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First catalytic dihydroamination of a phosphaalkyne. Crystal and molecular structure of *trans*-[$PdCl_2\{P(Pr^iNH)_2CH_2Bu^t\}_2$]

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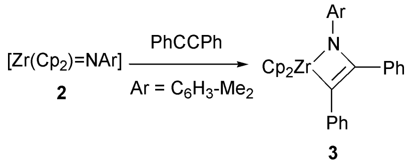
Treatment of a dichloromethane solution of Bu^tCP, containing a catalytic amount of $TiCl_4$, with an excess of the primary amines RNH_2 (R = Pr^i, Bu^t) quantitatively affords the corresponding bis-dialkylaminophosphine $P(Bu^tNH)_2$-CH_2Bu^t. $P(Pr^iNH)_2CH_2Bu^t$ is structurally characterised by a single crystal X-ray diffraction study of its bis-*trans*-$PdCl_2$ complex.

The direct addition of nucleophiles HNR_2 to alkenes and alkynes has been shown to be kinetically unfavourable due to high activation barriers caused by unfavourable approach of the substrates.[1] Catalysis is therefore of fundamental importance for the amination of alkynes, by providing alternative lower energy kinetic pathways. A survey of the literature in this area reveals a stronger precedence for catalytic *intra*-molecular hydroamination of alkynes employing complexes of titanium,[2] nickel,[3] palladium,[4] gold[5] and lanthanides.[6] In contrast, catalytic *inter*-molecular hydroamination of alkynes appears much more difficult and these reactions are often hampered by low turnover numbers. The use of Hg^{II} reagents appears to be the most general route for the hydroamination of alkenes and alkynes[7,8] and examples of thallium,[9] lanthanides,[10] uranium and thorium[11] containing catalysts exist.

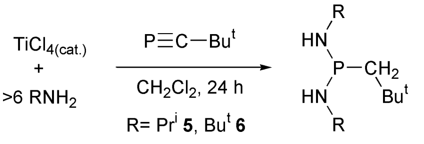
Recently, Bergman *et al.*[12] have demonstrated the utility of the zirconocene diamide $[Zr(\eta^5\text{-}C_5H_5)_2(NHC_6H_3\text{-}Me_2)_2]$ **1** for the stoichiometric and catalytic addition of amines to internal alkynes and allenes, yielding enamines and imines respectively. The thermolysis (α-elimination) of **1** yields the transient imide '$[Zr(\eta^5\text{-}C_5H_5)_2(NC_6H_3\text{-}Me_2)]$' **2** which catalyses the addition of alkynes (RCCR, R = Me, Ph) to 2,6-dimethylaniline. Although intermediates have not been observed during the catalytic cycle, the proposed intermediate metallacyclobutene complex $[Zr(\eta^5\text{-}C_5H_5)\{N(C_6H_3\text{-}Me_2)(Ph)CC(Ph)\}]$ **3**, formed from a stoichiometric [2 + 2] addition of diphenyl acetylene to the metal nitrogen unsaturated bond of **2**, has been prepared and structurally characterised (see Scheme 1).



Scheme 1

Although phosphaalkynes, RCP, contain a slightly polarised bond[13] their similarity in reactivity to alkynes is now very well established.[14] However, although nucleophilic, *trans*-metallations and 1,2-additions have been described,[13] there are no examples to date of hydroaminations of this class of unsaturated molecule. Recently we have been interested in the cycloaddition chemistry of the phosphaalkyne Bu^tCP with Ti and Zr imides.[15] The reaction of Bu^tCP with the transient imide '$[Cp_2ZrN(C_6H_3\text{-}Me_2)]$' **2** affords the azaphosphacyclobutadiene complex $[\overline{Cp_2ZrN}(C_6H_5\text{-}Me_2)PC(Bu^t)]$ **4** which is isostructural with **3**. The $\underline{MNPC}$ fragment in **4** is in agreement with the expected bond polarity of the unsaturated reactive sites.

During the course of this work we have discovered that the reaction of catalytic amounts of $TiCl_4$ with the primary amines RNH_2 (R = Bu^t, Pr^i) followed by the addition of $PCBu^t$ yields the dialkyldiaminophosphines $P(NHR)_2CH_2Bu^t$ (R = Pr^i **5**,† Bu^t **6**†) in near quantitative yields (90–95%) (Scheme 2). No reaction occurs in the absence of $TiCl_4$.



Scheme 2

Compounds **5** and **6** are colourless oils which can be easily purified from the crude reaction mixtures by sublimation *in vacuo* on to a cold finger (liquid nitrogen, 60–70 °C, 10^{-2} mbar, yield 95%). The ^1H NMR spectrum of **5** displays the expected five signals. The septet at δ 3.16 and two doublets at δ 1.40, 1.31 are assigned to the methine, methylene and NH protons respectively, the NH resonance being broadened by ^{14}N quadrupolar coupling. The singlet at δ 1.1 is attributed to the *tert*-butyl protons, and the doublet of doublets at δ 1.03 is assigned to the diastereotopic methyl groups of the isopropyl units which are further coupled to the methine protons. The ^{31}P-$\{^1H\}$ NMR spectrum displays a singlet at δ 57.2. In order to unambiguosly assign the connectivity of **5**, the bis-diaminophosphine complex *trans*-$[PdCl_2\{P(Pr^iNH)_2CH_2(Bu^t)\}_2]$ **7**† was prepared from the reaction of $[PdCl_2(NCPh)_2]$ **8** and 2 equiv. **5** in acetone. Crystals suitable for X-ray analysis were grown from a concentrated toluene solution cooled to −50 °C and the molecular structure is depicted below together with relevant bond lengths and angles (Fig. 1).‡ The structure is unremarkable, but serves to confirm the dihydroamination of the phosphaalkyne. The bis-aminophosphine units adopt a

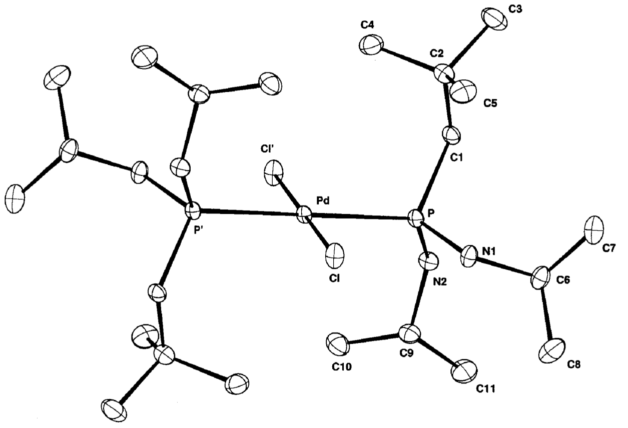


Fig. 1 Molecular structure of $[PdCl_2\{(NHPr^i)_2PCH_2(Bu^t)\}]$ **7**. Selected distances (Å) and angles (°): Pd–P 2.313(1), P–C(1) 1.829(3), P–N(1) 1.667(2), P–N(2) 1.662(2), Å. P–Pd–Cl′ 87.19(4), N(2)–P–N(1) 103.8(1) P–Pd–Cl 92.81(4) N(1)–P–C(1) 110.0(1), N(2)–P–Pd 116.32(9), N(1)–P–Pd 112.26(8), C(1)–P–Pd 114.49(9)°. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

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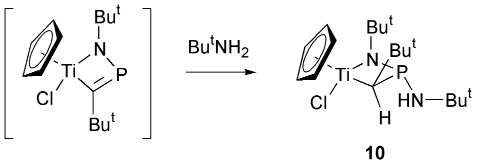

Scheme 3

trans-orientation in **7** and the phosphorus atoms display a tetrahedral coordination geometry.

Surprisingly, a survey of the literature shows a relative paucity of structural information on diaminophosphines and only $P(Ar^*NH)_2Ar$ ($Ar^* = C_6H_2Bu^t{}_3$-2,4,6)[16] and $P(Ar_fNH)_2Ar^*$ ($Ar_f = C_6H_2(CF_3)_3$-2,4,6)[17] have been crystallographically characterised. A few complexes of the group 6 metals have also been reported.[18]

The mechanism of formation of the diaminophosphine has not been fully determined, however Winter *et al.*[19] reported that treatment of $TiCl_4$ with an excess of primary amines affords imido complexes of type $[TiCl_2(NR)(NH_2R)_x)]$ **9** which clearly are likely candidates for the active catalytic species. Furthermore, in unpublished results Regitz and Asmus[20] have recently shown that the reaction of $[Ti(\eta^5\text{-}C_5H_5)Cl_3]$ with Bu^tNH_2 and $PCBu^t$ in toluene yields $[Ti(\eta^5\text{-}C_5H_5)Cl\{PNBu^t(NHBu^t)CHBu^t\}]$ **10**, (probably *via* a [2 + 2] addition of $PCBu^t$ to the intermediate titanium imide $[Ti(C_5H_5)Cl(NBu^t)]$, followed by a 1,2 addition of NH_2Bu^t across the activated P=C bond) (Scheme 3).

The mechanism of formation of the diaminophosphines **5** and **6** by di-hydroamination of $PCBu^t$ probably proceeds *via* the intermediacy of $[TiCl_2(NR)(NH_2R)_x)]$ **9** and $[TiCl_2(NR)P(NHR)CHBu^t]$ which is analogous to **10**, the excess $[NH_3Bu^tCl]$ formed subsequently removing the resulting substrate '$\{PNR(NHR)CHBu^t\}$' *via* a double protonation step.

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Notes and references

† *Characterisation data* for: $P(NHPr^i)_2CH_2{}^tBu$ **5**: ^1H NMR (d_6-benzene, 295 K) δ 2.36 [sept, 1H, CH, $^3J_{(HH)}$ 6.4 Hz], 1.4 [d, 2H, CH_2, $^2J_{(HP)}$ 2.5 Hz], 1.31 [d, 2H, $NHC(CH_3)_3$, $^3J_{(HH)}$ 7.14 Hz], 1.11 [s, $PCH_2C(CH_3)_3$], 1.05, 1.0 [d × 2, 12H, $CH(CH_3)_2$]. $^{31}P\text{-}\{^1H\}$ NMR δ 57.16.

$P(NHBu^t)_2CH_2Bu^t$ **6**: ^1H NMR (d_6-benzene, 295 K): δ 1.19 [s, 18H, $CH_2C(CH_3)_3$], 1.09 [s, 9H, $C(CH_3)_3$], 1.27 [d, br, 2H, CH_2]. $^{13}C\text{-}\{^1H\}$ NMR δ 55.9 [d, $C(CH_3)_3$, $^2J_{(CP)}$ 6.83 Hz], 50.97 [d, PC, $^1J_{(CP)}$ 14 Hz], 32.69 [d, $NHC(CH_3)_3$, $^3J_{(CP)}$ 8.93 Hz], 31.80 [d, $CH_2C(CH_3)_3$, $^2J_{(CP)}$ 9.03 Hz], 31.1 [d, $NHC(CH_3)_3$, $^2J_{(CP)}$ 12.28 Hz] $^{31}P\text{-}\{^1H\}$: NMR δ 40.88. EI-MS *m/z* (%): 246 (30) $[M]^+$, 233 (13) $[M - (Me)]^+$, 175 (80) $[M - (NHBu^t) - (Me)]$.

$[PdCl_2\{P(NH_2Pr^i)_2CH_2Bu^t\}_2]$ **7** ^1H NMR (d_6-benzene, 295 K): δ 3.5 [s, br, 2H, NH], 2.8 [sept., 2H, $CH(CH_3)_2$, $^3J_{(HH)}$ 7.1 Hz], 1.8 [d, 4H, CH_2P, $^2J_{(HP)}$ 3.92 Hz], 1.39 [s, 9H, $C(CH_3)_3$,], 1.05 [d, 12H, $CH(CH_3)_2$, $^3J_{(HH)}$ 4.1 Hz] 1.19 [d, 12H, $CH(CH_3)_2$, $^3J_{(HH)}$ 4.1 Hz]. $^{13}C\text{-}\{^1H\}$ NMR: δ 44.3 $[C(CH_3)_3]$, 41.1 [*pseudo*-t, PCH_2, $^1J_{(PC)}$ 22 Hz], 32.6 [br, $C(CH_3)_3$], 31.09 [NCH], 26.1, 25.6 [d, $CH(CH_3)_2$]. $^{31}P\text{-}\{^1H\}$ NMR δ 64.8. EI-MS *m/z* (%): 614 (25) $[M]^+$, 543 (5) $[M - (CC(CH_3)_3]^{+\cdot}$ Analysis calculated for $C_{22}H_{54}Cl_2N_4P_2Pd$: C, 43.04; H, 8.87. Found: C, 43.00; H, 8.90%.

‡ *Crystal data* for $C_{36}H_{66}Cl_2N_4P_2Pd$ **7**: $M = 794.2$, triclinic, $a = 7.869(3)$, $b = 10.919(3)$, $c = 12.754(5)$ Å, $\alpha = 90.44(3)$, $\beta = 103.26(3)$, $\gamma = 95.81(3)°$, $U = 1060.6(6)$ Å^3, $T = 173(2)$ K, space group $P\bar{1}$ (no. 2), $Z = 1$, λ(Mo-Kα) = 0.71073 Å, 5107 reflections measured which were used in all calculations. Final R indices for $[I > 2\sigma(I)]$ with 4563 reflections was $R1 = 0.038$. Single crystals of $[PdCl_2\{P(NH_2Pr^i)_2CH_2(Bu^t)\}_2]$ were grown from a saturated toluene solution (−53 °C), mounted in inert oil and transferred to the cold gas stream of the diffractometer. The structure was solved using direct methods and refined by full-matrix least-squares on F^2. CCDC 182/1830. See http://www.rsc.org/suppdata/cc/b0/b007512o/ for crystallographic files in .cif format.

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