ORGANOMETALLICS
Communication

Organometallics **2010,** *29,* 5757–5758 5757
DOI: 10.1021/om100778f

Synthesis and Chemistry of 2-Phosphafurans

Matthew P. Duffy, Yuhan Lin, Feny Ho, and Francois Mathey*

Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371

Received August 11, 2010

2-Phosphafurans (1,2-oxaphospholes) are among the simplest and least well-known members of the broad family of aromatic heterophospholes.[1] In fact, only one compound of this class has ever been described in the literature, as an unstable product formed via a complex route that was characterized by NMR at low temperature.[2] We wish to present here the straightforward synthesis of a 2-phosphafuran as a reasonably stable species and to give some preliminary results concerning its chemistry. Our approach is based on the availability of the transient chlorophosphinidene complex [Cl−P−W(CO)$_5$].[3] This species, as generated from a chlorophosphole complex and dimethyl acetylenedicarboxylate, reacts at 80 °C with benzylideneacetophenone in toluene to give the corresponding [1 + 4] cycloadduct **1** as a mixture of two isomers. This, in turn, reacts with *N*-methylimidazole between −20 °C and room temperature to give a red solution of the very reactive phosphafuran complex **2** (Scheme 1). This species is characterized by its ^{31}P resonance at low field: $\delta(^{31}P)$ 223.7 ($^1J_{PW}$ = 296 Hz). It can be kept without noticeable decomposition for 1 h at room temperature and for 2 weeks at −25 °C. Its identity was definitively established by a series of trapping reactions (Scheme 2). The X-ray crystal structures of **3** and **4** are shown in Figures 1 and 2.

Selected NMR data for **3**−**5** are given in ref 4. Full experimental data are available in the Supporting Information.

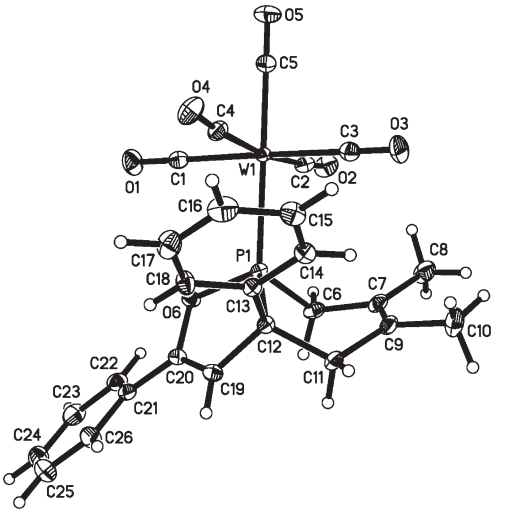
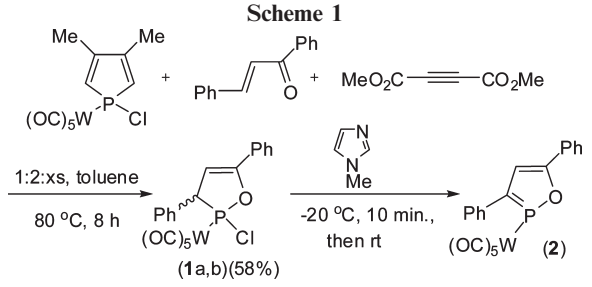
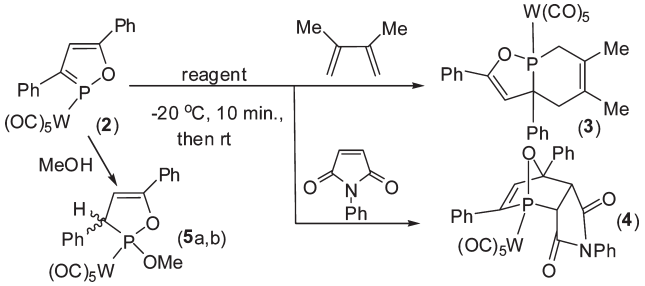


Figure 1. Molecular structure of **3**.

Scheme 1



Scheme 2



2-Phosphafurans are computed to be reasonably aromatic with an ASE (aromatic stabilization energy) of ca. 13.2 kcal mol^{-1}.[5] Thus, this explains why it is possible to synthesize these species by dehydrochlorination of **1** with a mild base. On the

*To whom correspondence should be addressed. E-mail: fmathey@ntu.edu.sg.

(1) Review: Schmidpeter, A., Heterophospholes. In *Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Mathey, F., Ed.; Elsevier: Oxford, U.K., 2001; pp 363−461.

(2) Mack, A.; Bergsträβer, U.; Reiss, G. J.; Regitz, M. *Eur. J. Org. Chem.* **1999**, 587.

(3) Duffy, M. P.; Mathey, F. *J. Am. Chem. Soc.* **2009**, *131*, 7534.

(4) Data for **3**: ^{31}P NMR (CD_2Cl_2) δ 159.6, $^1J_{PW}$ = 281 Hz; ^{1}H NMR (CD_2Cl_2) δ 1.82 (br s, Me), 1.86 (s, Me), 5.63 (d, J_{HP} = 17.8 Hz, =CH); ^{13}C NMR (CD_2Cl_2) δ 20.86 (d, J_{CP} = 2.5 Hz, CH_3), 21.19 (d, J_{CP} = 2.5 Hz, CH_3), 43.37 (s, CH_2), 45.12 (d, J_{CP} = 9.8 Hz, CH_2), 61.09 (d, J_{CP} = 17.1 Hz, P−C−Ph), 106.56 (d, J_{CP} = 3.7 Hz, =CH), 157.36 (d, J_{CP} = 6.1 Hz, =C(Ph)O), 195.95 (d, J_{CP} = 7.4 Hz, cis CO), 199.75 (d, J_{CP} = 29.5 Hz, trans CO). Data for **4**: ^{31}P NMR (CD_2Cl_2) δ 117.8, $^1J_{PW}$ = 308 Hz; ^{1}H NMR (CD_2Cl_2): δ 4.05 (dd, J_{HH} = 7.7 Hz, J_{HP} = 2.7 Hz, CH−CO), 4.38 (dd, J_{HH} = 7.7 Hz, J_{HP} = 3.2 Hz, CH−CO); ^{13}C NMR (CD_2Cl_2) δ 51.93 (s, CH(CO)), 53.84 (d, J_{CP} = 7.3 Hz, P−CH(CO)), 98.23 (d, J_{CP} = 3.7 Hz, Ph−CO), 142.68 (s, =CH), 171.51 (s, NCO), 172.97 (s, NCO), 194.35 (d, J_{CP} = 8.5 Hz, cis CO), 197.29 (d, J_{CP} = 34.1 Hz, trans CO). Data for **5a**: ^{31}P NMR (CD_2Cl_2) δ 171.9, $^1J_{PW}$ = 331 Hz; ^{1}H NMR (CD_2Cl_2) δ 3.42 (d, J_{HP} = 12.4 Hz, OMe), 4.86 (dd, J_{HH} = 2.3 Hz, J_{HP} = 14.6 Hz, CH−P), 6.01 (dd, J_{HH} = 2.3 Hz, J_{HP} = 18.3 Hz, =CH); ^{13}C NMR (CD_2Cl_2) δ 55.45 (d, J_{CP} = 3.9 Hz, OMe), 62.91 (d, J_{CP} = 18.2 Hz, CH−P), 103.61 (s, =CH), 157.08 (d, J_{CP} = 6.7 Hz, PhC−O), 195.82 (d, J_{CP} = 8.7 Hz, cis CO), 198.55 (d, J_{CP} = 34.6 Hz, trans CO). Data for **5b** ^{31}P NMR (CD_2Cl_2) δ 185.6, $^1J_{PW}$ = 336 Hz; ^{1}H NMR (CD_2Cl_2) δ 3.75 (d, J_{HP} = 11.4 Hz, OMe), 4.45 (dd, J_{HH} = 3.7 Hz, J_{HP} = 9.6 Hz, CH−P), 6.04 (dd, J_{HH} = 3.7 Hz, J_{HP} = 19.3 Hz, =CH); ^{13}C NMR (CD_2Cl_2) δ 55.20 (d, J_{CP} = 8.7 Hz, OMe), 59.68 (d, J_{CP} = 13.5 Hz, CH−P), 103.99 (s, =CH), 157.80 (d, J_{CP} = 6.7 Hz, PhC−O), 195.32 (d, J_{CP} = 9.6 Hz, cis CO), 198.68 (d, J_{CP} = 35.5 Hz, trans CO).

(5) Cyrañski, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. v. R. *J. Org. Chem.* **2002**, *67*, 1333.

Published on Web 10/14/2010

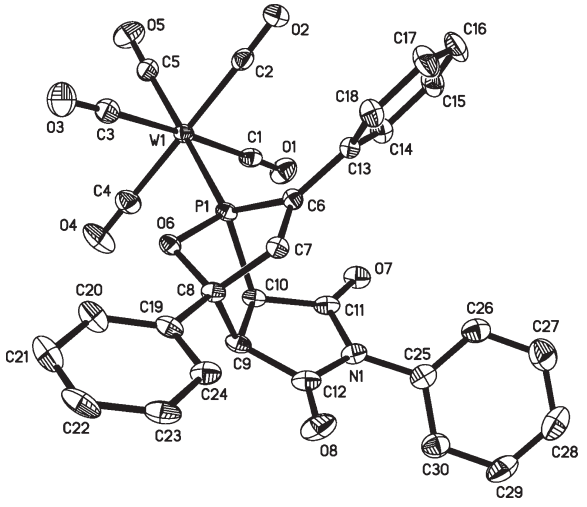
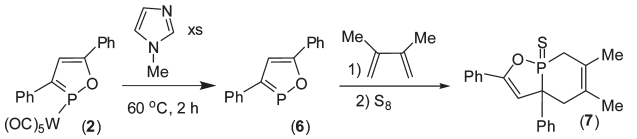


Figure 2. Molecular structure of **4**.

other hand, this aromaticity is not high enough to suppress the reactivity of the P=C double bond. Indeed, it is striking to see that **2** behaves as a nonaromatic 2*H*-phosphole in terms of reactivity.[6] Of course, these observations concern the complexed phosphafurans and it must be recalled that P-complexation is known to significantly reduce the aromaticity of related species such as phosphinines.[7] Thus, the free species might have a different reactivity. We discovered that it suffices to heat **2** at 60 °C for 2 h in the presence of an excess of *N*-methylimidazole to get the free phosphafuran **6**, which displays a ^{31}P resonance at 285.5 ppm in toluene with no P−W coupling (Scheme 3). This reaction suggests that the phosphafuran is a poor P-donor.

(6) Mathey, F. *Acc. Chem. Res.* **2004**, *37*, 954.
(7) Mathey, F.; Alcaraz, J.-M. *Tetrahedron Lett.* **1984**, *25*, 207.

Scheme 3



Phosphafuran **6** can be kept at room temperature for 10 days without noticeable decomposition. It reacts at room temperature with an excess of 2,3-dimethylbutadiene to give the [2 + 4] cycloadduct (δ(^{31}P) 144 ppm in toluene) whose sulfurization gives **7**, which was fully characterized (including a X-ray crystal structure analysis).[8] Clearly, the complexation by tungsten provides some kinetic stability to the 2-phosphafuran ring by steric protection as it does for 2*H*-phospholes[9] but does not fundamentally alter the reactivity of the ring.

Acknowledgment. We thank Nanyang Technological University and the Singapore Ministry of Education Research Fund Tier 2 (MoE 2009-T2-2-065) for financial support of this work and Dr. Li Yongxin (NTU) for the X-ray crystal structure analyses.

Supporting Information Available: Text and figures giving full experimental details and characterization data and CIF files giving X-ray data for **3**, **4**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

(8) Data for **7**: ^{31}P NMR (CD_2Cl_2) δ 123.5; ^{1}H NMR (CD_2Cl_2) δ 1.74 (d, J_{HP} = 5.0 Hz, Me), 1.79 (s, Me), 5.74 (d, J_{HP} = 24.7 Hz, =CH); ^{13}C NMR (CD_2Cl_2) δ 20.67 (d, J_{CP} = 6.7 Hz, CH_3), 21.29 (d, J_{CP} = 2.9 Hz, CH_3), 41.66 (d, J_{CP} = 56.6 Hz, CH_2), 42.53 (s, CH_2), 55.01 (d, J_{CP} = 59.4 Hz, P−C−Ph), 107.19 (d, J_{CP} = 5.8 Hz, =CH), 156.97 (s, =C(Ph)O). The structure has been checked by X-ray analysis (see the Supporting Information).
(9) Holand, S.; Charrier, C.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1984**, *106*, 826.