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A Phosphinine 2-Carboxaldehyde

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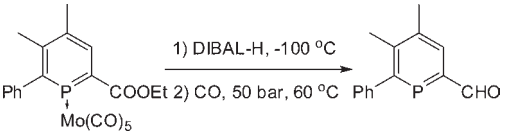
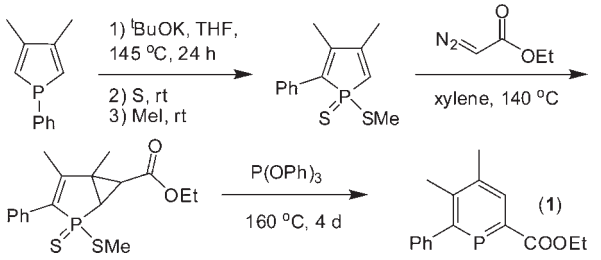
ABSTRACT



The first phosphinine 2-carboxaldehyde was synthesized as shown and transformed into an alkene via a Wittig reaction without destruction of the phosphinine ring.

Whereas some 6000 references are related to the 2-pyridinecarboxaldehyde according to *Chemical Abstracts*, to the best of our knowledge, nothing is known of the corresponding phosphorus derivative.[1] This gap represents a serious limitation for the incorporation of the phosphinine ring into more complex structures. We have been able to synthesize the first representative of this class of compounds as reported hereafter. We first synthesized the phosphinine ester **1** as shown in Scheme 1. This compound has already been obtained,[2] but this approach is different and relies on a previously described route.[3] The 6-phenyl substituent is used for imparting additional stability to the ring. The first step involves a [1,5] migration of

Scheme 1. Synthesis of Phosphinine Ester **1**



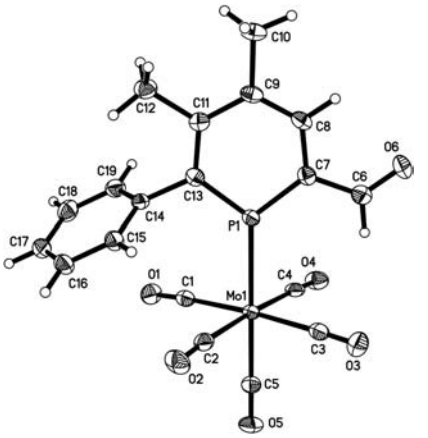


Figure 1. Molecular structure of **3**.

the phenyl group from P to Cα giving the 2-phenylphospholide as already described.[4] All of our attempts to reduce the ester group of **1** failed because most hydrides react both at the ester functionality and at the highly electrophilic P. It was thus necessary to protect P. We chose the complexation by molybdenum pentacarbonyl because the P−Mo bond is relatively weak and the steric protection of P is significant. A similar approach with $W(CO)_5$ as the complexing group was successfully used in lithiation experiments on 2-bromophosphinines.[5]

(1) A λ^5- phosphinine 4-carboxaldehyde has been described: Dimroth, K.; Kaletsch, A. *Chem. Ber.* **1987**, *120*, 1245.

(2) Chen, H.; Li, J.; Wang, H.; Liu, H.; Duan, Z.; Mathey, F. *Eur. J. Inorg. Chem.* **2011**, 1540.

(3) Holand, S.; Ricard, L.; Mathey, F. *J. Org. Chem.* **1991**, *56*, 4031.

(4) Holand, S.; Jeanjean, M.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 98.

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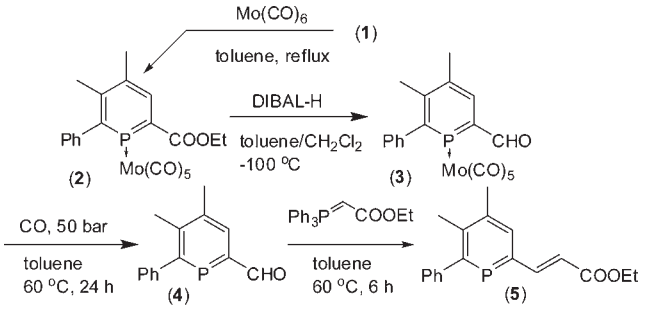
It proved possible to selectively reduce the ester group of the molybdenum complex **2** by diisobutylaluminum hydride at −100 °C to attain the corresponding aldehyde **3** in an acceptable yield (39%) (Scheme 2)

Scheme 2. Synthesis and Reactivity of the Phosphinine 2-Carboxaldehyde



Complex **3** was fully characterized by NMR spectroscopy[6] and X-ray crystal structure analysis (Figure 1). The formyl group appears at 10.29 ($^3J_{HP}$ = 4.6 Hz) on the proton spectrum and at 190.67 ppm ($^2J_{CP}$ = 27.1 Hz) on the carbon spectrum ($CDCl_3$). The formyl group is coplanar with the phosphinine ring whereas the phenyl ring is forced to rotate out of this plane by 79.7° due to the steric repulsion by the complexing group. The two P−C bonds are inequivalent at 1.719(3) [P−C(CHO)] and 1.729(3) Å. The P−Mo bond is relatively short at 2.4761(8) Å. All of these data are very close to those of the parent phosphinine $Mo(CO)_5$ complex.[7] The problem then was to remove the complexing group without altering the aldehyde functionality. The use of a chelating diphosphine proved to be uneffective. The use of carbon monoxide under pressure proved to be satisfactory. Since the reaction is an equilibrium, the displacement is not complete, but a conversion of 83% was achieved under 50 bar of CO at 60 °C and **4** was recovered in yields as high as 75% due to the very low rate of the reverse complexation reaction at room temperature. In **4**, both the carbonyl carbon and the phosphorus are highly electrophilic. DFT calculations on 2-formylphosphinine at the RB3YP/6-311+G(D,P) level show that the LUMO is highly localized at both P and the formyl carbon (Figure 2). The problem was then to check whether it is possible to perform a selective reaction at the aldehyde. The Wittig reaction of a stabilized ylid[8] with **4** afforded the corresponding alkene **5** in 91% yield. The aldehyde **4** is thus a good building block for the synthesis of complex structures containing phosphinines. Since these phosphinines have already found numerous uses in homogeneous catalysis[9] and that some applications in conjugated materials for optoelectronics are starting to appear,[10] it seems clear that this advance offers several interesting perspectives.

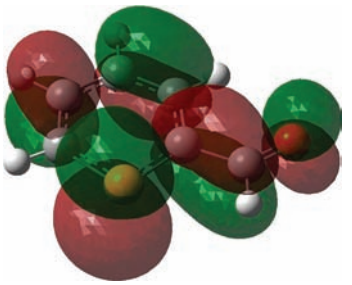


Figure 2. LUMO of 2-formylphosphinine (Kohn−Sham).

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Supporting Information Available. Experimental section and X-ray data for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) (**3**): ^{31}P NMR ($CDCl_3$): δ 212.5; ^{1}H NMR ($CDCl_3$): δ 2.16 (d, J_{HP} = 2.7 Hz, 3H, CH_3), 2.51 (d, J_{HP} = 5.5 Hz, 3H, CH_3), 7.21−7.51 (m, 5H, Ph), 8.28 (d, $^3J_{HP}$ = 14.6 Hz, 1H, =CH ring), 10.29 (d, $^3J_{HP}$ = 4.6 Hz, 1H, CHO); ^{13}C NMR ($CDCl_3$): δ 20.51 (d, J_{CP} = 4.5 Hz, CH_3), 23.25 (d, J_{CP} = 3.7 Hz, CH_3), 128.38 (d, J_{CP} = 2.4 Hz, =CH), 128.99 (d, J_{CP} = 1.1 Hz, =CH), 130.35 (d, J_{CP} = 8.2 Hz, =CH), 138.17 (d, J_{CP} = 21.5 Hz, =C), 140.12 (d, J_{CP} = 17.4 Hz, =C), 140.25 (d, $^2J_{CP}$ = 14.2 Hz, =CH), 150.30 (d, J_{CP} = 10.7 Hz, =C), 152.91 (d, J_{CP} = 6.2 Hz, =C), 167.84 (d, J_{CP} = 9.0 Hz, =C), 190.67 (d, $^2J_{CP}$ = 27.1 Hz, CHO), 203.21 (d, $^2J_{CP}$ = 11.0 Hz, *cis*-CO), 208.93 (d, $^2J_{CP}$ = 32.7 Hz, *trans*-CO); HRMS *m*/*z* 464.9440 (calcd for $C_{19}H_{12}MoO_6P$ 464.9426) (**4**): ^{31}P NMR ($CDCl_3$): δ 215.1; ^{1}H NMR ($CDCl_3$): δ 2.30 (d, J_{HP} = 1.9 Hz, 3H, CH_3), 2.53 (d, J_{HP} = 3.3 Hz, 3H, CH_3), 7.29−7.48 (m, 5H, Ph), 8.30 (d, $^3J_{HP}$ = 5.0 Hz, 1H, =CH ring), 10.14 (d, $^3J_{HP}$ = 2.6 Hz, 1H, CHO); ^{13}C NMR ($CDCl_3$): δ 19.49 (s, CH_3), 23.48 (d, J_{CP} = 2.1 Hz, CH_3), 127.48 (d, J_{CP} = 2.0 Hz, =CH), 128.29 (s, =CH), 129.40 (d, J_{CP} = 8.6 Hz, =CH), 136.45 (d, J_{CP} = 13.2 Hz, =CH), 141.19 (d, J_{CP} = 14.9 Hz, =C), 142.81 (d, $^2J_{CP}$ = 25.6 Hz, =C), 146.75 (d, J_{CP} = 10.6 Hz, =C), 160.37 (d, $^1J_{CP}$ = 46.9 Hz, =C—P), 171.69 (d, $^1J_{CP}$ = 48.4 Hz, =C—P), 193.11 (d, $^2J_{CP}$ = 44.9 Hz, CHO); HRMS *m*/*z* 227.0626 (calcd for $C_{14}H_{12}OP$ 227.0626). (**5**): ^{31}P NMR ($CDCl_3$): δ 195.2; ^{1}H NMR ($CDCl_3$): δ 1.35 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 2.23 (d, J_{HP} = 1.9 Hz, 3H, CH_3), 2.47 (d, J_{HP} = 3.4 Hz, 3H, CH_3), 4.27 (q, 2H, OCH_2), 6.67 (dd, $^3J_{HH}$ = 15.8 Hz, $^4J_{HP}$ = 3.2 Hz, 1H, =CH substituent), 7.28−7.45 (m, 5H, Ph), 7.81 (d, $^3J_{HP}$ = 5.4 Hz, 1H, =CH ring), 7.92 (dd, $^3J_{HH}$ = 15.8 Hz, $^3J_{HP}$ = 12.2 Hz, 1H, =CH substituent); ^{13}C NMR ($CDCl_3$): δ 14.33 (s, CH_3), 18.89 (s, CH_3), 23.52 (s, CH_3), 60.47 (s, OCH_2), 117.61(d, J_{CP} = 22.8 Hz, =CH), 127.19 (s, =CH), 128.29 (s, =CH), 129.40 (d, J_{CP} = 8.6 Hz, =CH), 136.08 (d, J_{CP} = 13.0 Hz, =CH), 140.71 (d, J_{CP} = 14.4 Hz, =C), 142.56 (d, J_{CP} = 12.2 Hz, =C), 142.95 (d, J_{CP} = 25.5 Hz, =C), 146.77 (d, $^2J_{CP}$ = 29.3 Hz, =CH substituent), 159.37 (d, $^1J_{CP}$ = 48.2 Hz, =C—P), 166.93 (s, CO), 171.45 (d, $^1J_{CP}$ = 48.2 Hz, =C—P), 193.11 (d, $^2J_{CP}$ = 44.9 Hz, CHO); HRMS *m*/*z* 297.1038 (calcd for $C_{18}H_{18}O_2P$ 297.1044).

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The authors declare no competing financial interest.