Inorganic Chemistry
Communication

Inorg. Chem. **2009**, *48*, 8063–8065 **8063**
DOI: 10.1021/ic901072z

Modeling the Direct Activation of Dihydrogen by a P_2C_2 Cyclic Biradical: Formation of a Cyclic Bis(P−H λ^5-phosphorane)

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Received June 4, 2009

The synthesis of a remarkable cyclic bis(P−H λ^5-phosphorane) is reported. A stable phosphorus-heterocyclic biradical, 1,3-diphosphacyclobutane-2,4-diyl, sequentially accepts negatively and positively charged hydrogen atoms to afford 2,4-diphospha-1,3-cyclobutadiene with a diylidic structure containing two P−H bonds.

The family of 1,3-diphosphacyclobutane-2,4-diyls is an intriguing class of compounds of much popular interest because of their singlet organic biradical character.[1] Niecke and co-workers reported a room-temperature stable compound containing the 1,3-diphosphacyclobutane-2,4-diyl skeleton[2a] and have provided much new fundamental information on these uniquely stable biradicals.[2b−2d] Recently, we developed an alternative and versatile synthetic method for air-stable 1,3-diphosphacyclobutane-2,4-diyls by utilizing a bulky phosphaalkyne (−C≡P).[3a] This newest class of stable biradicals has shown that 1,3-diphosphacyclobutane-2,4-diyls have intriguing physical and chemical properties of 1,3-diphosphacyclobutane-2,4-diyl.[3b,3c] Furthermore, in addition to the C_2P_2 biradicals, several related cyclic biradicals have been investigated.[4−6]

1,3-Diphosphacyclobutane-2,4-diyls display several transformations unique to the four-membered heterocyclic biradical upon thermolysis[2a,2b,3a,3b,4b] and photolysis.[2c,4c] In addition to light and heat, chemical stimuli were also employed to explore the unusual reactivity of the phosphorus-heterocyclic organic biradicals. Chalcogenation afforded the corresponding phosphine chalcogenide accompanying a valence transformation at phosphorus,[3b] whereas protonation on a carbon atom afforded a phosphorus-heterocyclic cation.[2d] These chemical transformations represent not only some of the highly varied chemoselectivity observed for 1,3-diphosphacyclobutane-2,4-diyls but also considerable utility of the heterocyclic biradical moiety in terms of molecular trapping.[4d]

This paper reports the reaction of a stable 1,3-diphosphacyclobutane-2,4-diyl with a hydride reagent followed by subsequent protonation. In contrast to the previous finding on the protonation of 1,3-diphosphacyclobutane-2,4-diyl,[2d] a hydride is transferred to one of the phosphorus atoms to afford a cyclic anion bearing a P−H bond. The subsequent protonation of the cyclic anion transfers a proton to the remaining phosphorus to form a di-λ^5-phosphacyclobutadiene containing two P−H bonds. The properties of this novel four-membered phosphacycle were investigated by X-ray structure determination and computational modeling.

A tetrahydrofuran solution of the biradical **1**[3a] reacts with a solution of $LiAlH_4$ to produce an intermediate change in color from blue to red (Scheme 1). As a result of the regioselective hydride attack on the less-hindered phosphorus atom, an anionic species **2** can be identified

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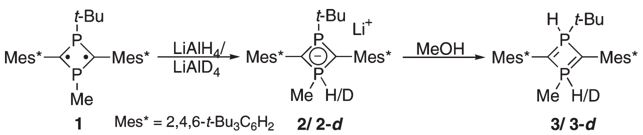
Scheme 1. Stepwise Addition of Hydride and Proton to **1**, Leading to the Formation of **3** via **2**



from the ^{31}P NMR spectrum of the reaction mixture [δ −37.1 (ddq, $^2J_{PP}$ = 49.3 Hz, $^1J_{PH}$ = 322.1 Hz, $^2J_{PH}$ = 9.9 Hz, MePH), 143.8 (d, $^2J_{PP}$ = 49.3 Hz, P-*t*-Bu)]. Regioselective attack on the less-congested MeP center corresponds to addition to the lowest unoccupied molecular orbital of the singlet 1,3-diphosphacyclobutane-2,4-diyls.[2a] The lower field ^{31}P NMR chemical shift in **2** is consistent with a phosphorus center that is similar to the λ^5-phosphorus centers reported for four-membered dimethylenephosphoranes.[3b] The higher-field ^{31}P NMR resonance in **2** exhibits a large $^1J_{PH}$ constant, confirming the P−H moiety. The $^2J_{PP}$ constant of **2** (49.3 Hz) is considerably smaller than that observed for **1** (362.8 Hz)[3a] and is comparable to that of a 1,3-diphosphacyclobutenide anion (86.8 Hz),[7] which is a precursor of **1**. The small J_{PP} constant of **2** relative to **1** might be due to perturbation of hydride on the lone pair of phosphorus. Analogously, from **1** and LiAlD$_4$, the corresponding anion **2-*d*** [δ_P −37.4 (dt, $^2J_{PP}$ = 50.3 Hz, $^1J_{PD}$ = 50.3 Hz, MePD), 144.1 (d, $^2J_{PP}$ = 50.3 Hz, P-*t*-Bu)] is generated (see the Supporting Information).

When air-sensitive **2** was mixed with methanol, regioselective protonation on the remaining trivalent phosphorus took place to afford a novel phosphorus-heterocyclic compound bearing two P−H bonds (**3**) in moderate yield as an air-stable yellow-green solid [mp 130−132 °C (dec), 73% yield]. In the ^{31}P NMR spectrum, both of the phosphorus atoms show large $^1J_{PH}$ constants characteristic of P−H bonds [δ 3.3 ($^1J_{PH}$ = 405.0 Hz), 47.1 ($^1J_{PH}$ = 405.0 Hz)]. The $^2J_{PP}$ coupling in **3** ($^2J_{PP}$ = 92.0 Hz) is smaller than that observed for **1** (362.8 Hz),[3a] indicating the effect of the higher valency of phosphorus.[8] In ^{1}H NMR, the PH protons are observed at low field (δ 7.45 and 8.40), which are similar to those in phosphorus ylides bearing P−H bonds.[9] Also, the P−H groups of **3** were characterized by the IR absorption data [2286 cm^{-1} (KBr)]. In the ^{13}C NMR spectrum, the sp^2 carbon in the four-membered ring has a higher field chemical shift (δ 12.6) compared to **1** (δ 111.3),[3a] consistent with a contribution from the ylidic $\equiv$P$^+$−C$^-$< structure.[10,11] The UV spectrum of **3** [λ_{max} (CH$_2$Cl$_2$) 400 nm (log ε 4.2)] is obviously different from that of **1** because of the absence of the biradical moiety. In the case of **2-*d***, protonation was successful and also afforded the corresponding HD adduct, **3-*d***. Furthermore, **3** is oxidized by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone to re-form **1**.

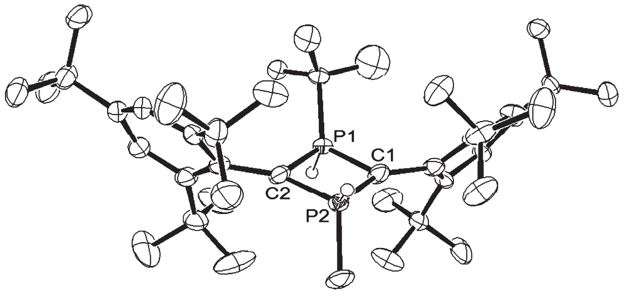


Figure 1. ORTEP drawing for molecular structure **3** (major form) with 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): P1−C1 1.697(5), P1−C2 1.720(5), P1−C$_{t\text{-Bu}}$ 1.854(4), P2−C1 1.755(4), P2−C2 1.773(5), P2−C$_{Me}$ 1.828(5), C1−C$_{Mes*}$ 1.484(6), C2−C$_{Mes*}$ 1.496(6), C1−P1−C2 93.3(2), C1−P2−C2 89.6(2), P1−C1−P2 89.2(2), P1−C2−P2 87.8(2).

Compound **3** was subjected to single-crystal X-ray diffraction. Unfortunately, in spite of many attempts (numerous crystals were investigated along with multiple solvent systems and crystallization conditions), it was not possible to find a refined model for the experimental X-ray diffraction data that was free from disorder problems. Nonetheless, the central core of the molecule did refine fairly well and provided reasonable geometric parameters. Figure 1 shows one of the solved structures in which the hydrogen atoms were assigned based on the diffraction data.[12] The four-membered ring of the major form is almost planar (dihedral angle of P1−C1−P2−C2: 3°),[13] and the bulky aryl groups (Mes* groups) are not coplanar to avoid steric congestion (tilting angle: 60°). The diffraction data refined to show rotational disorder of the *tert*-butyl attached to phosphorus and the phosphorus centers were disordered (80/20) over ring flip-like positions, with additional disorder in methylene chloride as the solvent.

The carbon atoms in the four-membered ring (C1 and C2) appear essentially planar [Σ(angles) = 360 and 359°], and the sums of the C−P−C angles (P1, 336°; P2, 323°) reveal pyramidal phosphorus centers comparable to those of **1** (341 and 319°).[3a] Steric hindrance around the carbon atoms in the four-membered ring (C1 and C2) causes distortion of the Mes* moiety (dihedral angle of C1−C$_{ipso}$−C$_{ortho}$−C$_{meta}$: 150°).[14] Steric congestion is also relieved by the trans orientation of the *tert*-butyl and methyl groups relative to the four-membered ring. The (Me)P−C distances in the ring are longer than the (*t*-Bu)P−C distances, in contrast to expectations based on the steric bulk and electron-donating property of the attached substituents (Me *vs* *t*-Bu).

To investigate the properties of **3** and related molecules, we performed density functional theory (DFT) calculations for

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(12) Crystallographic parameters of **3**: space group *C*2/*c* (No. 15), a = 28.5576(7) Å, b = 8.8932(2) Å, c = 34.006(1) Å, β = 96.0431(6)°, V = 8588.4(4) Å^3, Z = 8. Data: 9217 (R_{int} = 0.066). Variables: 450. R_1 = 0.125, R_W = 0.262. The positions of the hydrogen atom on phosphorus were refined. CCDC 670462 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(13) We considered the possibility of the presence of a minor constituent with a slightly puckered four-membered ring that could account for the structural disorder problems. However, time and conditions could be expected to lead to changing ratios of C,H- and P,H-reduced products that were not observed experimentally. NMR spectroscopic data also consistently indicated only a single product. Hence, we are confident that only the PHPH product is present in as a single conformation.

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4 (68.8) 5 (0.0) 5' (1.4) 6 (39.2)

Figure 2. Calculated relative energies (in kcal mol^{-1}) for optimized structures **4**−**6** at the B3LYP/DGDZVP2 level of theory.

model compounds **4**−**6**, where *t*-Bu and Mes* groups on the four-membered ring are replaced by Me, at the B3LYP/DGDZVP2 level.[15−17] As displayed in Figure 2, **4** (the model for **3**) is predicted to be less stable than **5** at this level of theory. Compound **5′** is one of the geometrical isomers of **5**, and its stability is slightly inferior to that of **5**. Compound **6** (a possible intermediate in the double tautomerization process) shows stability between those of **4** and **5**. Theoretical models suggest that C,C-reduced product **5** is the most stable structure on the energy surface connecting the regioisomeric P,P-, P,C-, and C,C-reduced forms (including all their geometric isomers; see the Supporting Information) of the biradical **1** after the addition of 1 equiv of dihydrogen. However, experimental and/or theoretical data remain to be obtained to determine the magnitudes (heights) of the barriers separating the various geometric and regio isomers. Additionally, steric congestion of **3** is expected to play an important role in stabilizing the four-membered ring structure containing two P−H bonds of pentavalent phosphorus atoms. The regioselective attack of hydride on the less hindered phosphorus atom is explicable by the steric encumbrance around the phosphorus atoms.

Additional DFT calculations [B3LYP/DGDZVP2] for a four-membered cyclic anion [HMeP(CMe)$_2$PMe]$^-$ as a model structure of **2** indicated inferior stability to its isomeric C-reduced form (see the Supporting Information), consistent with the predicted relative energies of **5** and **6** (*vide supra*). Nevertheless, no isomeric form of **3** (C,C- or C,P-reduced) through [1,2]-hydrogen migration was observed experimentally, suggesting either the presence of high barriers separating these structures or steric encumbrance associated with the C-reduced forms (*vide supra*). The regioselectivity in the protonation of **2** is likely to be also affected by the steric encumbrance of the Mes* group preventing protonation at the carbon center.

Optimization of the "near-experimental" molecules bearing *t*-Bu and 2,6-*t*-Bu$_2$C$_6$H$_3$ substituents at the DFT level also predicts the C,C-reduced isomer to be the most stable isomer by 26 kcal mol^{-1} [MP2 single-point calculations at the DFT geometries give 29 kcal mol^{-1}] over the observed P,P-reduced isomer (Figure 3).[18] The choice of substituents on the actual (experimental) system is likely to be the determining factor for the regiochemistry of reduction and protonation (*i.e.*, P,P reduction *vs* C,P and/or C,C reduction).

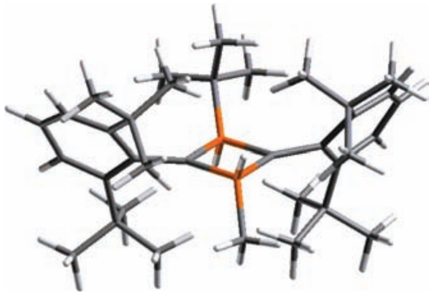

Figure 3. DFT-optimized structure of the P,P-reduced isomer of the "near-experimental" system at the B3LYP/DGDZVP2 level of theory.

The results reported here describe that a stable phosphorus-heterocyclic biradical sequentially accepts negatively and positively charged hydrogens (hydride and then proton), while retaining the basic four-membered quasi-planar structure resulting in the formation of a remarkable bis(P−H λ^5-phosphorane). We have also recently made the preliminary observation of the uncatalyzed addition of dihydrogen directly to **1** at high pressures of dihydrogen. At low pressures (with 1 equiv of dihydrogen), this reaction appears sluggish, but studies in our laboratory are ongoing in relation to a hydrogen storage venture.[19,20]

Acknowledgment. This work was supported, in part, by the Program Research, Center for Interdisciplinary Research and the Support for Young Researchers, Graduate School of Science, Tohoku University, Casio Science Promotion Foundation, the NSF (Grants CHE-0413521 and CHE-0342921), the U.S. DOE (Grant DE-FG02-86ER13465), and the DOE, Office of Energy Efficiency and Renewable Energy under the Hydrogen Storage Grand Challenge (Grant DE-PS36-03GO93013). We acknowledge Prof. David A. Dixon and Dr. Shenggang Li, The University of Alabama, for their helpful comments and MP2 single-point calculations, and Prof. Hidehiro Uekusa and Kotaro Fujii, Tokyo Institute of Technology, for their valuable comments on X-ray analysis.

Supporting Information Available: Experimental procedures, spectroscopic data, and structural parameters for compound **3**, computational results, and the complete ref 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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