Hydrozirconation of an η^2-ligated phosphaalkyne. A new synthetic route to η^2-ligated phosphaalkenes

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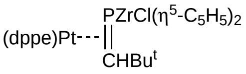
The phosphaalkyne complex [Pt(dppe)(η^2-Bu^{t}C≡P)] undergoes ready hydrozirconation with [ZrHCl(η^5-C_5H_5)$_2$] to give the metallaphosphaalkene complex [Pt(dppe){η^2-Bu^{t}CH=PZrCl(η^5-C_5H_5)$_2$}] which is a useful precursor for the synthesis of η^2-phosphaalkene complexes.

The recent report of the formation of a phosphaalkenyl ruthenium(II) complex by hydroruthenation of the phosphaalkyne Bu^{t}C≡P[1,2] prompts us to describe the first examples of the facile conversion of the η^2-ligated Bu^{t}C≡P by a synthetic route which offers considerable potential for the synthesis of a range of η^2-ligated Bu^{t}CH=PX derivatives.

Thus treatment of [Pt(dppe)(η^2-Bu^{t}C≡P)] **1**[3] with the Schwartz reagent, [ZrHCl(η^5-C_5H_5)$_2$], quantitatively affords the η^2-ligated metallaphosphaalkene complex [Pt(dppe){η^2-Bu^{t}CH=PZrCl(η^5-C_5H_5)$_2$}] **2** which occurs as a single isomer.†

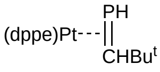


$$\mathrm{(dppe)Pt}{-}{-}{-}\begin{array}{l}\mathrm{PZrCl(\eta^5\text{-}C_5H_5)_2}\\ || \\ \mathrm{CHBu^t}\end{array}$$

2

It is interesting to note that the [ZrCl(η^5-C_5H_5)$_2$] fragment adds solely to the phosphorus atom which is at the positive end of the dipole in uncoordinated Bu^{t}C≡P. Hydrozirconation of phosphaalkenes R_2C=PR′ has been the subject of a very recent review,[3] where it was pointed out that the course of these reactions depends strongly on the nature of the substituents attached to phosphorus or carbon.

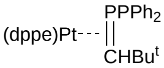
Treatment of **2** with H_2O at −60 °C in thf for 1 h readily affords the yellow η^2-phosphaalkene complex [Pt(dppe)(η^2-Bu^{t}CH=PH)] as a 3 : 1 mixture of *cis*- and *trans*-isomers **3a** and **3b**.‡ The uncoordinated phosphaalkene is unknown.



$$\mathrm{(dppe)Pt}{-}{-}{-}\begin{array}{l}\mathrm{PH}\\ || \\ \mathrm{CHBu^t}\end{array}$$

3

The synthetic potential of the intermediate **2** in the generation of other phosphaalkene complexes is illustrated by its reaction with Ph_2PCl leading to ready elimination of [$ZrCl_2$(η^5-C_5H_5)$_2$] and formation of the diphenylphosphino-phosphaalkene complex [Pt(dppe)(η^2-Bu^{t}CH=PPh$_2$)] **4** as a mixture of *cis*- and *trans*-isomers.§



$$\mathrm{(dppe)Pt}{-}{-}{-}\begin{array}{l}\mathrm{PPPh_2}\\ || \\ \mathrm{CHBu^t}\end{array}$$

4

The field of metallaphosphaalkene complexes has recently been reviewed by Weber[4] but the synthesis of **2** represents a new approach; furthermore as discussed elsewhere,[5] the reactivity of **2** towards halogeno-compounds offers considerable synthetic potential to generate other metallaphosphaalkene complexes by treatment with appropriate metal halides.

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Footnotes

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† NMR data for **2**: ^{31}P {^{1}H} (121.4 MHz, C_6D_6); δ 47.7 (dd, CH_2PPh_2, $^2J_{PP}$ 53.9, $^2J_{PP}$ 35.5, $^1J_{PPt}$ 3233.6 Hz), 52.7 (dd, PCBu^t, $^2J_{PP}$ 35.5, $^2J_{PP}$ 15.3, $^1J_{PPt}$ 282.2 Hz). ^{13}C{^{1}H} (75.4 MHz, C_6D_6); δ 30.5 (dd, CH_2, J_{CP} 33.0, J_{CP} 15.9, $^2J_{CPt}$ 16.0 Hz), 33.2 (dd, CH_2, J_{CP} 32.4, J_{CP} 14.7, $^2J_{CPt}$ 19.0 Hz), 33.8 (dd, CH_3, J_{CP} 6.1, J_{CP} 5.7, $^3J_{CPt}$ 32.9 Hz), 74.1 (ddd, CH, J_{CP} 83.6, J_{CP} 50.0, $^2J_{CP}$ 3.7, J_{CPt} 341.3 Hz), 109.6–109.7 (m, C_5H_5), 126.5 (s, Ph), 126.9 (dd, Ph, J_{CP} 8.4, J_{CP} 0.8 Hz), 127.3 (d, Ph, J_{CP} 6.0 Hz), 127.6 (d, Ph, J_{CP} 9.9 Hz), 128.1 (dd, Ph, J_{CP} 42.5, J_{CP} 1.1, J_{CPt} 54.7 Hz), 129.3 (dd, Ph, J_{CP} 38.8, J_{CP} 10.0 Hz), 130.9 (d, Ph, J_{CP} 11.0, J_{CPt} 11.2 Hz), 131.4 (d, Ph, J_{CP} 12.6, J_{CPt} 19.0 Hz), 133.1 (d, Ph, J_{CP} 12.6, J_{CPt} 21.8 Hz), 134.4 (dd, Ph, J_{CP} 13.7, J_{CP} 2.4, J_{CPt} 24.2 Hz); quaternary carbons unidentified. ^{1}H (300 MHz, C_6D_6); δ 1.28 (s, 9 H, CH_3), 2.00 (m, 4 H, CH_2), 4.19 (ddd, 1 H, CH, J_{HP} 7.5, J_{HP} 7.5, J_{HP} 3.8, $^2J_{HPt}$ 55.6 Hz), 5.80–6.01 (m, 10 H, C_5H_5), 6.80–8.21 (m, 20 H, Ph).

‡ *NMR data for* **3a** *and* **3b**: **3a** ^{31}P{^{1}H} (C_6D_6); δ 154.7 (dd, PH, J_{PP} 52.1, J_{PP} 11.0, J_{PPt} 286.7, J_{PH} 138.5 Hz), 51.8 (dd, PPh_2, J_{PP} 52.1, J_{PP} 45.8, J_{PPt} 3226.1 Hz), 56.9 (dd, PPh_2, J_{PP} 45.8, J_{PP} 11.0, J_{PPt} 2929.7 Hz). ^{13}C{^{1}H} (thf); δ 27.5 (dd, CH_2, J_{CP} 32.6, J_{CP} 14.1, $^2J_{CPt}$ 13.9 Hz), 31.5 (dd, CH_2, J_{CP} 33.6, J_{CP} 18.1, $^2J_{CPt}$ 20.5 Hz), 33.8 (dd, CH_3, J_{CP} 8.5, J_{CP} 5.8, $^3J_{CPt}$ 30.7 Hz), 69.6 (ddd, CH, J_{CP} 65.9, J_{CP} 52.0, J_{CP} 4.2 Hz), 126.5–134.3 (m, Ph); quaternary carbons unidentified. ^{1}H (C_6D_6); δ 1.41 (s, 9 H, CH_3), 2.00 (m, 4 H, CH_2), 2.70 (ddd, PH, $^1J_{HP}$ 150, $^3J_{HP}$ 12.5, $^3J_{HH}$ 9.6, $^2J_{HPt}$ 51.8 Hz), 4.38 (dddd, 1 H, CH, $^2J_{HP}$ 18.8, $^3J_{HH}$ 9.6, $^3J_{HP}$ 3.0, $^3J_{HP}$ 3.1, $^2J_{HPt}$ 58.0 Hz), 6.99–8.15 (m, 2 Ph). **3b** ^{31}P{^{1}H} for the minor product: δ −167.0 (dd, PH, $^3J_{PP}$ 49.9, J_{PP} 6.2, J_{PPt} 325.6, J_{PH} 145.8 Hz), 50.3 (dd, PPh_2, J_{PP} 49.9, J_{PP} 48.0, J_{PPt} 3237.7 Hz), 56.9 (dd, PPh_2, J_{PP} 48.0, J_{PP} 6.2, J_{PPt} 2929.7 Hz).

§ *NMR data for* **4**: ^{31}P{^{1}H} (CD_2Cl_2) δ −80.0 (ddd, PCH, $^1J_{PP}$ 213.2, $^2J_{PP}$ 54.0, $^2J_{PP}$ 9.6, $^1J_{PPt}$ 297.9 Hz), −12.7 (ddd, PPh_2, $^1J_{PP}$ 213.2, $^3J_{PP}$ 9.4, $^3J_{PP}$ 5.8, $^2J_{PPt}$ 38.0 Hz), 51.5 (ddd, CH_2PPh_2, $^2J_{PP}$ 54.0, $^2J_{PP}$ 39.8, $^3J_{PP}$ 5.8, $^1J_{PPt}$ 3198.0 Hz), 53.9 (ddd, CH_2PPh_2, $^2J_{PP}$ 39.8, $^2J_{PP}$ 9.6, $^3J_{PP}$ 5.4, $^1J_{PPt}$ 2951.5 Hz).

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