Syntheses of complexes containing the novel 1,2,3-azadiphosphole and 1,2,5-azadiphosphole ring systems: crystal and molecular structure of $[Ir(\eta^5-C_5Me_5)(\eta^4-(Bu^tCPNBu^tPCBu^t)]]$

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The first examples of complexes containing the novel 1,2,5-azadiphosphole and 1,2,3-azadiphosphole ring systems are presented, together with the molecular structure of [Ir(η^{5} -C₅Me₅)(η^{4} -(Bu^tCPNBu^tPCBu^t)] as established by a single crystal X-ray diffraction study.

Transition metal-promoted syntheses of unsaturated P-heterocycles has received considerable attention in recent years in the quest for sophisticated ligands containing sp2- and/or sp3hybridised phosphorus atoms in heterocyclic rings.¹ Tungsten complexes of 2H-1,2-azaphosphole,² 2H-1,3,2-diazaphosphole³ and 2H-1,4,2-diazaphosphole^{3,4} rings can be obtained using the dual precursor potential of 2H-azaphosphirene complexes via intermediate terminal phosphanediyl and nitrilium phosphane-ylide complexes, the former giving rise to 3and 4-membered and the latter to 5-membered P-heterocycles. The planar, aromatic 1,2,4-azadiphosphole ring systems, $P_2C_2Bu_2^tNR^5$ (R = Prⁱ, Et, Ph, Tol, Prⁿ, Cy, Bu^tCH₂) on the otherhand, have recently been reported via coupling reactions involving the phospha-alkyne, PCBut, with the imido fragment of $[TiCl_2(NR)(py)_3]$ (R = Prⁱ, Et, Ph, Tol) or $[VCl_3(NR)]$ (R = Prⁱ, Prⁿ, Cy, Bu^tCH₂) complexes.⁵ We now describe the syntheses of complexes containing the previously unknown 1,2,3-azadiphosphole and 1,2,5-azadiphosphole ring systems; we also provide first evidence for 1,2,4-azadiphosphole complexes.

Extending our three-component reaction concept³ towards phospha-alkynes, we have now observed that 2*H*-azaphosphirene complex 1⁶ react with 1-piperidinonitrile (2 equiv.) and an excess of Bu⁴CP⁷ **2a** or 1-AdCP⁸ **2b** (Ad = adamantyl) in toluene at elevated temperature to give the 1,2,3-azadiphosphole complexes **3a,b** and 1,2,4-azadiphosphole complexes **4a,b**. Based on observations made earlier, *cf*. ref. 3 we assume that a transiently formed *C*-1-piperidino-substituted nitrilium phosphane-ylide complex react with the phospha-alkynes in [4 + 2] cycloaddition reactions to yield the two regioisomers, which were formed in ratios of 8:1 (**3a**:**4a**) and 3:1 (**3b**:**4b**) respectively. Unfortunately, even using low-temperature column chromatography, only complex **3b** could be separated by extraction and subsequent crystallisation (Scheme 1).

Bergman and co-workers,⁹ synthesised the monomeric imido complex [Ir(η^5 -C₅Me₅)(NBu^t)] from [{Ir(η^5 -C₅Me₅)Cl₂}₂] and 4 equiv. of LiNHBu^t in THF and described its cycloaddition reaction with dimethyl acetylenedicarboxylate to afford the structurally characterised compound [Ir(η^5 -C₅Me₅){NBu^t-(MeO₂CCCCO₂Me)₂}], which contains an η^4 -coordinated pyrrole ring. Since phospha-alkynes, PCR, are known to behave very like alkynes,¹ we have extended this type of cyclisation reaction and find that [Ir(η^5 -C₅Me₅)(NBu^t)] **5** on treatment with an excess of PCBu^t **2a** in toluene at ambient temperature afforded the η^4 -ligated 1,2,5-azadiphosphole ring complex **6**.¶

The E.I. mass spectra[†] exhibited the molecular ions of **3b** and **6**, which are consistent with the proposed formulations. The

molecular structures of 3b and 6 were deduced by NMR spectroscopy[‡] (¹³C, ³¹P) (vide infra) and confirmed by a single crystal X-ray diffraction study§ in the case of 6 (Fig. 1). The ³¹P{¹H} NMR spectra of complexes **3** and **4** displayed the expected AB-type spectra with low-field resonances for the two-coordinated phosphorus centers and with typical magnitudes of phosphorus-phosphorus coupling constants (for 3 ca. 294 Hz; for 4 ca. 34 Hz). Additionally, complex 3b shows signals in its ¹³C{¹H} NMR spectrum at δ 180.3 (m) and 196.5 (dd, ${}^{1}J_{(PC)}$ 61.1 Hz, ${}^{2}J_{(PC)}$ 9.7, *C*=P), which were readily assigned to the imino- and the phosphaalkene-carbon atoms respectively. The ${}^{31}P{}^{1}H$ NMR spectrum of **6** displayed a singlet (δ 0.26) implying a symmetrical environment for the two P atoms. The three signals (δ 1.92, 1.48, 1.07) observed in the ¹H NMR spectrum were readily assigned to C₅Me₅, PCBu^t and NBut respectively. Further insight into the structure of this molecule was gained from the ${}^{13}C{}^{1}H$ NMR spectrum which showed two pseudo triples (δ 34.7 ${}^{3}J_{(PC)}$ 6.51 Hz, 28.7 ${}^{3}J_{(PC)}$ 7.28 Hz) in an intensity ratio of 2:1 which were assigned to the methyl resonances of the two sets of non-equivalent tert-butyl groups, thereby establishing the connectivity of both phosphorus nuclei with nitrogen.

The molecular structure of complex **6** which was confirmed by a single crystal X-ray analysis of crystals grown from a saturated pentane solution (-50 °C), is shown in Fig. 1 together



Scheme 1 Reaction of complex 1 with 1-piperidinonitrile and phosphaalkynes 2a,b§



Scheme 2 Reaction of $[Ir(\eta^5\text{-}C_5Me_5)(NBu^t)]$ 5 with the phospha-alkyne PCBut 2a.¶



Fig. 1 Molecular structure of $[Ir(\eta^{5-}C_5Me_5)(\eta^{4-}(Bu^{t}CPNBu^{t}PCBu^{t})]$ 6. Selected distances (Å) and angles (°): P(1)–C(1) 1.846(7), C(2)–P(2) 1.837(11), P(1)–N 1.718(7), P(2)–N 1.733(6), C(2)–C(1) 1.427(12), Ir–C(2) 2.161(11), Ir–C(1) 2.173(5), Ir–P(2) 2.333(2), Ir–P(1) 2.338(3), C(18)–C(19) 1.433(14) Å. N–P(2)–C(2) 101.3(4), N–P(1)–C(1) 101.2(3), P(1)–N–P(2) 98.9(3), C(2)–C(1)–P(1) 108.8(5), C(1)–C(2)–P(2) 109.1(7), P(2)–N–C(11) 121.8(4), P(2)–C(2)–C(7) 118.6(7), C(1)–C(2)–C(7) 132.0(8)°. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

with principal bond lengths and angles. The IrC₅Me₅ fragment is η^4 -ligated to the 1,2,5-azadiphosphole ring resulting in the nitrogen atom becoming pyramidalised and it lies out of the plane formed by P(2)–C(2)–C(1)–P(1), (dihedral angle between P(2)–C(2)–C(1)–P(1) and P(1)–N–P(2), 44.2(3)°). The longer Ir–P(1)/Ir–P(2) (av. 2.335 Å) bond lengths compared with Ir– C(2)/Ir–C(1) (av. 2.167 Å) causes the P(2)–C(2)–C(1)–P(1) fragment to tilt away from the plane of the C₅Me₅ ring (dihedral angle between P(1)–C(1)–C(2)–P(2) and C(15)–C(16)–C(17)– C(18)–C(19), 7.7°). The C(1)–C(2) bond distance (1.427(12) Å) lies within the range expected for η^4 -bonded systems, whereas the P(1)–C(1) and P(2)–C(2) distances (1.846(7), 1.837(11) Å) are considerably longer than anticipated for P=C double bonds. This is the first structurally characterised metal complex containing a 1,2,5-azadiphosphole derivative.

It is interesting to note that Regitz and co-workers¹⁰ recently proposed, on the basis of ${}^{31}P{}^{1}H{}$ NMR spectroscopic data, the possible intermediacy of a 1,2,5-azadiphosphole ring system in the metal-mediated formation of azatetraquadricyclanes from phosphaalkynes. Complex **1**, which has a formal electron count of 18e, was found to be remarkably stable and column chromatography (silica gel, pentane) in air resulted in only very slight decomposition of the sample (1% loss), likewise attempts to displace the heterocycle from iridium by carbonylation of the metal centre proved unsuccessful.

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Notes and references

† Satisfactory elemental analysis were obtained for complexes **3b** and **6**. NMR data were recorded in [²H₆]benzene solutions (295 K) at 75.5 MHz (¹³C) and 81.0 (³¹P), using TMS and 85% H₃PO₄ as standard references; *J*/Hz. *Selected spectroscopic data for* **3**, **4** and **6**. ³¹P [¹H] NMR: **3a**: δ 340.4 (d, ¹*J*_(PP) 297.1), 91.2 (d, ¹*J*_(PP) 297.1, ¹*J*_(PW) 211.0). **4a**: δ 234.1 (d, ²*J*_(PP) 34.2), 107.6 (d, ²*J*_(PP) 34.2). **3b**: δ 341.8 (d, ¹*J*_(PP) 296.2), 93.3 (d, ¹*J*_(PP) 296.2, ¹*J*_(PW) 209.5). **4b**: δ 232.9 (d, ²*J*_(PP) 34.8), 105.8 (d, ²*J*_(PP) 34.8). **3b**: ¹³C [¹H] NMR: δ 2.7 [m_c, br, (SiCH₃)], 21.7 [m_c, (CH(SiCH₃)₂)], 23.9 [s, NCH₂CH₂CH₂], 25.9 [s, NCH₂CH₂], 29.4 [s, Ad C3/C5/C7], 36.7 [s, Ada C4/C6/C10], 42.9 [dd, *J*_(PC) 10.1, *J*_(PC) 11.8, Ad C1], 44.0 [d, ³*J*_(PC) 14.3, Ad C2/C8/C9], 54.7 [s, NCH₂], 180.3 [m_c, *C*=N], 196.5 [dd, ¹*J*_(PC) 61.1, ²*J*_(PC) 9.7, *C*=P], 197.3 [dd, *J*_(PC) 3.5, *J*_(PC) 4.5, *cis*-CO], 198.6 [d, *J*_(PC) 19.4 Hz, *trans*-CO]. EI-MS (pos.-CI, NH₃) *m*/*z* (%): 802 (80) [M]⁺. **6**: ³¹P [¹H] NMR: δ 0.26. ¹³C [¹H] NMR: δ 11.5 [C₅(CH₃)₅], 28.7 [t, NC(CH₃)₃, ³*J*_(PC) 7.28], 34.7 [*pseudo*-t, PCC(CH₃)₃, ³*J*_(PC) 6.51 Hz], 36.2 [*pseudo*-t, PCC(CH₃)₃, ²*J*_(PC) 8.21], 95.2 [m, PCC], 94.0 [C₅(CH₃)₅]. EI-MS *m*/*z* (%): S59 (30) [M]⁺.

‡ *Crystal data* for **6**: C₂₄H₄₂IrNP₂, M = 598.73, orthorhombic, space group *Pna2*₁ (no. 33), a = 20.067(2), b = 14.271(3), c = 8.775(5) Å, U = 2513(2) Å³, Z = 4, $D_c = 1.58$ Mg m⁻³, crystal dimensions $0.2 \times 0.2 \times 0.2$ mm, *F*(000) = 1200, T = 173(2) K, Mo-K α radiation, $\lambda = 0.71073$ Å. Data were collected on an Enraf-Nonius CAD4 diffractometer and of the total 4635 reflections measured 2151 having $I > 2\sigma(I)$ were used in the calculations. The final indices ($I > 2\sigma(I)$) were R1 = 0.022, wR2 = 0.049. CCDC 182/1727. See http://www.rsc.org/suppdata/cc/b0/b004692m/ for crystallographic files in .cif format.

§ *Experimental*: to a solution of 2.15 g (3.5 mmol) 2*H*-azaphosphirene complex **1** in 20 ml toluene was added 0.6 mL (5 mmol) 1-piperidinonitrile and 1.4 g (14 mmol) Bu^cCP or 2.5 g (14 mmol) 1-AdaCP. The solutions were heated with stirring at 75–80 °C for 3 h and the volatiles removed *in vacuo* (0.1 mbar). In the case of **3b**, the crude product was separated by extraction of the brown residue with light petroleum (60:40) and crystallised from *n*-pentane/toluene at -20 °C; yield 2.13 g, 19%.

¶ *Experimental*: to a stirred solution of $[Ir(\eta^5-C_5Me_5)(NBu^t)]$ (0.370 g, 0.9 mmol) in toluene (30 ml) was added dropwise, PCBu^t (0.232 g, 2.3 mmol) and the resulting black solution was allowed to stir for 24 h. The solvent was removed *in vacuo* and the residue sublimed (180 °C, 10⁻⁵ mbar) yielding a white waxy solid (yield 0.205 g, 40%). Crystals suitable for X-ray analysis were grown from a slowly cooled and concentrated pentane solution (-48 °C).

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