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Synthesis, characterisation and reactivity of the first diphosphaalkyne †

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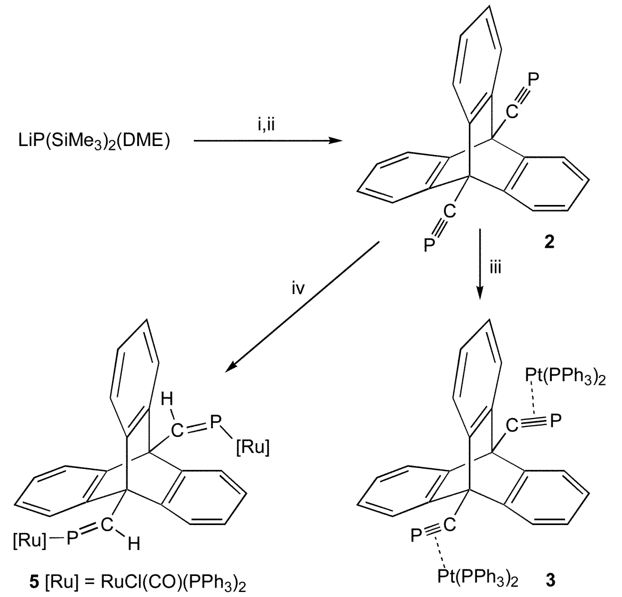
The first diphosphaalkyne, P≡CC(C_6H_4)$_3$CC≡P, has been synthesised and structurally characterised; its reaction with [Pt(C_2H_4)(PPh_3)$_2$] affords the complex, [{(PPh_3)$_2$Pt}$_2${μ-η^2:η^2-P≡CC(C_6H_4)$_3$CC≡P}], whilst its treatment with [RuHCl(CO)(PPh_3)$_3$] yields the bis-ruthenium phosphaalkenyl complex, [{(PPh_3)$_2$(CO)ClRu}$_2${μ-P=C(H)-C(C_6H_4)$_3$CC(H)=P}].

Since the preparation of the first stable phosphaalkyne, P≡CBu^t, in 1981,[1] these compounds have developed from being chemical curiosities to versatile and widely utilised starting materials for the preparation of organophosphorus cage, heterocyclic and acyclic compounds, phospha-organometallics and coordination complexes which display a variety of phosphaalkyne ligation modes.[2] The versatility of phosphaalkynes in this respect is largely due to the fact that their chemistry more closely mimics that of alkynes than nitriles. Their importance to organometallic and organophosphorus chemists is perhaps best illustrated by the fact that over 400 publications describing phosphaalkyne chemistry have appeared to date.[3] Despite this, there have been no reports of diphosphaalkynes save for a spectroscopic observation of the transient 1,4-diphosphabutadiyne, P≡C–C≡P,[4] and the preparation of the partially delocalised alkali metal phosphaethynolate salts, M(O–C≡P)$_2$, M = Mg, Ca, Sr, Ba.[5] If diphosphaalkynes could be developed they would have enormous potential as building blocks in the formation of organophosphorus polymers, phosphaalkynyl substituted organophosphorus heterocycles and cages, and coordination polymers. We have begun a study to explore this potential and report on the preparation and preliminary reactivity studies of the first diphosphaalkyne herein.

The reaction of 9,10-triptycenedicarbonyl chloride with 2 equivalents of [LiP($SiMe_3$)$_2$(DME)] led to the formation of the diphosphaalkene, (Me_3Si)P=C($OSiMe_3$)C(C_6H_4)$_3$CC($OSiMe_3$)=P($SiMe_3$) **1**, as a mixture of its *Z*,*Z*-, *Z*,*E*- and *E*,*E*-isomers. Treatment of **1** with a catalytic amount of KOH in DME afforded the diphosphaalkyne, **2**, in good yield (67%) as an air and moisture stable solid (Scheme 1). The ^{31}P{^{1}H} NMR spectrum ‡ of the compound displays a singlet (δ −15.7 ppm) in the normal region for phosphaalkynes.[2] In addition, an alkynic carbon resonance appears as a doublet ($^1J_{PC}$ = 47.1 Hz) at δ 164.0 ppm in its ^{13}C NMR spectrum. The molecular structure § of **2** is depicted in Fig. 1 and shows it to be monomeric with no intermolecular close contacts. Its P–C bond lengths (1.532 Å avge.) are comparable with those in other phosphaalkynes, *e.g.* 1.548(1) Å in P≡CBu^t,[6] and are consistent with localised triple bonded interactions. It is likely that the linear nature of the molecule and the separation of the two phosphaalkyne functionalities lends stability to the compound because the possibility of intramolecular phosphaalkyne coupling reactions is circumvented.

Initial efforts have been made to compare the reactivity of **2** to that of mono-phosphaalkynes and these have shown it to



Scheme 1 Reagents and conditions: i, Cl(O)CC(C_6H_4)$_3$CC(O)Cl, cyclohexane, −LiCl; ii, cat. KOH, DME, −(Me_3Si)$_2$O; iii, Pt(C_2H_4)(PPh_3)$_2$, toluene, −C_2H_4; iv, RuHCl(CO)(PPh_3)$_3$, CH_2Cl_2, −PPh_3.

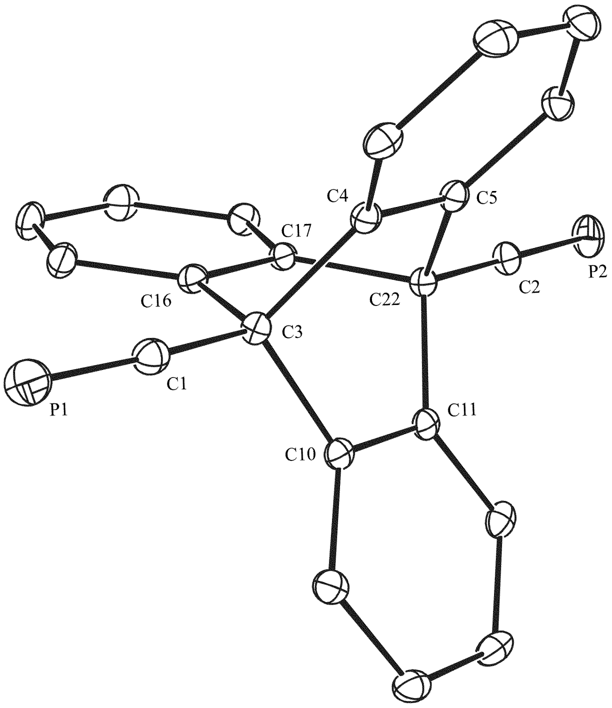


Fig. 1 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.531(2), P(2)–C(2) 1.533(2), C(1)–C(3) 1.473(3), C(2)–C(22) 1.476(3); C(3)–C(1)–P(1) 177.44(19), C(22)–C(2)–P(2) 179.52(19), C(1)–C(3)–C(16) 113.36(18), C(1)–C(3)–C(10) 113.70(19), C(1)–C(3)–C(4) 113.63(19), C(2)–C(22)–C(5) 113.65(19), C(2)–C(22)–C(11) 113.84(18), C(2)–C(22)–C(17) 113.04(18).

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† Electronic supplementary information (ESI) available: Synthesis of compounds **1**, **2**, **3** and **5**. See http://www.rsc.org/suppdata/dt/b3/b309061b/

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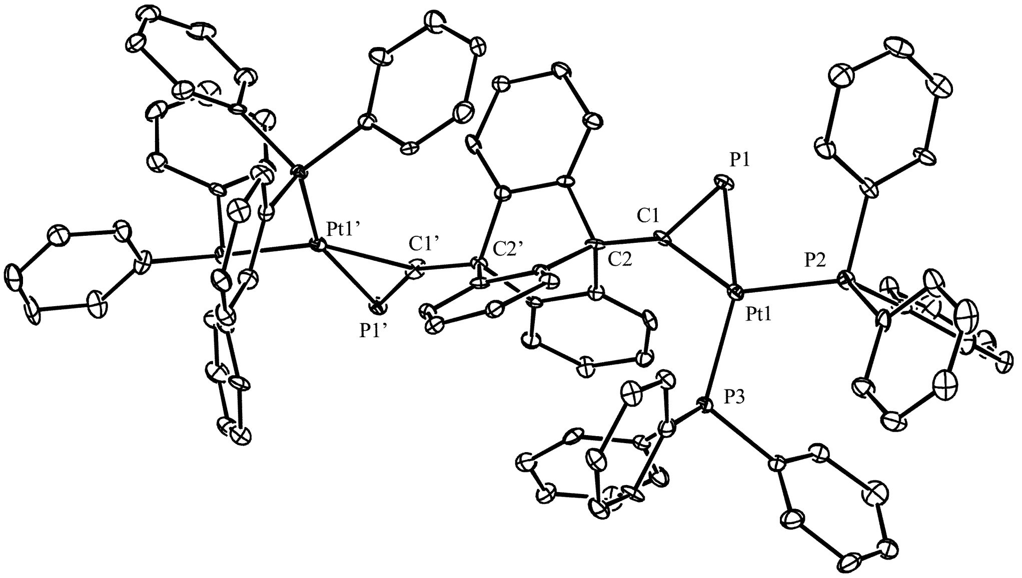

Fig. 2 Molecular structure of **3**. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.681(13), C(1)–C(2) 1.462(19), Pt(1)–C(1) 2.098(14), Pt(1)–P(2) 2.297(3), Pt(1)–P(3) 2.304(3), Pt(1)–P(1) 2.323(4); P(1)–C(1)–C(2) 142.6(10), C(1)–P(1)–Pt(1) 60.7(5), C(1)–Pt(1)–P(2) 140.4(3), C(1)–Pt(1)–P(3) 111.9(3), P(2)–Pt(1)–P(3) 107.36(13), C(1)–Pt(1)–P(1) 44.3(3), P(2)–Pt(1)–P(1) 96.24(13), P(3)–Pt(1)–P(1) 156.21(12). Symmetry operation: ′ $-x + 1$, y, $-z + 3/2$.

behave in a similar fashion. Its reaction with two equivalents of $[Pt(C_2H_4)(PPh_3)_2]$ led to ethylene displacement and the high yield (70%) formation of the bis-platinum(0) coordination complex, **3** (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of **3** is strongly suggestive of a symmetrical complex in which the phosphaalkyne moieties are η^2-bonded to the platinum fragments, as in the related complex, $[Pt(PPh_3)_2(\eta^2\text{-}P{\equiv}CBu^t)]$, **4**.[7] It exhibits three doublet of doublet resonances; two corresponding to the inequivalent PPh_3 ligands with satellites having couplings in the normal range ($^1J_{PtP}$ = 3273 and 3747 Hz), and one at low field (δ 94.9 ppm, *cf.* 84.1 ppm in **4**) which displays a very small $^1J_{PtP}$ coupling of 53 Hz, *cf.* 62 Hz in **4**. The magnitude of this coupling is consistent with the proposed alkyne like η^2-coordination of **2**, and the *ca.* 110 ppm downfield shift for this resonance upon coordination of the phosphaalkyne functionalities points towards significant back-bonding from the Pt centres into the π^*-orbitals of the P–C triple bonds.

The X-ray crystal structure of **3** was obtained (Fig. 2) and provides confirmation that **2** acts as a bifunctional ligand in this complex. In addition, it shows that the C(1) and P(1) centres have moved towards being sp^2-hybridised upon coordination, as the C(1)–P(1) bond length, 1.681(13) Å, *cf.* 1.672(17) Å in **4**, is 9.8% longer than the P–C bonds in **2** and, indeed, is in the normal P=C bond length range.[2] This combined with the fact that the PCC angles are no longer linear, *viz.* 142.6(10)°, *cf.* 132(2)° in **4**, provides strong evidence for the proposed back-bonding in this complex.

We have previously reported the facile hydrometallation of mono-phosphaalkynes with $[RuHCl(CO)(PPh_3)_3]$[8] and have shown that the resulting ruthenium–phosphaalkenyl complexes have a diverse and fascinating chemistry.[9] It was reasoned that if similar reactivity were demonstrated by **2** then its hydrometallation products may well be useful precursors to a variety of previously inaccessible diphosphaalkenes, metallophosphaalkenes and even unconjugated polyphosphaalkenes. Accordingly, the reaction of **2** with two equivalents of $[RuHCl(CO)(PPh_3)_3]$ led to the high yield (85%) formation of the bis-ruthenium phosphaalkenyl complex, **5** (Scheme 1). Unfortunately, X-ray quality crystals of this complex could not be obtained but all the spectroscopic evidence is compatible with the proposed structure. Its $^{31}P\{^1H\}$ NMR spectrum characteristically exhibits a very low field signal (δ 516.7 ppm) corresponding to the phosphaalkenyl P-centres, and a resonance at δ 39.9 ppm for the equivalent PPh_3 ligands. These shifts can be compared to those in the related complex, $[RuCl\{P{=}C(H)Bu^t\}(CO)(PPh_3)_2]$, **6** ($\delta$ 450.4, 33.9 ppm),[8] though in that complex a $^2J_{PP}$ coupling of 10 Hz was observed, whereas in **5** the signals are too broad for any coupling to be resolved. The ^1H NMR spectrum of the complex is as expected and exhibits an alkenic proton resonance at δ 7.98 ppm. In addition, a single CO stretching absorption (ν 1924 cm^{-1}, *cf.* 1929 cm^{-1} in **6**) can be seen in its infrared spectrum.

In summary, the preparation and structural characterisation of the first diphosphaalkyne has been described. Preliminary studies have shown its reactivity to mimic that of known mono-phosphaalkynes. We are currently examining the further chemistry of the bis-ruthenium phosphaalkenyl complex, **5**, in addition to exploring the cyclo-oligomerisation and polymerisation of **2**. The results of these studies will appear in forthcoming publications.

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Notes and references

‡ Selected data for **2**: mp 263–265 °C (decomp.); ^1H NMR (300.5 MHz, C_6D_6, 298 K): δ 6.85–6.87 (m, 6H, ArH), 7.86–7.91 (m, 6H, ArH); $^{13}C\{^1H\}$ NMR (75.6 MHz, C_6D_6, 298 K): δ 51.0 (d, C_3C, $^2J_{PC}$ = 17.4 Hz), 122.3, 125.9 (s, ArC), 143.0 (d, *quat*-ArC, $^3J_{PC}$ = 4.2 Hz), 164.0 (d, PC, $^1J_{PC}$ = 47.1 Hz); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ −15.7 (s, P≡C); MS APCI: *m*/*z* (%) 339 [MH^+, 100]; IR (Nujol) ν/cm^{-1}: 1555(m); Acc. mass EI: calc. for M^+ 338.0409, found 338.0411; **3**: mp 251–255 °C (decomp.); ^1H NMR (300.5 MHz, C_6D_6, 298 K): δ 6.39–7.18 (m, 60H, PPh_3), 6.54–6.58 (m, 6H, ArH), 7.60–7.64 (m, 6H, ArH); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 25.4 (dd, PPh_3, $^2J_{PP}$ = 21 and 11 Hz, $^1J_{PtP}$ = 3273 Hz), 28.9 (dd, PPh_3, $^2J_{PP}$ = 28 and 21 Hz, $^1J_{PtP}$ = 3747 Hz), 94.9 (dd, P≡C, $^2J_{PP}$ = 28 and 11 Hz, $^1J_{PtP}$ = 53 Hz); MS FAB (NOBA) *m*/*z* (%): 1776 [M^+, 6], 1514 [$M^+ - PPh_3$, 11], 1252 [$M^+ - 2PPh_3$, 8], 719 [$Pt(PPh_3)_2^+$, 100], 338 [$M^+ - 2Pt(PPh_3)_2$, 22]; IR (Nujol) ν/cm^{-1}: 1260(s), 1091(s), 1021(s), 803(s), 751(m), 690(m); **5**: mp 233–235 °C; ^1H NMR (300.5 MHz, C_6D_6, 298 K): δ 6.88–7.59 (m, 72H, ArH), 7.98 (br. m, 2H, CH=P); $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 39.9 (br. m, PPh_3), 516.7 (br. m., CH=P); MS FAB (noba) *m*/*z* (%): 688 [$Ru(PPh_3)_2(CO)Cl^+$, 7], 653 [$Ru(PPh_3)_2(CO)^+$, 11], 625 [$Ru(PPh_3)_2^+$, 10], 263 [PPh_3H^+, 100]; IR (Nujol) ν/cm^{-1}: 1924 ν(=CO).

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§ Crystal data for **2**: $C_{22}H_{12}P_2$, M = 338.26, monoclinic, space group $P2_1/n$, a = 8.1140(16), b = 10.161(2), c = 20.829(4) Å, β = 101.23(3)°, V = 1684.4(6) Å^3, Z = 4, D_c = 1.334 g cm^{-3}, F(000) = 696, μ(Mo-Kα) = 0.26 mm^{-1}, 150(2) K, 3732 unique reflections [R(int) 0.0860], R (on F) 0.0520, wR (on F^2) 0.1294 ($I > 2\sigma I$); **5**·Et_2O: $C_{98}H_{82}OP_6Pt_2$, M = 1851.64, monoclinic, space group $C2/c$, a = 24.329(5), b = 26.421(5), c = 13.270(3) Å, β = 105.04(3)°, V = 8238(3) Å^3, Z = 4, D_c = 1.493 g cm^{-3}, F(000) = 3696, μ(Mo-Kα) 3.56 mm^{-1}, 150(2) K, 7480 unique reflections [R(int) 0.1172], R (on F) 0.0873, wR (on F^2) 0.1940 ($I > 2\sigma I$). CCDC reference numbers 216489 and 216490. See http://www.rsc.org/suppdata/dt/b3/b309061b/ for crystallographic data in CIF or other electronic format.

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