosphine, and an ethyl ligand asymmetrically bound to the central nickel atom through a σ-bond [Ni(1)–C(52) 1.940(5) Å] and a β-agostic interaction [Ni(1)–C(51) 2.081(5), Ni(1)–H(51A) 1.644(19) Å]. As expected[2,3] the Ni–P bond lengths show evidence of the weak *trans*-influence exerted by the β-CH moiety [Ni(1)–P(1) 2.181(1) Å and Ni(1)–P(2) 2.214(1) Å]. The Ni(1)–C(52)–C(51) bond angle is acute [74.5(3)°] and the C(51)–C(52) bond length of 1.433(8) Å is substantially reduced relative to an ordinary C(sp^3)–C(sp^3) single bond distance of 1.54 Å.

Our previous work[3] on the platinum diphosphine 'ethyl' complexes $[Pt('C_2H_5')(L_2)]^+$ [L_2 = $Bu^t{}_2P(CH_2)_nPBu^t{}_2$, *n* = 2, 3; *o*-$(Bu^t{}_2PCH_2)_2C_6H_4$], has shown that there is a fine balance between the *cis*-ethene–hydride form $[PtH(\eta^2\text{-}C_2H_4)(L_2)]^+$ [L_2 = $Bu^t{}_2P(CH_2)_2PBu^t{}_2$] and the ethyl agostic form $[Pt(C_2H_5)(L_2)]^+$[L_2 = $Bu^t{}_2P(CH_2)_3PBu^t{}_2$, *o*-$(Bu^t{}_2PCH_2)_2$-$C_6H_4$] which is controlled by the ancillary diphosphine ligands, where the larger bite-angle favours the agostic form. Comparing similar complexes in the group reveals interesting trends. For example with $Bu^t{}_2P(CH_2)_2PBu^t{}_2$, for platinum the alkene hydride form is more thermodynamically stable than the

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‡ Selected ^1H NMR data for the cations **3b**, **3c** and **4a** in CD_2Cl_2: δ −1.63 (J_{PH} 9) for **3b**, −1.84 (J_{PH} 6) **3c**, 1.1 (J_{PH} 16 Hz) **4a**. The corresponding signal for **4c** is obscured by the Bu^t signals.

§ *Crystal data* for $C_{20}H_{45}BF_4P_2Ni$: *M* = 493.0, monoclinic, space group $P2_1/n$, *a* = 11.198(3), *b* = 14.510(5), *c* = 16.253(5) Å, β = 105.58(2)°, *U* = 2543.8(14) Å^3, D_c = 1.287 g cm^{-3}, *Z* = 4, *F*(000) = 1056, Mo-Kα X-radiation (graphite monochromator), λ = 0.71073 Å, μ(Mo-Kα) = 0.922 mm^{-1}. A yellow-orange cut block of dimensions 0.70 × 0.52 × 0.50 mm was used for measurement at 203 K. Intensity data in the range 3° < 2θ < 50° were collected using a θ–2θ scan technique on a Nicolet R3m/V diffractometer. The intensities of three reflections measured periodically showed a negligible decrease of less than 1% over the data collection. A total of 4855 reflections was collected of which 4428 (R_{int} = 2.77%) were independent and 3004 for which $F > 4.0\sigma(F)$ were used in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods. All hydrogen atoms were found from Fourier difference maps, including the bridging hydride H(51A). All but the hydride were placed in calculated positions and refined riding upon their respective parent atoms. The positional and thermal parameters of H(51A) were refined. At convergence *R* = 4.87% and R_w = 4.28%, $w = [\sigma^2(F) + 0.0002F^2]^{-1}$, *s* = 1.28, Δ/σ < 0.001. The absorption was corrected for, using a faced-indexed numerical technique with min/max transmission 81/85%. Calculations were performed using the SHELXTL-PLUS program package on a MicroVax II. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

agostic structure whereas the latter is more stable for palladium and nickel. Furthermore, although structurally similar the last two differ markedly in the activation barriers to β-elimination–ethene rotation which is much lower for palladium than nickel. These results highlight the subtle differences between the nickel sub-group metals with respect to some of the fundamental processes of organometallic chemistry, and should lead to a more complete understanding of the role of these metals in homogeneous catalysis.

We thank Dr A. Guy Orpen of the School of Chemistry, University of Bristol for helpful discussions and the SERC for support.

Received, 15th April 1991; Com. 1/01748I

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