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Phosphepines: Convenient Access to Phosphinidene Complexes

Mark L. G. Borst, Rosa E. Bulo, Christiaan W. Winkel, Danièle J. Gibney, Andreas W. Ehlers, Marius Schakel, Martin Lutz, Anthony L. Spek, and Koop Lammertsma*

Department of Organic Chemistry, Faculty of Sciences, Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands, and Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received February 8, 2005; E-mail: k.lammertsma@few.vu.nl

The cycloheptatriene−norcaradiene (CHT−NCD) equilibrium exemplifies a 6-el electrocyclic reaction with a modest barrier separating the valence tautomers **1C** and **2C**.[1] Less is known about the heterocyclic analogues (X = O, S, NR, PR) (Scheme 1). For those with an oxygen atom, benzene oxide **2O** is the more stable form, but entropy factors shift the equilibrium toward oxepin **1O** at room temperature.[2] Only the monocyclic form is observed for thiepins[3] **1S** and 1*H*-azepines[4] **1N**, and both require bulky groups and/or extended conjugation for stability. Of the phosphorus analogue, phosphepine **1P**, only its oxide[5] and 2,7-dialkyl-substituted[6] and annelated[7,8] derivatives are known, but without structural details. Here we describe a computational analysis of the **1P**−**2P** equilibrium and present new stable phosphepine derivatives and a novel application.

Phosphepines equilibrate with phosphanorcaradienes (benzene phosphines) such as CHT with NCD. DFT calculations for the parent system give an energetic preference for NCD **2P** over CHT **1P** (ΔE_{2-1} −4.2 kcal/mol, Table 1) with a modest **1P** → **2P** barrier (10.6 kcal/mol), reflecting the same behavior as the thia analogues (ΔE_{2-1} −7.8 (**S**) kcal/mol). A 1,5-sigmatropic shift relates NCD **2P** with the 15.5 kcal/mol less stable 7-phosphanorbornadiene **3P**, neither of which is known experimentally, except for a strained derivative of **3P**,[10] presumably due to release of the phosphorus group to give pentamers, $(PR)_5$.

Transition metal coordination at phosphorus stabilizes **1P** over **2P** because the distal C−C bond is weakened by σ,π-interactions (Scheme 2), reversing the order for $W(CO)_5$ (ΔE_{2-1} 1.5 kcal/mol). Due to extended conjugation, benzannelation has an even stronger influence, reversing the CHT−NCD equilibrium in favor of **1P** by 11.0 kcal/mol. These cumulative electronic effects give a 16.8 kcal/mol energetic preference of benzophosphepine $W(CO)_5$ complex over its valence isomer **2P** with a 24.7 kcal/mol barrier for electrocyclization.[11]

On the basis of these calculations benzophosphepine complexes **7** are expected to be stable at room temperature. Indeed, **7** could be synthesized from the complexed phosphine and 1,2-diethynylbenzene (**5**) by a modified Märkl's procedure[7] (Scheme 3). Dialkyne **5** was obtained in 91% yield from commercially available *o*-phthaldialdehyde (**4**) by a one-carbon homologation−oxidation sequence. The base-promoted double hydrophosphination of **5** with PH_2Ph−$W(CO)_5$ (**6a**) gave 3*H*-3-benzophosphepine−$W(CO)_5$ **7a** in 74% yield as yellow crystals. $W(CO)_5$ coordination causes shielding of the ^{31}P NMR resonance (δ −15 vs −33 ppm), shielding of the C1,C5 ^{13}C NMR resonances (by 6 ppm), and reduces the $^2J_{CP}$ coupling constants (1.6 vs 21.1 Hz).[7] Distinctive are the coupling constants for the olefinic protons with a sizable $^3J_{HH}$ (12.4 Hz) and with a $^3J_{HP}$ (33.4 Hz) being much larger than the $^2J_{HP}$ (21.3 Hz).

The crystal structure (C_s-symmetry) shows alternating C=C bonds (no homoaromaticity) for the boat-shaped phosphepine ring (Figure 1) that has the phosphorus atom shifted out of the hydrocarbon plane by 67.20(13)°. The orthogonal phenyl group is on the mirror plane and bisects the C1−P−C1i angle. The P−C1-(C1i) bonds are very short (1.814(3) Å).

Because the phosphorus group is introduced in the final step, the synthesis allows for versatility in substituents and metal complexes. Illustrative is the condensation of **5** with $PhPH_2$−$Mn(CO)_2Cp$ that gives manganese-complexed phosphepine **7b** (35%). The molecule in the crystal shows again C_s-symmetry, but has a flatter phosphepine ring with a dihedral angle of 34.49(8)° between the C1−P1−C1i and hydrocarbon planes (Figure 2). This is best explained by a steric effect of the Cp, hanging over the phosphepine ring, in which C=C bond alternation is again evident. The orthogonal phenyl group bisects the C1−P−C1i angle, and the Mn−P bond has a normal distance of 2.1954(5) Å.[12] The more shielded ^{31}P NMR resonance at +64 ppm points to less electrophilic character for the phosphorus group than in **7a**; the ^{1}H and ^{13}C NMR parameters are similar, including the $^2J_{HP}$ (20.7 Hz) and $^3J_{HP}$ (32.1 Hz) coupling constants.

Scheme 1. Valence Isomers of Cyclohexatriene

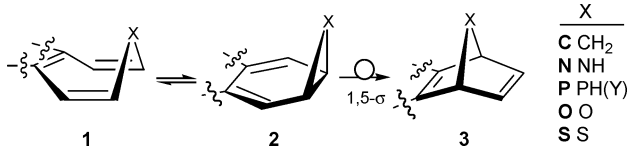
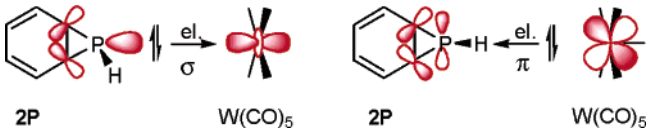


Table 1. B86-P88/*TZP* Relative Energies (in kcal/mol) for **1P**, **2P**, **3P**, and Their $W(CO)_5$ and Benzannelated Derivatives[a]

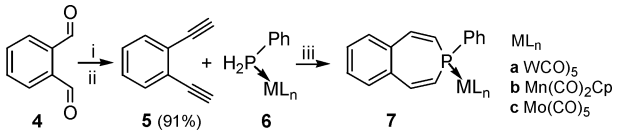
R(Y)	1P	2P	3P
H	0.0	−4.2	11.3
H($W(CO)_5$)	0.0	1.5	7.8
H + benzo[b]	0.0	11.0	4.2
H($W(CO)_5$) + benzo-[b]	0.0	16.8	1.3

[a] The lone pair and $W(CO)_5$ group occupy the axial (**1**) or *syn* (**2**, **3**) position.[9] [b] Benzannelation as indicated in Scheme 1.

Scheme 2. HOMO−LUMO Interactions between **2P** and $W(CO)_5$



Scheme 3. Synthesis of Benzophosphine Complex **7**[a]



[a] Reaction conditions: i) CBr_4, PPh_3; ii) LDA; iii) KOH, THF, at 25 °C.

10.1021/ja050817y CCC: $30.25

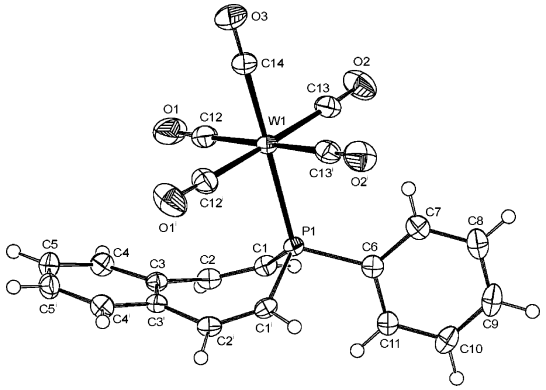


Figure 1. ORTEP diagram of 3-phenyl-benzophosphepine-$W(CO)_5$.

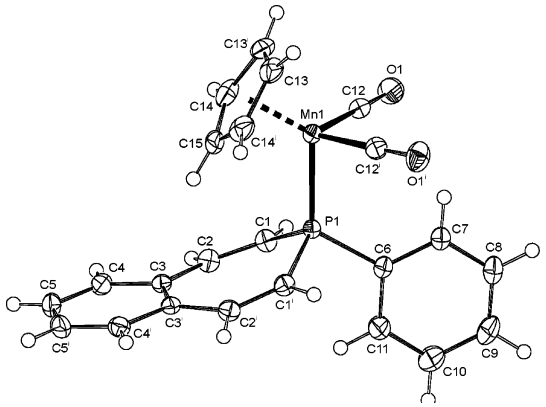
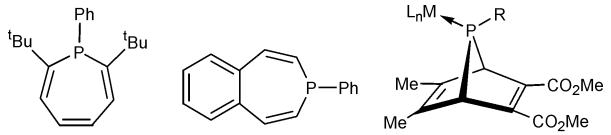


Figure 2. ORTEP diagram of 3-phenyl-benzophosphepine-$Mn(CO)_2Cp$.

Chart 1 Stabilized Phosphepines and Phosphinidene Precursor 10.

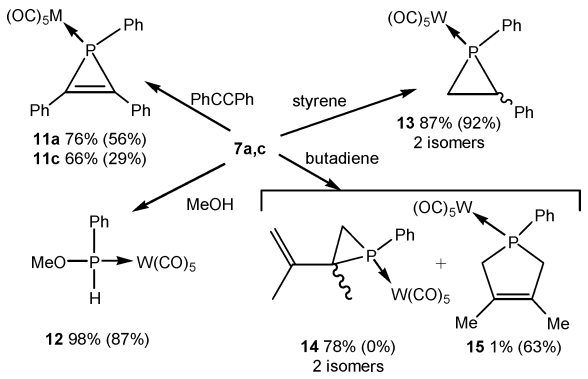


8 **9** **10**

Phosphepines **8** and **9** are known to decompose readily to the aromatic hydrocarbon and $(RP)_5$, presumably by expelling [RP] from the NCD intermediates[7,8] (Chart 1). Interestingly, in the case of complex **7** this would result in the expulsion of a transition metal-stabilized phosphinidene [R−P═ML_n]. Extremely few synthetic routes enable access to such phosphinidene complexes,[13] especially those with electrophilic properties. In fact, cheletropic elimination from complexed 7-phosphanorbornadienes **10** is the only general route to generate [R−P═$M(CO)_5$],[13a] but its synthesis is longer, less flexible to metal variation, and requires, for milder conditions, a catalyst that can alter the course of the reaction.[14] Nevertheless, in situ trapping of the transient species has led to a plethora of useful organophosphorus compounds.[15]

Benzophosphepine **7a** reacts with the test set of molecules, first used for the reaction with **10**, to give at 75−80 °C the same addition/insertion products,[13a,16,17] but in better yields (Scheme 4) and requiring only removal of solvent and naphthalene (by sublimation). The 30 °C advantage in reaction temperature is evident from the formation of vinylphosphirane **14** from 2,3-dimethyl-butadiene, whereas phospholene **15** is the main product with **10a**[13] due to a 1,3-sigmatropic shift that occurs above 80 °C.[16] Reaction of molybdenum complex **7c**, obtained from **5** and $PhPH_2$−$Mo(CO)_5$ (67%), with tolan gives phosphirene **11c** in 66% yield versus 29% with **10c**.[17] Access to unprecedented far less electrophilic

Scheme 4. Phosphinidene Reactions of **7** (and **10**)



phosphinidenes is illustrated by the reaction of manganese complex **7b** with phenylacetylene that results in a $Mn(CO)_2Cp$ complexed phosphirene (81%, ^{31}P NMR δ −59.0), suggesting the intermediacy of the novel phosphinidene [R−P═$Mn(CO)_2Cp$].

In conclusion, we presented a very short synthesis to diverse stable 3*H*-3-benzophosphepine complexes that are excellent precursors to electrophilic phosphinidene complexes, requiring very mild reaction conditions and an extremely simple workup.

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Supporting Information Available: Experimental section including NMR spectra and computational data. X-ray crystallographic data for **7a**, **b** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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