Syntheses of complexes containing the novel 1,2,3-azadiphosphole and 1,2,5-azadiphosphole ring systems: crystal and molecular structure of [Ir(η^5-C$_5$Me$_5$)(η^4-(Bu^{t}CPNBu^{t}PCBu^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-C$_5$Me$_5$)(η^4-(Bu^{t}CPNBu^{t}PCBu^t)] as established by a single crystal X-ray diffraction study.

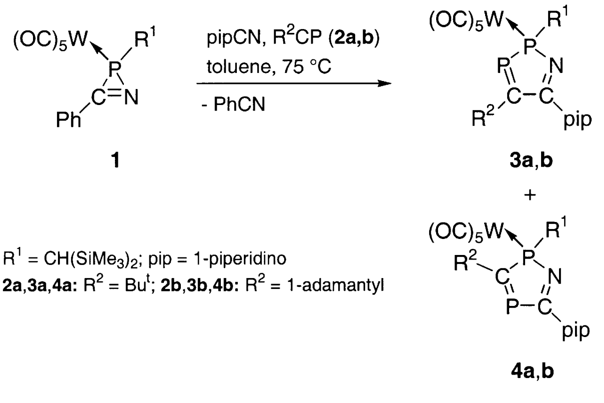
Transition metal-promoted syntheses of unsaturated P-heterocycles has received considerable attention in recent years in the quest for sophisticated ligands containing sp^2- and/or sp^3-hybridised phosphorus atoms in heterocyclic rings.[1] Tungsten complexes of 2*H*-1,2-azaphosphole,[2] 2*H*-1,3,2-diazaphosphole[3] and 2*H*-1,4,2-diazaphosphole[3,4] rings can be obtained using the dual precursor potential of 2*H*-azaphosphirene complexes *via* intermediate terminal phosphanediyl and nitrilium phosphane-ylide complexes, the former giving rise to 3- and 4-membered and the latter to 5-membered P-heterocycles. The planar, aromatic 1,2,4-azadiphosphole ring systems, P$_2$C$_2$Bu$^t_2$NR[5] (R = Pr^i, Et, Ph, Tol, Pr^n, Cy, Bu^{t}CH$_2$) on the otherhand, have recently been reported *via* coupling reactions involving the phospha-alkyne, PCBu^t, with the imido fragment of [TiCl$_2$(NR)(py)$_3$] (R = Pr^i, Et, Ph, Tol) or [VCl$_3$(NR)] (R = Pr^i, Pr^n, Cy, Bu^{t}CH$_2$) 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 concept[3] towards phospha-alkynes, we have now observed that 2*H*-azaphosphirene complex **1**[6] react with 1-piperidinonitrile (2 equiv.) and an excess of Bu^{t}CP[7] **2a** or 1-AdCP[8] **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).

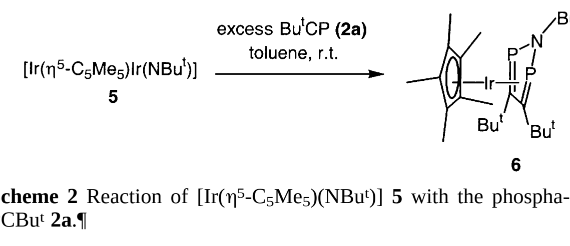
Bergman and co-workers,[9] synthesised the monomeric imido complex [Ir(η^5-C$_5$Me$_5$)(NBu^t)] from [{Ir(η^5-C$_5$Me$_5$)Cl$_2$}$_2$] and 4 equiv. of LiNHBu^t in THF and described its cycloaddition reaction with dimethyl acetylenedicarboxylate to afford the structurally characterised compound [Ir(η^5-C$_5$Me$_5$){NBu^t-(MeO$_2$CCCCO$_2$Me)$_2$}], 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-C$_5$Me$_5$)(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‡ (^{13}C, ^{31}P) (*vide infra*) and confirmed by a single crystal X-ray diffraction study§ in the case of **6** (Fig. 1). The ^{31}P{^{1}H} 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 ^{13}C{^{1}H} NMR spectrum at δ 180.3 (m) and 196.5 (dd, $^1J_{(PC)}$ 61.1 Hz, $^2J_{(PC)}$ 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 ^{1}H NMR spectrum were readily assigned to C$_5$Me$_5$, PCBu^t and NBu^t 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 $^3J_{(PC)}$ 6.51 Hz, 28.7 $^3J_{(PC)}$ 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 phospha-alkynes **2a**,**b**§



Scheme 2 Reaction of [Ir(η^5-C$_5$Me$_5$)(NBu^t)] **5** with the phospha-alkyne PCBu^t **2a**.¶

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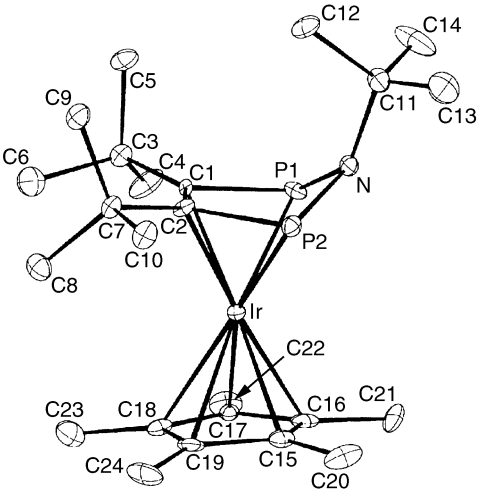

Fig. 1 Molecular structure of $[Ir(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}(Bu^tCPNBu^tPCBu^t)]$ **6**. Selected distances (Å) and angles (°): P(1)–C(1) 1.846(7), C(2)–P(2) 1.837(11), P(1)–N 1.718(7), P(2)–N 1.733(6), C(2)–C(1) 1.427(12), Ir–C(2) 2.161(11), Ir–C(1) 2.173(5), Ir–P(2) 2.333(2), Ir–P(1) 2.338(3), 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 IrC_5Me_5 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 C_5Me_5 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-workers[10] recently proposed, on the basis of $^{31}P\{^1H\}$ 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 $[^2H_6]$benzene solutions (295 K) at 75.5 MHz (^{13}C) and 81.0 (^{31}P), using TMS and 85% H_3PO_4 as standard references; J/Hz. *Selected spectroscopic data for* **3**, **4** *and* **6**. $^{31}P\{^1H\}$ NMR: **3a**: δ 340.4 (d, $^1J_{(PP)}$ 297.1), 91.2 (d, $^1J_{(PP)}$ 297.1, $^1J_{(PW)}$ 211.0). **4a**: δ 234.1 (d, $^2J_{(PP)}$ 34.2), 107.6 (d, $^2J_{(PP)}$ 34.2). **3b**: δ 341.8 (d, $^1J_{(PP)}$ 296.2), 93.3 (d, $^1J_{(PP)}$ 296.2, $^1J_{(PW)}$ 209.5). **4b**: δ 232.9 (d, $^2J_{(PP)}$ 34.8), 105.8 (d, $^2J_{(PP)}$ 34.8). **3b**: $^{13}C\{^1H\}$ NMR: δ 2.7 [m_c, br, ($SiCH_3$)], 21.7 [m_c, ($CH(SiCH_3)_2$)], 23.9 [s, $NCH_2CH_2CH_2$], 25.9 [s, NCH_2CH_2], 29.4 [s, Ad *C*3/*C*5/*C*7], 36.7 [s, Ada *C*4/*C*6/*C*10], 42.9 [dd, $J_{(PC)}$ 10.1, $J_{(PC)}$ 11.8, Ad *C*1], 44.0 [d, $^3J_{(PC)}$ 14.3, Ad *C*2/*C*8/*C*9], 54.7 [s, NCH_2], 180.3 [m_c, *C*=N], 196.5 [dd, $^1J_{(PC)}$ 61.1, $^2J_{(PC)}$ 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, NH_3) *m/z* (%): 802 (80) $[M]^+$. **6**: $^{31}P\{^1H\}$ NMR: δ 0.26. $^{13}C\{^1H\}$ NMR: δ 11.5 [$C_5(CH_3)_5$], 28.7 [t, $NC(CH_3)_3$, $^3J_{(PC)}$ 7.28], 34.7 [*pseudo*-t, $PCC(CH_3)_3$, $^3J_{(PC)}$ 6.51 Hz], 36.2 [*pseudo*-t, $PCC(CH_3)_3$, $^2J_{(PC)}$ 8.21], 95.2 [m, PCC], 94.0 [$C_5(CH_3)_5$]. EI-MS *m/z* (%): 559 (30) $[M]^+$.

‡ *Crystal data* for **6**: $C_{24}H_{42}IrNP_2$, $M = 598.73$, orthorhombic, space group $Pna2_1$ (no. 33), $a = 20.067(2)$, $b = 14.271(3)$, $c = 8.775(5)$ Å, $U = 2513(2)$ Å^3, $Z = 4$, $D_c = 1.58$ Mg m^{-3}, crystal dimensions 0.2 × 0.2 × 0.2 mm, $F(000) = 1200$, $T = 173(2)$ K, Mo-Kα 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^tCP 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 $[Ir(\eta^5\text{-}C_5Me_5)(NBu^t)]$ (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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