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Synthesis of a η^2-2,3-diphosphabutadiene complex of zerovalent platinum from the corresponding η^2-phosphaalkyne complex

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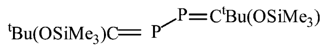
Hydrozirconation of the η^2-phosphaalkyne complex [Pt(dppe)(η^2-^{t}BuCP)] with [ZrHCl(η^5-C_5H_5)$_2$], followed by treatment with the chlorophosphaalkene ClP=C($SiMe_3$)$_2$ affords the η^2-2,3-diphosphabutadiene complex [Pt(dppe)(η^2-^{t}BuC(H)=PP=C($SiMe_3$)$_2$]. In the presence of [Pt(PPh_3)$_2$] the latter undergoes an addition reaction with water to afford the structurally characterised Pt(II) complex [Pt(dppe)(^{t}BuCH_2P(O)HPC($SiMe_3$)$_2$]

In spite of the considerable activity over the past few years in the area of unsaturated organophosphorus compounds, there are relatively few reports of 2,3-diphosphabutadienes of the type $R^1R^2C{=}PP{=}CR^3R^4$ and to date mainly symmetric compounds ($R^1R^2 = R^3R^4$) have been described.[1–6] Two different methods affording the symmetrical 2,3-diphosphabutadiene ^{t}Bu(OSiMe$_3$)C=PP=C^{t}Bu(OSiMe$_3$) **1** are known (i) by treatment of ^{t}Bu(OSiMe$_3$)C=PSiMe$_3$ with C_2Cl_6 and (ii) reacting $Me_3SiP{=}PSiMe_3$ with ^{t}BuCOCl. The unsymmetrical 2,3-diphosphabutadiene, ^{t}Bu(OSiMe$_3$)C=PP=CPh(SiMe$_3$), rearranges on heating in acetonitrile to give **1** together with the unstable 2,3-diphosphabutadiene Ph(SiMe$_3$)C=PP=CPh(SiMe$_3$), which then polymerises. The latter compound, as well as the diphosphane Ph_2PPPh_2, also resulted from thermolysis of Ph(SiMe$_3$)C=PPh$_2$

Since it is well known that ligation of unstable multiply bonded species to transition metal complexes can enhance their stability, we now describe a totally new synthetic route to an η^2-ligated unsymmetrical 2,3-diphosphabutadiene using this strategy. Previously,[7] we described the synthesis of the zerovalent platinum complex **4** containing the η^2-ligated **unstable** phosphaalkene ^{t}BuC(H)=PH , *via* hydrozirconation of the η^2-phosphaalkyne complex [Pt(dppe)(η^2-^{t}BuCP)] **2** with [ZrHCl(η^5-C_5H_5)$_2$], followed by protolysis of the resulting η^2-metallaphosphaalkene complex [Pt(dppe)(η^2-^{t}BuC(H)=PZrCl(η^5-C_5H_5)$_2$] **3**. Subsequently Heydt, Regitz and Schroder[8] have synthesised the corresponding phosphaalkene complex [Pt(PPh_3)$_2$(η^2-^{t}BuC(H)=P^{t}Bu] **5** by direct reaction of the **stable** phosphaalkene ^{t}BuC(H)=P^{t}Bu with [Pt(PPh_3)$_2$(C_2H_4)].

We now find that treatment of **3** with the chlorophosphaalkene ClP=C($SiMe_3$)$_2$ readily affords the unsymmetrical 2,3-diphosphabutadiene complex [Pt(dppe)(η^2-^{t}BuC(H)=PP=C($SiMe_3$)$_2$] **6**, whose identity was unambiguously established by its characteristic $^{31}P\{^1H\}$ NMR spectrum‡ which exhibited (i) the expected four different types of phosphorus nuclei, with a large one bond coupling constant ($^1J_{P^AP^B}$ = 260.5 Hz) for the two adjacent P atoms of the diphosphabutadiene and (ii) the characteristic ^{195}Pt satellites of the appropriate magnitude around each of the the resonances of P^A (368.4 Hz), P^B (68.2 Hz), P^C (3390 Hz) and P^D (3166 Hz). The $^{195}Pt\{^1H\}$ NMR spectrum of **4** was totally consistent with the proposed structure, showing the required 16-line pattern from coupling to the four non-equivalent phosphorus centres.‡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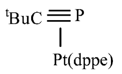
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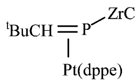
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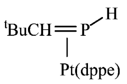
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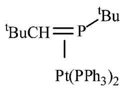
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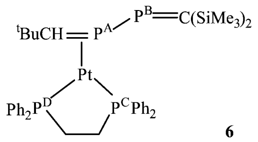
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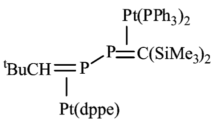
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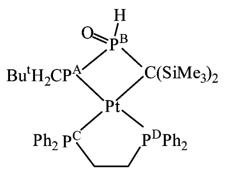
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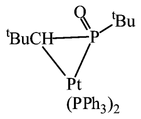
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The further ligating potential of the 2,3-diphosphabutadiene unit in **6** as a 4e donor, was explored in its reaction with [Pt(PPh_3)$_2$(C_2H_4)] in an attempt to form [Pt(dppe)(η^2-η^2-^{t}BuC(H)=PP=C($SiMe_3$)$_2$Pt(PPh_3)$_2$] **7**. Although the product could not be isolated, support for its formulation came from the observation that whereas **6** is unreactive towards water, complex **7** on work-up readily lost the [Pt(PPh_3)$_2$] fragment in the adventitious presence of water readily to afford the platinum (II) complex [Pt(dppe)(^{t}BuCH_2P(O)HPC($SiMe_3$)$_2$] **8**. The latter which was fully structurally characterised by a single crystal X-ray diffraction study,§(See Figure 1), showed the expected ^{1}H and ^{31}P NMR spectra,‡ is presumably formed by insertion of the retained [Pt(dppe)] fragment into the intermediate diphosphirane ring system ^{t}BuCH_2PP(OH)C($SiMe_3$)$_2$, which arises from H_2O addition to the unsaturated –C=P–P=C system, followed by an Arbusov-type rearrangement of the resulting –P(OH) bond to afford the pentavalent –P(O)H unit. The molecular structure of **8** also confirms the formation of the P–P bond, as proposed in the synthesis of **6** from **3**.

We showed previously[9,10] the quantitative nature of insertion reactions of the zerovalent d^{10} transition metal-ligand fragments [M(PR_3)$_2$], (M = Ni, Pd, Pt), into both phosphirene and phosphirane rings, to afford the corresponding four-membered metalla-phospha-cyclobutene and metalla-phospha-cyclobutane ring systems respectively. Interestingly the structurally

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† (Deceased)

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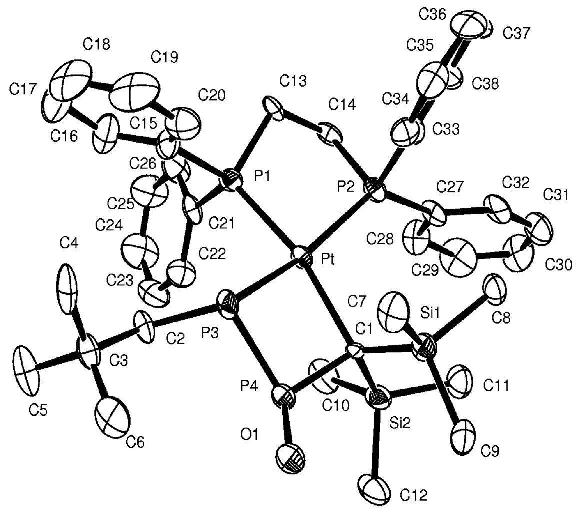

Fig. 1 Molecular structure of **8**, with selected bond lengths (Å) and bond angles (°). Pt–C(1) 2.190(9), Pt–P(1) 2.264(3), Pt–P(2) 2.321(3), Pt–P(3) 2.364(3), P(3)–P(4) 2.150(4), P(4)–C(1) 1.793(9), P(4)–O(1) 1.470(8); P(1)Pt(P2) 83.80(10), P(3)PtC(1) 79.9(2), P(3)Pt(P1) 93.63(10), P(2)PtC(1)105.9(2), P(3)P(4)C(1) 95.4(3), PtP(3)P(4) 81.21(12), PtC(1)P(4) 94.7(4).

related complex [Pt(PPh$_3$)$_2$(η^2-^{t}BuC(H)=P(O)^{t}Bu] **9** can be obtained directly by controlled peracid oxidation of **5**.[8]

Notes and references

‡ NMR data for **6**: ^{31}P{^{1}H} (121.4 MHz, C_6D_6); δ 1.5 (dd, P^{A}, ${}^{1}J_{P^AP^B}$ 260.4, ${}^{2}J_{P^AP^D}$ 56.6, ${}^{1}J_{P^APt}$ 368.4 Hz); δ 282.6 (dd, P^{B}, ${}^{1}J_{P^BP^A}$ 260.5, ${}^{3}J_{P^BP^D}$ 11.0, ${}^{2}J_{P^BPt}$ 68.2 Hz); δ 47.3 (d, P^{C}, ${}^{2}J_{P^CP^D}$ 27.7, ${}^{1}J_{P^CPt}$ 3390 Hz); δ 43.1 (ddd, P^{D}, ${}^{2}J_{P^DP^A}$ 56.7, ${}^{2}J_{P^DP^C}$ 27.7, ${}^{3}J_{P^DP^B}$ 11.0, ${}^{1}J_{P^DPt}$ 3166 Hz). ^{195}Pt{^{1}H} (53.779 MHz, C_6D_6) δ −5246 (dddd, ${}^{1}J_{P^CPt}$ 3389, ${}^{1}J_{P^DPt}$ 3166, ${}^{1}J_{P^APt}$ 368.1, ${}^{2}J_{P^BPt}$ 67.8 Hz). NMR data for **8**: ^{31}P{^{1}H} (121.4 MHz, C_6D_6); δ −38.0 (ddd, P^{A}, ${}^{1}J_{P^AP^B}$ 194, ${}^{2}J_{P^AP^D}$ 106, ${}^{2}J_{P^AP^C}$ 9.8, ${}^{1}J_{P^APt}$ 586 Hz); δ 35.9 (d, P^{D},${}^{2}J_{P^AP^D}$ 106, ${}^{1}J_{P^DPt}$ 2350 Hz); δ 38.5 (t, P^{C}, ${}^{2}J_{P^AP^C}$ 12.4, ${}^{3}J_{P^BP^C}$ 12.4, ${}^{1}J_{P^CPt}$ 2627 Hz); δ 47.4 (dd, P^{B}, ${}^{1}J_{P^AP^B}$ 193, ${}^{3}J_{P^BP^C}$ 12.7, ${}^{2}J_{PtP^B}$ 336 Hz). The one bond coupling ${}^{1}J_{P^BH}$ is 400 Hz)

§ *Crystal data*: for **8**: $C_{38}H_{54}OP_4PtSi_2.3.5(C_4H_8O)$ (M = 1154.3, monoclinic, space group $C2/c$ (no. 15), a = 27.187(5), b = 19.897(8), c = 20.892(6) Å, β = 92.94(2)°, V = 11286(6) Å^3, T = 173(2) K, Z = 8, μ (Mo–Kα) = 2.68 mm^{-1}, λ = 0.71073 Å, 7980 reflections collected, 7801 independent (R_{int} = 0.046), 5652 with $I > 2\sigma I$, R_1 = 0.061, wR_2 = 0.147 for $I > 2\sigma I$, R_1 = 0.091, wR_2 = 0.168 for all data collection–Enraf-Nonius CAD4. The structure was refined on F^2 using SHELXL-93. There are 5 poorly defined thf molecules; two in general positions and three lying across 2-fold rotation axes, which were included with all non-H atoms as C and with H atoms omitted. CCDC 203326. See http://www.rsc.org/suppdata/cc/b3/b301335a/ for crystallographic data in .cif or other electronic format.

1 R. Appel, O. Kündgen and F. Knoch, *Chem. Ber.*, 1985, **118**, 1352.
2 R. Appel, V. Barth and F. Knoch, *Chem. Ber.*, 1983, **116**, 938.
3 V. D. Romanenko, L. S. Kachkovskaya and L. N. Markovsky, *J. Gen. Chem. USSR*, 1985, **55**, 1898.
4 G. Märkl and H. Sejpka, *Tet. Lett.*, 1986, **27**, 171.
5 R. Appel, Chapter 4 in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Edited by M. Regitz and O. J. Scherer, Georg Thieme Verlag, Stuttgart, New York 1991.
6 K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*, John Wiley and Sons, Publishers, 1998.
7 M. H. A Benvenutti, N. Cenac and J. F. Nixon, *Chem. Commun.*, 1997, 1327.
8 H. Heydt, M. Regitz and M. Schroder, unpublished results, (H. Heydt, personal communication); M. Schroder, Doctoral Dissertation, 1999, University of Kaiserslautern, Germany.
9 S. S. Al-Juaid, D. Carmichael, P. B. Hitchcock, A. Marinetti, F. Mathey and J. F. Nixon, *J. Chem. Soc., Dalton Trans.*, 1991, 905.
10 D. Carmichael, P. B. Hitchcock, J. F. Nixon, F. Mathey and L. Ricard, *J. Chem. Soc., Dalton Trans.*, 1993, 1811.