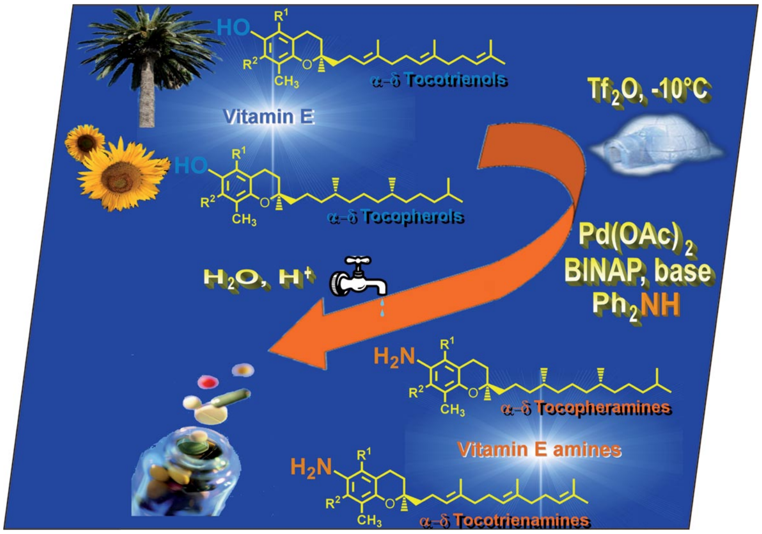
HUNGARY
ITALY
GERMANY
GREECE
BELGIUM
FRANCE
ChemPubSoc Europe
SWEDEN
CZECH REPUBLIC
AUSTRIA
PORTUGAL
SPAIN
NETHERLANDS

A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

COVER PICTURE

The cover picture shows the easy and efficient Pd-catalyzed transformation of the pool of vitamin E (VE) compounds (tocopherols and tocotrienols coming from natural sources) into the corresponding VE amines in enantiopure form. The latter are promising therapeutic agents and building blocks of VE analogues that showed high antitumoral activity. Details are discussed in the article by F. Mazzini, T. Netscher, P. Salvadori et al. on p. 2063ff.



CONTENTS

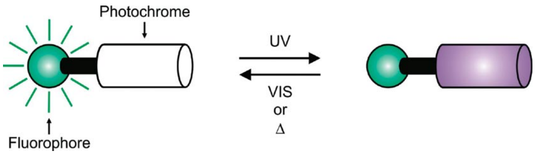
MICROREVIEW

Photoswitchable Fluorophores

J. Cusido, E. Deniz,
F. M. Raymo* 2031–2045

Fluorescent Switches Based on Photochromic Compounds

Keywords: Electron transfer / Energy transfer / Fluorescence / Molecular switches / Photochromism



Molecular constructs with photoswitchable fluorescence can be assembled from fluorescent and photochromic components. In the resulting systems, the photoinduced transformation of one component modulates the emission of the other.

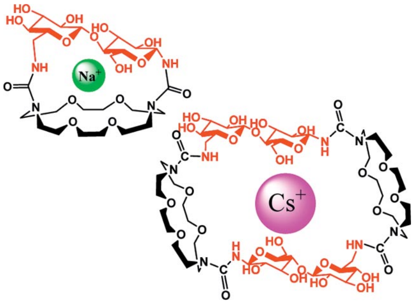
SHORT COMMUNICATIONS

Glycocryptands

S. Porwanski, A. Marsura* 2047–2050

Tandem Staudinger–Aza-Wittig Templated Reaction: De Novo Synthesis of Sugar–Ureido Cryptands

Keywords: Cryptands / Template synthesis / Carbohydrates / Crown compounds



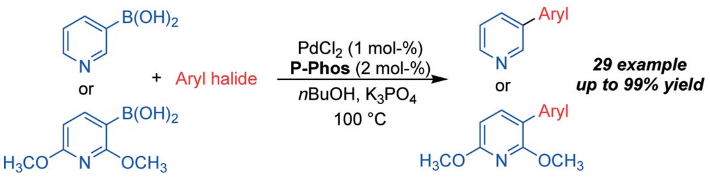
1,6′-Diazidocellobiosyl units react with diazacrown ethers under template-effect conditions to afford chiral, macrobicyclic or macrotricyclic glycocryptands by a tandem Staudinger–aza-Wittig reaction. The macrocyclisation step was shown to be under cation size control.

Suzuki Cross-Couplings

X.-L. Fu, L.-L. Wu, H.-Y. Fu, H. Chen,*
R.-X. Li 2051–2054

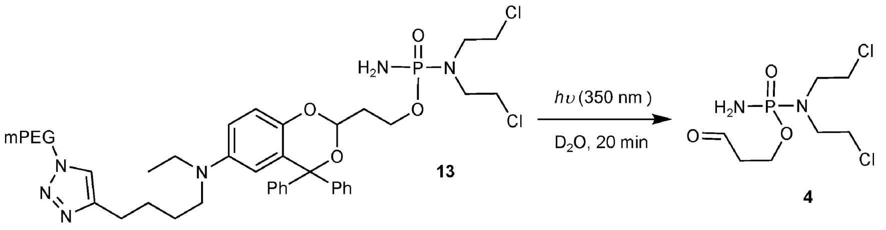
Efficient Diphosphane-Based Catalyst for the Palladium-Catalyzed Suzuki Cross-Coupling Reaction of 3-Pyridylboronic Acids

Keywords: Nitrogen heterocycles / Boron / Cross-coupling / Phosphane ligands / Palladium



Pyridine-derived boronic acids do not readily participate in Suzuki cross-coupling reactions. We have developed a catalyst system derived from $PdCl_2$ and P-Phos, which exhibits high catalytic activity in the Suzuki reaction between 3-pyridylboronic acid and a variety of aryl halides.

Drug Release



A novel photoactivated phosphamide mustard prodrug (**13**) equipped with a new phototrigger was designed and synthesized. The prodrug is water soluble and stable under laboratory lighting. It effectively released aldophosphamide (**4**) upon irradiation at 350nm.

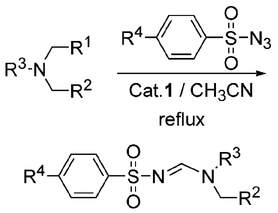
P. Wang,* M. Mondal, Y. Wang 2055–2058

Photolabile Carbonyl Protecting Group: A New Tool for Light-Controlled Release of Anticancer Agents

Keywords: Protecting groups / Photolabile groups / Prodrugs / Phosphorus / Antitumor agents / Drug delivery

Imidation of Amines

Simple copper salt catalyzed *C*-imidation of tertiary amines with sulfonyl azides under mild conditions was achieved in moderate to high yields (up to 96%).



N. Liu, B.-Y. Tang, Y. Chen, L. He* 2059–2062

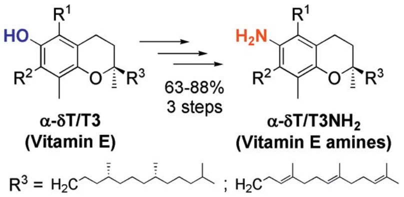
Catalyzed Imidation of Tertiary Amines by Simple Copper Salts

Keywords: Amines / Sulfur / Imidation / Copper

FULL PAPERS

Vitamin E Amines

Tocopheryl amide derivatives (VE amides) show very interesting and promising pro-apoptotic activity against various tumor cell lines. Key precursors of VE amides are the corresponding tocopheryl- and tocotrienylamines. An efficient and easy synthesis of enantiopure VE amines by palladium-catalyzed *N*-arylation is reported.



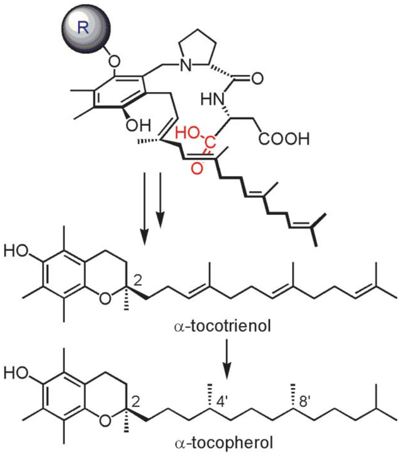
F. Mazzini,* T. Netscher, P. Salvadori* 2063–2068

Efficient Synthesis of Vitamin E Amines

Keywords: Amination / Antitumor agents / Palladium / Arylation / Vitamins

Vitamin E

A common synthetic route to α-tocotrienol and α-tocopherol has been achieved by a biomimetic cyclisation that yields the chromanol ring, the α-tocopherol being formed by diastereoselective hydrogenation of the α-tocotrienol. The chirality at C2 of the chromanol was induced by a covalently attached chiral dipeptide.



J. Chapelat, A. Chougnet, W.-D. Woggon* 2069–2076

Biomimetic Chromanol Cyclisation: A Common Route to α-Tocotrienol and α-Tocopherol

Keywords: Biomimetic synthesis / Chromanols / Vitamins / Cyclization / Peptides

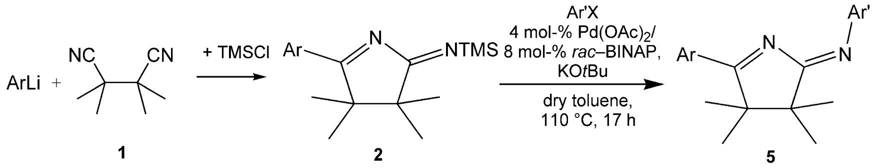
CONTENTS

Dihydropyrrolimines

S. Janich, R. Fröhlich, A. Wilken,
J. von Zamory, A. Wakamiya,
S. Yamaguchi,
E.-U. Würthwein* .... 2077−2087

3,4-Dihydro-3*H*-pyrrol-2-imines as Conformationally Restrained 1,3-Diazabutadienes: Synthesis, Structural Properties and Protonation

Keywords: Nitrogen heterocycles / Cross-coupling / Acidity / Fluorescence



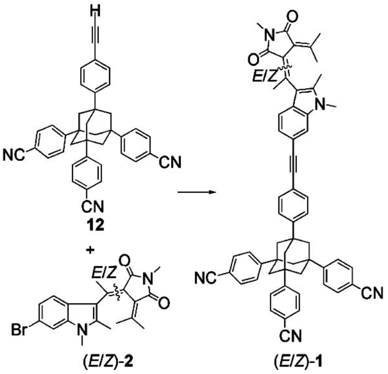
3,4-Dihydro-3*H*-pyrrol-2-imines **2**, conformationally restrained 1,3-diazabuta-1,3-diene derivatives, were easily accessible from aryllithium species and succinonitrile **1** after trapping with TMSCl. Palladium-catalysed C−N bond-forming reactions gave *N*-arylated compounds **5**, displaying interesting pH dependent colour changes and fluorescence properties.

Photoswitch Linker Conjugate

S. Zarwell, S. Dietrich,
C. Schulz, P. Dietrich, F. Michalik,
K. Rück-Braun* .... 2088−2095

Preparation of an Indolylfulgimide-Adamantane Linker Conjugate with Nitrile Anchoring Groups through Palladium-Catalyzed Transformations

Keywords: Fulgimides / Photochromism / Tripods / Cross-coupling / Cyanides



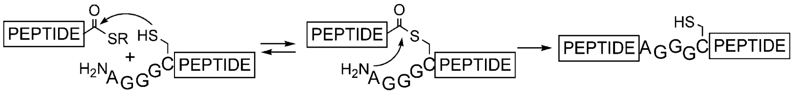
The tripodal adamantane ethynylene linker **12**, containing nitrile groups for metal−molecule contacts, has been synthesized by means of a palladium-catalyzed cyanation. Sonogashira conditions have been developed for the coupling of the linker **12** with the novel 6-bromo-substituted indolylfulgimide **2** to give the indolylfulgimide linker conjugate **1**.

Protein Synthesis

C. Haase, O. Seitz* .... 2096−2101

Internal Cysteine Accelerates Thioester-Based Peptide Ligation

Keywords: Coupling / Peptides / Macrocycles / Synthetic methods / Thioester



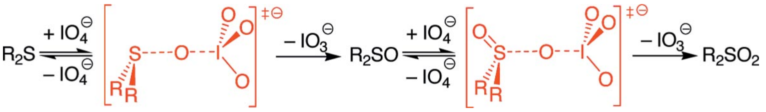
Rate acceleration factors of up to 25 can be achieved when a sequence internal cysteine assists thioester-based ligation reactions. The investigation reveals a strong sequence dependence and suggests optimal distances between the internal cysteine residue and the N-terminal amino group. Internal cysteine ligation can include sites such as Pro-Cys sites which are difficult to approach directly by conventional native chemical ligation.

Oxygen-Transfer Mechanism

F. Ruff,* A. Fábián, Ö. Farkas,
Á. Kucsman .... 2102−2111

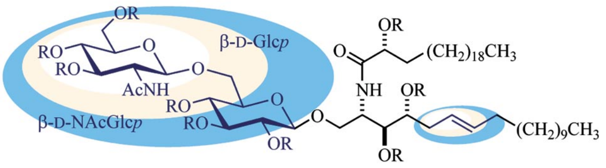
Mechanism for the Oxidation of Sulfides and Sulfoxides with Periodates: Reactivity of the Oxidizing Species

Keywords: Oxidation / Sulfides / Sulfoxides / Iodine / Density functional calculations / Reaction mechanisms



Sulfides and sulfoxides are oxidized with periodate species of different reactivities ($HIO_4 >> H_5IO_6 > IO_4^- > H_4IO_6^- >> H_3IO_6^{2-}$) by one-step oxygen-transfer reactions that involve very early transition states.

Glycolipids from Sponges



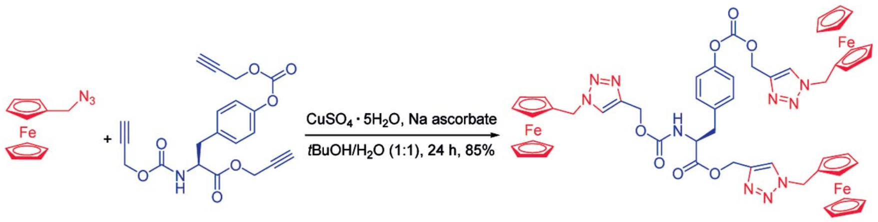
The Caribbean sponge *Amphimedon compressa* contains two novel glycosphingolipids, amphiceramide A (**1a**) and B (**2a**), which possess an unusual Δ^6-phytosphingosine. The saccharide chain of amphiceramide A is composed of a β-glucose residue glycosylated at the 6-position by an *N*-acetyl-β-glucosamine and has never been found before in a natural product.

V. Costantino, E. Fattorusso,
C. Imperatore, A. Mangoni,*
R. Teta .... 2112−2119

Amphiceramide A and B, Novel Glycosphingolipids from the Marine Sponge *Amphimedon compressa*

Keywords: Amines / Carbohydrates / Glycolipids / Sponges / Structure elucidation

Ferrocene Conjugates



Ferrocene conjugates with amino acids were synthesized employing copper-catalyzed 1,3-dipolar cycloaddition. Ethynylferrocene and ferrocene-derived azides were used for labeling. Diverse amino acid derived azides and alkynes were synthesized and labeled with ferrocene. A few conjugates were characterized by cyclic voltammetry.

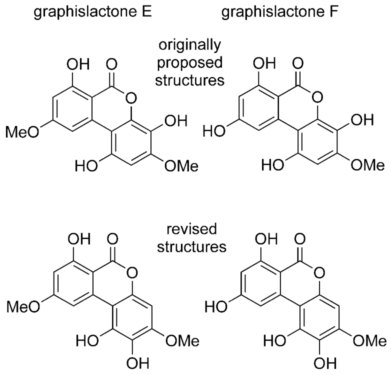
V. S. Sudhir, C. Venkateswarlu,
O. T. M. Musthafa, S. Sampath,*
S. Chandrasekaran* .... 2120−2129

Click Chemistry Inspired Synthesis of Novel Ferrocenyl-Substituted Amino Acids or Peptides

Keywords: Click chemistry / Amino acids / Ferrocenes / Cyclic voltammetry / Cycloaddition

Total Synthesis

Concise syntheses of ulocladol and of the lichen metabolites graphislactones A, C−F, and H are presented. NMR spectroscopic data of graphislactones E and F showed that the originally proposed structures were incorrect. Corrected structures matching the published data were synthesized.

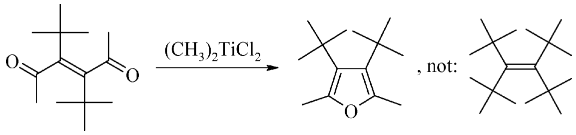


M. Altemöller, T. Gehring, J. Cudaj,
J. Podlech,* H. Goesmann, C. Feldmann,
A. Rothenberger .... 2130−2140

Total Synthesis of Graphislactones A, C, D, and H, of Ulocladol, and of the Originally Proposed and Revised Structures of Graphislactones E and F

Keywords: Polyketides / Lichen metabolites / Resorcylic lactones / Cross-coupling / Dakin reaction / Total synthesis

Highly Hindered Olefins



Although the conditions to prepare the still unknown tetra-*tert*-butylethene from a "half-*tert*-butylated diketone" were ideal, the system found a way to escape the intended route and produced a fully alkylated furan derivative instead upon treatment with dimethyltitanium dichloride.

O. Klein, H. Hopf,*
J. Grunenberg .... 2141−2148

The Ever-Elusive Tetra-*tert*-butylethene (TTBE, 3,4-Di-*tert*-butyl-2,2,5,5-tetramethylhex-3-ene): Further Insight on Its Preparation

Keywords: Diynes / Methylation / Titanium / Oxygen heterocycles / Cyclization

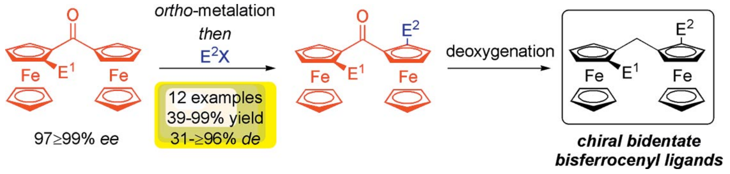
CONTENTS

Planar-Chiral Bisferrocenes

D. Enders,* E. A. Jonas,
T. Klumpen 2149–2162

Efficient Asymmetric Synthesis of Planar-Chiral Bisferrocenes

Keywords: *ortho*-Metalation / Ferrocenes / P ligands / Asymmetric synthesis / Metallocenes



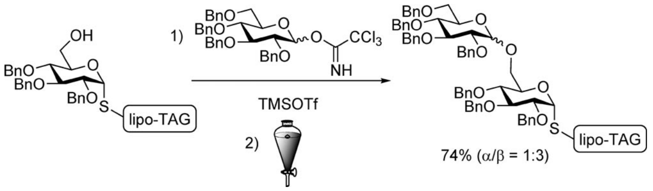
The resident planar-chirality in monosubstituted diferrocenyl ketones is capable of efficiently directing an *ortho*-metalation/functionalization reaction in a highly diastereoselective manner allowing rapid access to a large array of (pseudo) C_2-symmetric chiral diferrocenyl ligands.

Lipophilic Tagging

L. Encinas, J. L. Chiara* 2163–2173

Lipophilic Thioglycosides for the Solution-Phase Synthesis of Oligosaccharides Using Biphasic Liquid-Liquid Separation

Keywords: Carbohydrates / Thioglycosides / Glycosylation / Lipophilic tagging / Liquid-liquid extraction



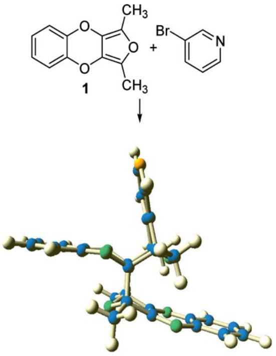
A simple "heavy" lipophilic tag readily prepared from inexpensive gallic acid can greatly simplify the purification steps in oligosaccharide synthesis by means of liquid-liquid extraction with two immiscible organic solvents. A single tag is sufficient to ensure a high affinity of the tagged molecule for alkane solvents even in the case of highly polar substrates. Simple and efficient tagging and detagging procedures are described.

Benzodioxin Dienophiles

C. Bozzo, N. Mur, P. Constans,
M. D. Pujol* 2174–2178

Furo[3,4-*b*]benzodioxin Cycloadditions – A One-Pot Synthesis of Functionalized Bis-Adducts

Keywords: Cycloaddition / Fused-ring systems / Polycycles / Dienophiles / Oxygen heterocycles



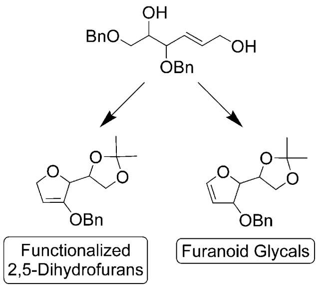
Furo[3,4-*b*]benzodioxin **1** reacts with a suitable dienophile to give a mono-adduct that proves the first reaction transforms the C4a–C10a bond into a double bond. Subsequently, the internal double bond of the 1,4-benzodioxin framework acts a new dienophile in a second cycloaddition reaction. With this uninterrupted cycloaddition sequence, the formation of stable bis-adducts was observed.

E2 Elimination

P. Pal, B. Kumar,
A. K. Shaw* 2179–2184

Synthesis of Enantiomerically Pure Highly Functionalized Furanoid Glycal and 2,5-Dihydrofuran Building Blocks

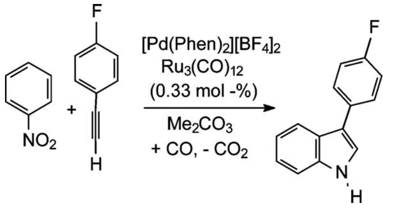
Keywords: Alcohols / Glycals / Elimination / Oxygen heterocycles / Allylic compounds



Differently protected enantiomerically pure furanoid glycals and highly functionalized 2,5-dihydrofurans were synthesized from glycal-derived allylic alcohols.

3-Arylindole Synthesis

3-Arylindoles, including that constituting the skeleton of Fluvastatin and other pharmaceutically active compounds, can be obtained regioselectively in one step from unfunctionalized nitroarenes and alkynes under CO pressure in the presence of a palladium−phenanthroline catalyst. The addition of $Ru_3(CO)_{12}$, dimethyl carbonate, or both to the reaction mixture improves the selectivity.



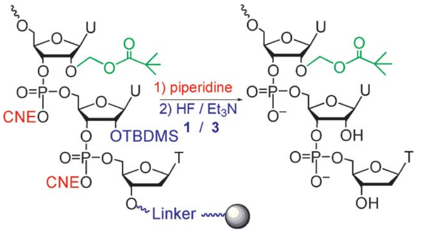
F. Ragaini,* F. Ventriglia, M. Hagar, S. Fantauzzi, S. Cenini .... 2185−2189

Synthesis of Indoles by Intermolecular Cyclization of Unfunctionalized Nitroarenes and Alkynes: One-Step Synthesis of the Skeleton of Fluvastatin 💻

Keywords: Alkynes / Arenes / Nitrogen heterocycles / Palladium / Carbonylation

Oligonucleotide Synthesis

An optimized fluoride ion treatment releases base-sensitive oligonucleotides connected to solid supports through the Q-linker or a silyl-type linker. It was applied to the preparation of chimeric oligoribonucleotides containing pivaloyloxymethyl groups and a 2′-OH group leading to modified biolabile RNA with high efficiency and purity.

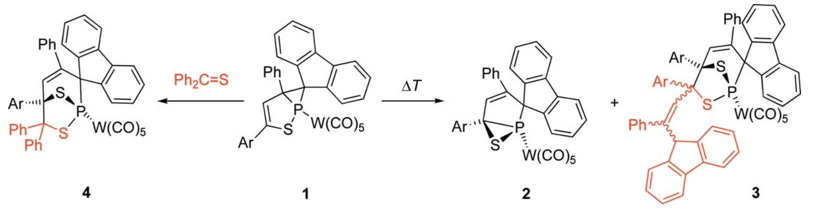


T. Lavergne, N. Parey, J.-J. Vasseur, F. Debart* .... 2190−2194

Efficient Release of Base-Sensitive Oligonucleotides from Solid Supports using Fluoride Ions 💻

Keywords: Oligonucleotides / Solid supports / Ribonucleosides / Fluorine / Protecting groups

Phosphirane Chemistry



4 **1** **2** **3**

Phosphirano-[1,2]thiaphosphole−$W(CO)_5$ complexes **1** undergo a thermal valence isomerization to form 2*H*-phospholothiaphosphiranes **2** and fragmentation/cycloaddition to generate bicyclic 1,3,2-dithiaphospholanes **3**. The latter ring system is also formed from **1** or its uncomplexed analogues and thiobenzophenone. Thus, the thermal behavior of phosphiranes **1** is different from that of the 6,6-diphenyl-substituted relatives.

S. Maurer, T. Jikyo, G. Maas* .... 2195−2207

Unexpected Thermal Reactivity of Phosphirano-[1,2]thiaphosphole *P*−$W(CO)_5$ Complexes

Keywords: Cycloaddition / Diazo compounds / Spiro compounds / Phosphorus heterocycles / Sulfur heterocycles

---

* Author to whom correspondence should be addressed.

💻 Supporting information on the WWW (see article for access details).