A metallacyclic λ⁵-phosphaalkenyl complex of ruthenium(II): X-ray structure of [Ru{κ²-P(=O)CBu^{t}C(=O)}(CNBu^t)$_2$(PPh$_3$)$_2$]

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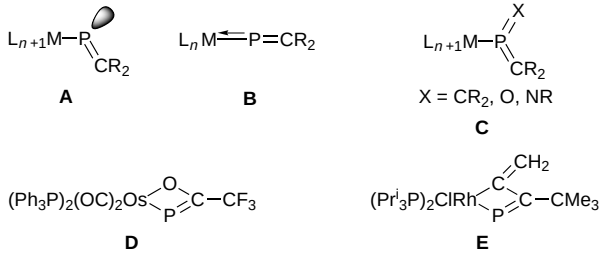
The reaction of [Ru(P=CHBu^t)Cl(CO)(PPh$_3$)$_2$] 1 or [Ru(P=CHBu^t)Cl(CNBu^t)(CO)(PPh$_3$)$_2$] 2b with excess pivalo isonitrile under aerobic conditions provides the novel metallacyclic λ⁵-phosphaalkenyl-*P* complex [Ru{κ²-P(=O)CBu^{t}C(=O)}(CNBu^t)$_2$(PPh$_3$)$_2$], which has been crystallographically characterised.

The λ³-phosphaalkenyl-*P* complex [Ru(P=CHBu^t)Cl(CO)(PPh$_3$)$_2$] **1**[1] is intriguing in that despite effective atomic number considerations for ruthenium, both the spectroscopic features and the emerging reactivity profile[2–4] point to a nucleophilic phosphorus centre (**A**). The RuCl(CO)(PPh$_3$)$_2$ fragment, possessing 15 valence electrons might be expected to commandeer three electrons from the phosphaalkenyl ligand **B** and thereby enforce linearity and attendant electrophilic character at phosphorus. This is, however, not the case. We have interpreted this counter-intuitive behaviour with reference to a similar dichotomy which prevails for nitrosyl ligands bound to metal centres with high d-occupancies.[1] One aspect of the 'semi-bent' nature of the phosphaalkenyl ligand in **1** is that the ruthenium centre readily, though reversibly, accepts two-electron ligands, resulting in a metal centre which requires bent (one-electron) phosphaalkenyl coordination. The resulting nucleophilic nature of the phosphorus centre has been demonstrated by its reduction to a complex of the unusual fluorophosphine Bu^{t}CH$_2$PHF ligand *via* the reaction of the isonitrile adduct [Ru(P=CHBu^t)Cl(CNC$_6$H$_3$Me$_2$-2,6)(CO)(PPh$_3$)$_2$] **2a** with HBF$_4$.[2] Herein we wish to report a curious transformation of **1** into a metallacyclic phosphaalkenyl complex **3**. This is accompanied by oxidation of the phosphorus from λ³ to λ⁵ (**C**), resulting in a rare example of a trigonal phosphorus centre surrounded by three π-interactive substituents. A notable feature of **3** is that it is, we believe, the first example of a λ⁵-phosphaalkenyl-*P* complex.



Whilst complex **1** readily forms a 1:1 adduct **2a** with CNC$_6$H$_3$Me$_2$-2,6, the same reaction with pivalo isonitrile (CNBu^t) is somewhat more complex. Under strict control of reagent stoichiometry and reaction conditions it is possible to prepare the adduct [Ru(P=CHBu^t)Cl(CNBu^t)(CO)(PPh$_3$)$_2$] **2b**, spectroscopic data for which are comparable to those for **2a**.§ On occasion however, complex **2b** is contaminated with a second product, which is also formed in low yield from **2b** on standing in solution. This second compound is the exclusive product if an excess of CNBu^t is used, under aerobic conditions. Spectroscopic data§ and a crystallographic study (Fig. 1)¶ confirm the identity of the new compound as the novel metallacyclic λ⁵-phosphaalkenyl-*P* complex [Ru{κ²-P(=O)CBu^{t}C(=O)}(CNBu^t)$_2$(PPh$_3$)$_2$] **3**. Of note amongst the spectroscopic data for **3**, is the ^{31}P{^{1}H} NMR resonance for the phosphaalkenyl centre which appears as a triplet [δ 47.0 ^2J(P$_2$P) 25.2 Hz], to substantially higher field of those observed for **2b** [δ 389.8 ^2J(P$_2$P) 11.7 Hz] or **1** [δ 450.4 ^2J(P$_2$P) 10.0 Hz]. The phosphoryl group contributes to a strong absorption in the infrared spectrum at 1198 cm^{-1}(Nujol), whilst the acyl group is apparent at 1644 cm^{-1}. All other spectroscopic data are as expected and unremarkable.

The geometry at ruthenium is essentially octahedral with *cis*-interligand angles in the range 85.2(2)–96.1(3)°, the exception being P(1)–Ru–C(2) which is contracted to 66.5(2)° by virtue of the constraints of chelation. The two ruthenium isonitrile distances are 1.988(10) and 2.037(10) Å suggesting that the *trans* influence of the phosphaalkenyl ligand is comparable to that of the acyl component of the metallacycle. The principle structural feature of interest is the metallacycle, the unsaturation of which is reflected in the coplanarity to within 0.03 Å of the atoms C(5), C(1), P(1) O(3), C(2), O(4) and Ru, a planarity which extends to include the CN groups of the isonitriles. Owing to the novelty of **3**, very little directly comparable structural data exists. Two metallacyclic λ³-phosphaalkenyl complexes have been structurally characterised (**D**[5] and **E**),[6]

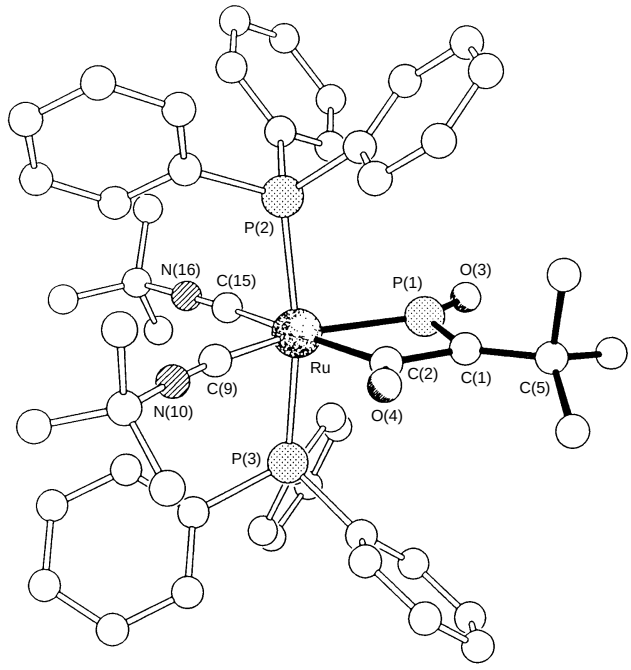
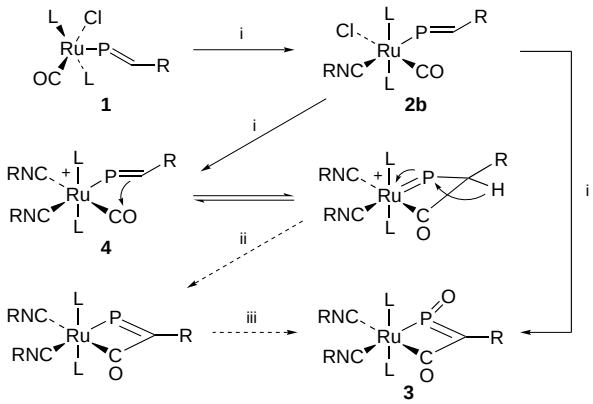


Fig. 1 Crystal structure of **3**

though perhaps more relevant here are the structural features of the phosphaalkene complexes [Ru{P(AuPPh$_3$)=CHBu^t}Cl$_2$(CO)(PPh$_3$)$_2$] **4**[3] and [Ru(PMe=CHBu^t)ClI(CO)(PPh$_3$)$_2$] **5**[4] where the Ru–P separations are 2.296(2) and 2.280(2) Å, respectively. The Ru–P(1) bond length of 2.350(2) Å in **3** thus indicates a substantially reduced degree of Ru–P multiple bond character, consistent with a perhaps surprising decrease in apparent π-acidity for the λ^5-phosphorus centre, notwithstanding the perturbations associated with chelation. This counter-intuitive result is possibly due to the co-ordination of a competitive π-acceptor *trans* to P(1), whilst the phosphaalkene ligands in **4** and **5** are *trans* to π-donor ligands. The P(1)–C(1) separation of 1.713(11) Å is marginally longer than the P=C bond lengths of 1.664(9) and 1.657(8) Å, found for **4** and **5**, respectively but falls within the range 1.68–1.72 Å found for free phosphaalkenes,[7] indicating substantial double bond character. In contrast the C(1)–C(2) bond at 1.54(1) Å is long for a single C_{sp^2}–C_{sp^2} bond length.

It remains for the mechanism to be established whereby **3** forms from **1** or **2b**, however we would make the following points which taken together support the route proposed in Scheme 1. The reaction proceeds in polar solvent mixtures suggesting ruthenium–chloride ionisation occurs. This is supported by the formation and isolation of the salt *cis*,*cis*,*trans*-[Ru(P=CHBu^t)(CO)(CNBu^t)$_2$(PPh$_3$)$_2$]Cl **4**§ when **1** is treated with 2 equiv. of pivaloisonitrile and isolated immediately. The β-position of vinyl ligands is typically nucleophilic in nature, in particular for later transition metals, and it seems reasonable to expect a similar property for phosphavinyl ligands. The carbonyl ligand will be activated towards nucleophilic attack as a result of the complex being cationic. Ring closure could provide the saturated metallacycle shown, and the proton which is α to both phosphorus and a carbonyl group would be expected to be acidic. Deprotonation then leads to unsaturation of the metallacycle. The aerial oxidation of the phosphorus centre is, in contrast to **1**, an endearing feature of which is its remarkable aerobic stability. Nevertheless, the Ru(CNBu^t)$_2$(PPh$_3$)$_2$ fragment would be expected to be particularly π-basic, activating the π-acid phosphorus centre towards oxidation. Notably the conversion of **4** to **3** is accelerated by addition of a non-nucleophilic base (DBU). We have so far been unsuccessful in isolating the intermediates between **4** and **3**, however the alternative route of deprotonation prior to cyclisation seems less favourable, given that it would produce a 20-valence electron phosphaalkyne complex of zerovalent ruthenium.[8]



Scheme 1 L = PPh$_3$, R = Bu^t. *Reagents*: i, CNR; ii, −HCl; iii, O$_2$.

The chemistry of λ^3 phosphaalkenyl ligands has seen substantial growth in recent times.[1–6,9] With the advent of a λ^5 example, it will be interesting to see how their respective coordination chemistries compare.

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Notes and References

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§ Selected data for new complexes [25 °C, IR Nujol(CH$_2$Cl$_2$), NMR (CDCl$_3$), satisfactory microanalytical data obtained]. **2b**: IR: 2148 (2148) [ν(CN)], 1930 (1961) [ν(CO)] cm^{-1}. NMR: ^{1}H δ 0.79 (s, 9 H, PCCCH$_3$), 0.97 (s, 9 H, NCCH$_3$), 7.24–7.95 (m, 31 H, C$_6$H$_5$ + P=CH) ^{31}P{^{1}H} δ 389.8 [t, ^2J(P$_2$P) 11.7 Hz], 24.6 [d, ^2J(P$_2$P) 11.7 Hz]. FABMS: *m/z* 874 [MH]$^+$, 772 [MH − HP=CHBu^t]$^+$, 744 [MH − HP=CHBu^t − CO]$^+$, 709 [MH − HP=CHBu^t − Cl − CO]$^+$. **3**: IR: 2169, 2028 (2171, 2038) [ν(CN)], 1644 (1606) [ν(CO)] cm^{-1}. NMR ^{1}H δ 0.61 (s, 9 H, PCCCH$_3$), 0.86 (s, 9 H, NCCH$_3$), 1.27 (s, 9 H, NCCH$_3$) 7.27–8.09 (m, 30 H, C$_6$H$_5$). ^{31}P{^{1}H} δ 47.0 [t, ^2J(P$_2$C) 25.2 Hz], 31.2 [dd, ^2J(P$_2$P) 25.2, 8.4 Hz]. FABMS: *m/z* 856 [M − CNBu^t]$^+$, 602 [M − CNBu^t − PPh$_3$]$^+$. **4**: IR: 2184(sh), 2163 (2179, 2156) [ν(CN)], 2003, 1980(sh) (2021) [ν(CO)] cm^{-1}. NMR: ^{1}H δ 0.66 (s, 9 H, PCCCH$_3$), 0.96 (s, 9 H, NCCH$_3$), 1.18 (s, 9 H, NCCH$_3$), 7.32–7.76 (m, 31 H, C$_6$H$_5$ + P=CHBu^t). ^{31}P{^{1}H} δ 336.9(s), 33.5(s). FABMS: *m/z* 921 [M]$^+$, 838 [M − CNBu^t]$^+$, 810 [M − CNBu^t] − CO]$^+$, 530 [M − CNBu^t − PPh$_3$]$^+$.

¶ *Crystal data* for **3**: $C_{52}H_{57}N_2O_2P_3Ru\cdot CH_2Cl_2$, M = 1020.9, triclinic, space group $P\bar{1}$ (no. 2), a = 13.616(1), b = 14.629(2), c = 15.473(3) Å, α = 89.93(1), β = 89.39(1), γ = 66.72(1)°, U = 2830.9(7) Å^3, Z = 2, D_c = 1.198 g cm^{-3}, μ(Cu-Kα) = 42.0 cm^{-1}, λ = 1.54178 Å, F(000) = 1060. A colourless prism of dimensions 0.27 × 0.20 × 0.05 mm was used. Data were measured on a Siemens P4/PC diffractometer with graphite monochromated Cu-Kα radiation (ω-scans). 7804 Independent reflections were measured ($2\theta \leqslant 116°$) of which 5605 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The structure was solved by direct methods and all the major occupancy non-hydrogen atoms of the complex were refined anisotropically by full-matrix least squares based on F^2 using absorption-corrected data to give R_1 = 0.082, wR_2 = 0.205 for the observed data and 530 parameters. The somewhat high R factors are a consequence of disorder in the Bu^t substituents and the included solvent molecule. CCDC 182/727.

1 R. B. Bedord, A. F. Hill and C. Jones, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 547.
2 R. B. Bedford, D. E. Hibbs, A. F. Hill, M. B. Hursthouse, K. M. A. Malik and C. Jones, *Chem. Commun.*, 1996, 1895.
3 R. B. Bedford, A. F. Hill, C. Jones, J. D. E. T. WIlton-Ely, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1997, 179.
4 R. B. Bedford, A. F. Hill, C. Jones, J. D. E. T. Wilton-Ely, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1997, 139; 1113.
5 D. S. Bohle, G. R. Clark, C. E. F. Rickard and W. R. Roper, *J. Organomet. Chem.*, 1988, **353**, 355.
6 P. Binger, J. Haas, A. T. Herrmann, F. Langhauser and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 310.
7 R. Appel, F. Knoll and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 731; A. H. Cowley, R. A. Jones, J. G. Lasch, N. C. Norman, C. A. Stewart, A. L. Stuart, J. L. Atwood, W. E. Hunter and H.-M. Zhang, *J. Am. Chem. Soc.*, 1984, **106**, 7015.
8 The complex [Ru(P≡CC$_6$H$_2$Bu$^t_3$)(CO)$_2$(PPh$_3$)$_2$] has however been described recently: R. B. Bedford, A. F. Hill, M. D. Francis, C. Jones and J. D. E. T. Wilton-Ely, *Inorg. Chem.*, 1997, **36**, 5142.
9 For a recent review, see: L. Weber, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 271.

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