

## Review

## Cooperative 1,1-addition reactions of vicinal phosphane/borane frustrated Lewis pairs

Allan Jay P. Cardenas<sup>a</sup>, Yasuharu Hasegawa<sup>b</sup>, Gerald Kehr<sup>b</sup>, Timothy H. Warren<sup>a,\*</sup>, Gerhard Erker<sup>b,\*\*</sup><sup>a</sup> Department of Chemistry, Georgetown University, Box 571227-1227, Washington, DC 20057, United States<sup>b</sup> Organisch-Chemisches Institut, Universität Münster, Corrensstraße 40, 48149 Münster, Germany

## Contents

1. Introduction .....	468
2. Reaction of vicinal P/B FLPs with isonitriles .....	469
3. Reaction of selected vicinal P/B FLPs with carbon monoxide .....	472
4. FLP reactions with nitric oxide: formation of the persistent P/B FLP-NO nitroxide radicals .....	475
5. 1,1-FLP addition reactions to mesityl azide .....	480
6. Conclusions .....	481
Acknowledgements .....	481
References .....	481

## ARTICLE INFO

## Article history:

Received 21 November 2014

Received in revised form 9 January 2015

Accepted 18 January 2015

Available online 28 January 2015

## Keywords:

Frustrated Lewis pairs

Nitric oxide

Carbon monoxide

Isonitriles

Cooperative addition

## ABSTRACT

The unsaturated vicinal phosphane/borane frustrated Lewis pairs (P/B FLPs)  $\text{Ph}_2\text{PC}(p\text{-tolyl})=\text{C}(\text{R})\text{B}(\text{C}_6\text{F}_5)_2$  ( $\text{R} = \text{C}_6\text{F}_5$  or  $\text{CH}_3$ ) react with *tert*-butyl isocyanide to give an equilibrium mixture of the starting materials, the borane/isonitrile adduct and the P/B addition product to the isonitrile carbon atom. The cooperative 1,1-adducts were exclusively formed upon treatment of these FLPs with *n*-butyl isocyanide. The saturated vicinal FLP  $\text{Mes}_2\text{PCH}_2\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2$  reacts analogously with carbon monoxide yielding the respective five-membered zwitterionic carbonyl heterocycle. Similarly cooperative CO addition was observed starting from a norbornane based vicinal P/B FLP. These saturated vicinal P/B FLPs (and several related systems) undergo analogous cooperative 1,1-addition reactions to nitric oxide (NO) to give the corresponding persistent five-membered heterocyclic FLP-NO nitroxide radicals. They were characterized spectroscopically and by X-ray diffraction and shown to undergo typical *N*-oxyl radical reactions. Some vicinal P/B FLPs also undergo 1,1-addition reactions to mesityl azide. Anomalous Staudinger reactions were observed to take place upon subsequent thermolysis or (in one case) photolysis.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

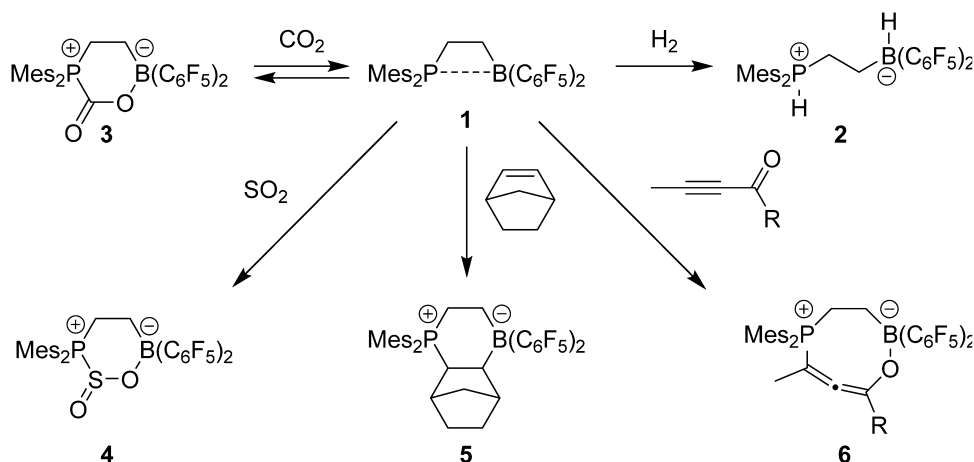
Attachment of sterically bulky substituents may effectively hinder Lewis acids and bases from undergoing the usual LA···LB adduct formation. Such frustrated Lewis pairs (FLPs) [1–4] then contain both the active Lewis acid and Lewis base compounds at the same time in solution. This creates the situation where both the Lewis acid and the Lewis base can separately exhibit their typical

reaction pattern, but in addition it offers the interesting possibility to have both components of the frustrated Lewis pairs react cooperatively with added substrates. This offers the chance to achieve some unprecedented reaction behavior and to actually find new reactions. The heterolytic splitting of dihydrogen [5–8] by the main group element derived FLPs under mild conditions is a typical example, a reaction that requires transition metals or metal complexes. This reaction has become the basis for developing a variety of main group element catalyzed hydrogenation reactions [9–26]. Some intramolecular vicinal phosphane/borane FLPs such as **1** have shown rather high reactivities in this hydrogen activation [7] and consequently in some metal-free catalytic transformation processes. The intramolecular FLP **1** and its congeners undergo a great variety of typical 1,2- (or 1,4-) addition reactions

\* Corresponding author. Tel.: +1 202 687 6362.

\*\* Corresponding author. fax: +49 2518336503.

E-mail addresses: [thw@georgetown.edu](mailto:thw@georgetown.edu) (T.H. Warren), [erker@uni-muenster.de](mailto:erker@uni-muenster.de) (G. Erker).

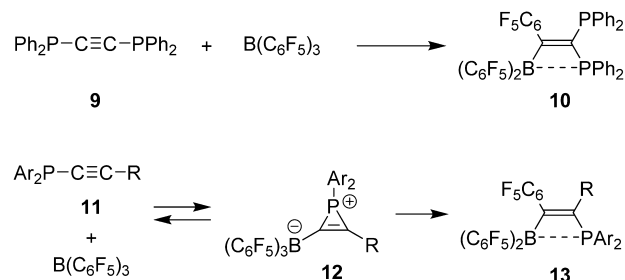
Scheme 1. FLP reactions of compound **1** [2–4].

to unsaturated molecules. Addition to carbon dioxide or sulfur dioxide are typical examples, but these FLP systems also add to organic carbonyl compounds, to alkenes, to enynes and diynes and even to  $\alpha,\beta$ -unsaturated ynones (see Scheme 1) [27–30].

With a few donor ligands  $X\equiv Y$ , for example, isonitriles or carbon monoxide and similar systems, there is an interesting option for competing bonding situations conceivable. These strong  $\sigma$ -donors might just form adducts with the Lewis acid component [31] of the FLP which leads to typical products (**7**, Scheme 2) of Lewis acid chemistry. There might, however, be in some cases the possibility that the adjacent phosphane Lewis base might become involved in the overall bonding situation. Its attack on the Lewis acid activated ligand would then result in the formation of a zwitterionic five-membered heterocyclic product (**8** in Scheme 2). In this case the intramolecular P/B FLP would have undergone a 1,1-addition reaction to the incoming small molecule  $X\equiv Y$ . We have actually identified a few such examples in the chemistry of intramolecular vicinal P/B FLPs and have examined their structure and reactivity. This will be illustrated and discussed in this account.

## 2. Reaction of vicinal P/B FLPs with isonitriles

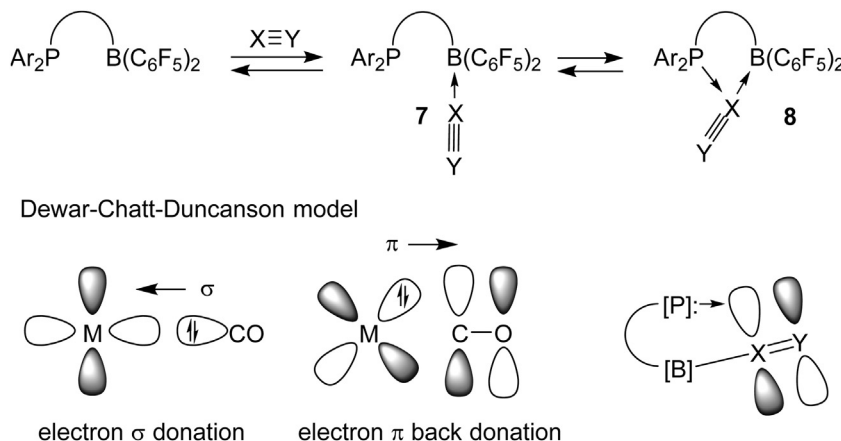
For this study we have used the unsaturated vicinal P/B FLPs **13** as substrates. This class of FLPs was conveniently prepared by means of the 1,1-carboration reaction [32–36] of the respective diarylphosphino-acetylenes **11**. The reaction of a variety of diarylphosphino-acetylenes with, for example,  $B(C_6F_5)_3$  resulted



Scheme 3. 1,1-Carboration reactions of phosphino-acetylenes [37,39].

in a clean and usually rapid 1,1-carboration reaction [37,38]. From separate studies using bis(diphenylphosphino)-acetylene (**9**) we knew that the  $PAR_2$  group in these systems was a good migrating group. In a few cases we were even able to observe and isolate the respective phosphirenium borate zwitterions **12** [39–41] which might possibly be considered as intermediates of these specific 1,1-carboration reactions (see Scheme 3).

For this study we selected diphenylphosphino-substituted systems, namely the FLPs **15** and **16** [42]. Both were prepared starting from the *p*-tolyl substituted diphenylphosphino-acetylene **14** (see Scheme 4). Its treatment with  $B(C_6F_5)_3$  gave the FLP **15**. The 1,1-carboration reaction of **14** with the borane  $(C_6F_5)_2BCH_3$  proceeded selectively by methyl group migrating from boron to carbon to give the unsaturated vicinal FLP **16**.



Scheme 2. Cooperative FLP bonding of CO and other small donor/acceptor ligands [31,42].

Download English Version:

<https://daneshyari.com/en/article/1300873>

Download Persian Version:

<https://daneshyari.com/article/1300873>

[Daneshyari.com](https://daneshyari.com)