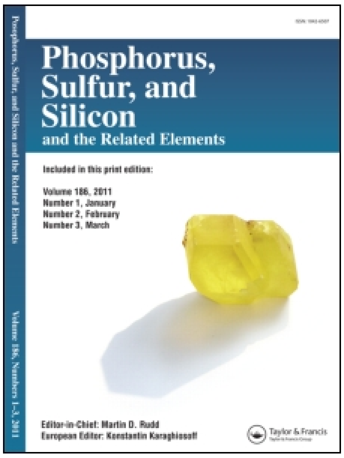

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Intramolecular Reactivity of π-Coordinated P-Heterocycles: How to Form Five-Membered Rings out of Phosphaalkynes

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INTRAMOLECULAR REACTIVITY OF π-COORDINATED P-HETEROCYCLES: HOW TO FORM FIVE-MEMBERED RINGS OUT OF PHOSPHAALKYNES

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Experimental and theoretical evidence is presented for a novel metal-dependent intramolecular reactivity of π-bonded, unsaturated P-heterocycles like 1,3-diphosphete and 1,3,5-triphosphinine. The nucleophilic attack of a P lone pair of 1,3-diphosphete toward a neighboring ligand leads to new bicyclic ligands with unique structural features. A metal-initiated intramolecular hydrogen transfer and C—C bond formation are observed for (1,3,5-triphosphinine)(COD)Fe to result in the formation of [(CO)$_5$Cr(4,5,6-trihydro-1,3,5-triphosphinine)(trihydropentalene)Fe].

Keywords: DFT calculations; iron; molybdenum; P-heterocycles, π-complexes

The cocyclization of terminal alkynes and *t*-BuC≡P **1** by reactive (arene)Fe(0) complexes leads to (1,3-diphosphinine)(1,3-diphosphete)Fe **2** complexes in good yield.[1] In contrast, the analogous cyclotrimerization/cyclodimerization product (1,3,5- triphosphinine)(1,3-diphosphete)Fe **3** is not observed in the absence of alkynes, but isomeric

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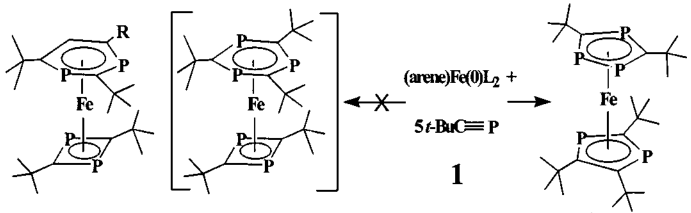


2 **3** **4**

FIGURE 1

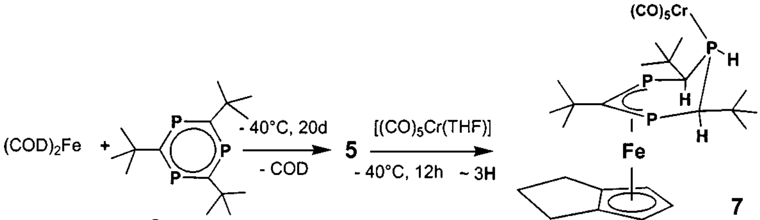
pentaphosphaferrocene **4** is formed (Figure 1) in a so far unexplained reaction.[2]

EXPERIMENTAL RESULTS

If 1,3,5-triphosphinine **6**[3] is reacted with (COD)$_2$Fe (COD = 1,5-cyclooctadine), (1,3,5-triphosphinine)(COD)Fe **5** is formed (Figure 2) in good yield.[4] To our surprise, **5** is thermolabile, whereas all complexes of the type (phosphinine)(COD)Fe are robust.[5] If (CO)$_5$(THF)Cr is added to **5**, a complex rearrangement process takes place that leads to the paramagnetic FeCr species **7**. This reaction gave a first hint at a pronounced intramolecular reactivity of a π-bonded triphosphinine.[4]

The second hint on the activation of an unsaturated P-heterocycle by π-co-ordination came from the observation of a temperature-dependent intramolecular bond formation between two ligands of tris(1,3-diphosphete)Mo **8**. The room-temperature structure of **8a** was determined earlier, and a short P—C distance between two of the rings has been stated,[6] but the reversible interring connection within **8b** takes place at low temperatures only (Figure 3).

This unpredictable intramolecular reactivity is believed to be caused by an activation of the organophosphorus π systems by the transition



6 **7**

FIGURE 2

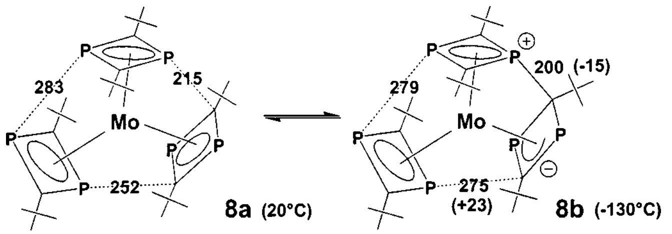


FIGURE 3 Schematic structures of **8a/b** in the solid state. (Data in pm.)

metals. Daucity Functional Theory (DFT) theoretical calculations seemed to be appropriate to analyze this assumption.

THEORETICAL CALCULATIONS

DFT calculations of the P—C bond formation (B3LYP/LanL2DZP[7]) on simplified **8′** (Me substituents) revealed C_s symmetric **8b′** as the energetic minimum. The calculated P—C interring bond distance is almost identical with the experimental value in the solid state at −130°C (201 vs. 200 pm). A transition structure (C_{2v}) with two identical interring P—C distances of 255 pm is 3.5 kcal/mol higher in energy than **8b′**, and **8a′** is destabilized by 0.8 kcal/mol with respect to **8b′**. This surprising result can be rationalized in chemical terms by a nucleophilic attack of the P lone pair on the carbon atom of the neighboring ring. The lone-pair-donating P atom forms a pyramidal phosphonium fragment structure, and the electrophilic ring is transformed into a carbon-bridged diphosphaallyl anion.

No energetic minimum with an aromatic ligand (**5a′**) (Figure 4) has been found by calculating the structure of (1,3,5-triphosphinine)(COD)Fe **5′** (H substituents; B3LYP/SV(P)[7]). A strong boatlike distortion of the triphosphinine is found instead, with a partial

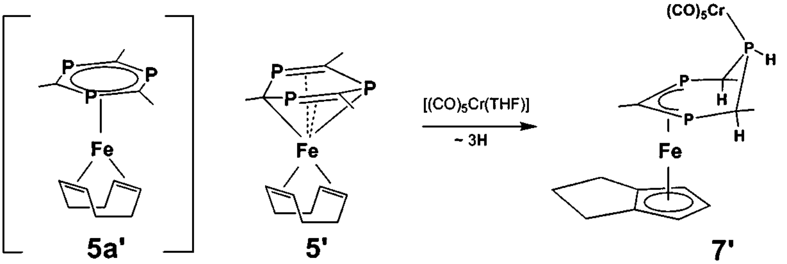


FIGURE 4

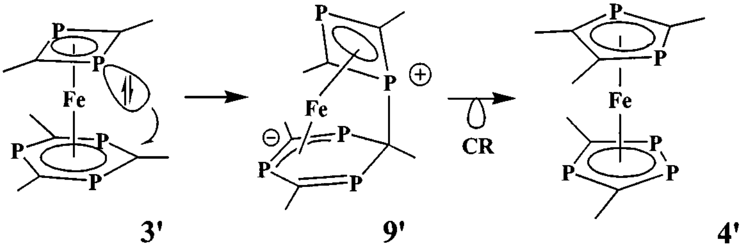


FIGURE 5

localization of two P=C double bonds. This theoretical finding is in line with the NMR spectra of **5** (^{31}P-NMR: AB_2 $\delta_A = 1.8$; $\delta_B = 5.4$; $J_{AB} =$ 32.8 Hz).

The molecular structure as determined in the solid state and the paramagnetism of **7** (triplet state) are precisely reproduced by the calculations. This proves the applicability of the DFT formalism. The calculated spin density distribution points to a strong diphosphaallyl–iron interaction. Also, **7′** plus THF is stabilized by 47 kcal/mol with respect to **5′** plus $(CO)_5(THF)Cr$. This difference in energy supplies the driving force of this unique hydrogen transfer and C—C bond-forming process.

According to DFT calculations, the aromatic ligand of (triphosphinine)(diphosphete)Fe **3′** (R = H) does not show the distortion of **5′**. In spite of its planarity, the ligand is activated by the Fe atom and allows a spontaneous rearrangement to form **4′**. This requires the transfer of one ring element from the triphosphinine to the diphosphete. As we learned about the intramolecular P—C bond formation between π ligands of Mo, we investigated this possibility for **3′**, too. The nucleophilic attack of a P lone pair of the diphosphete leads to the bent but not strained complex **9′** with a bicyclic η^4:η^3 ligand. Triplet species **9′** is only 13.5 kcal/mol higher in energy than **3′**. As for **7′**, the calculated structure of **4′** (Figure 5) is close to the experimental data of **4**.[2] The rearrangement is driven by the stabilization of **4′** by 52 kcal/mol with respect to **3′**.

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