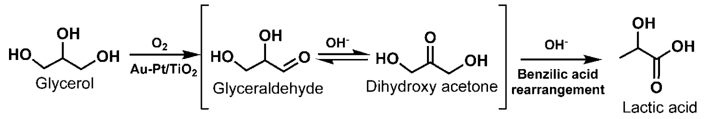
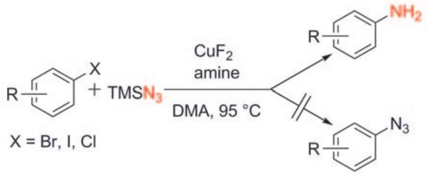
COMMUNICATIONS



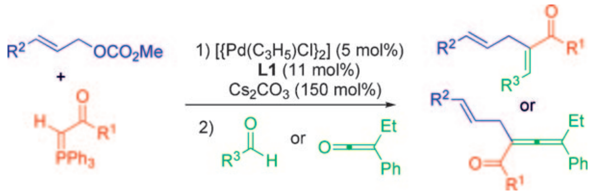
Go for the burn! A one-pot approach to the efficient synthesis of lactic acid through the aerobic oxidation of glycerol in the presence of bases at an atmospheric pressure of O_2 is reported, which combines two consecutive reactions, including oxidative dehydrogenation of glycerol to its dehydrogenated intermediates and their subsequent isomerization (see scheme).

Heterogeneous Catalysis



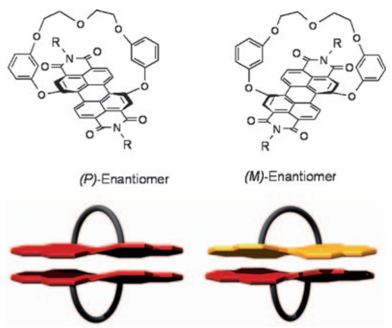
Look, no azide! Trimethylsilyl azide was reductively cross-coupled with a variety of aryl halides in the presence of a copper species and amines, such as triethylamine or aminoethanol, to give the corresponding primary aryl amine in good yields without the formation of the expected aryl azide (see scheme).

Azides for Aromatic Amination



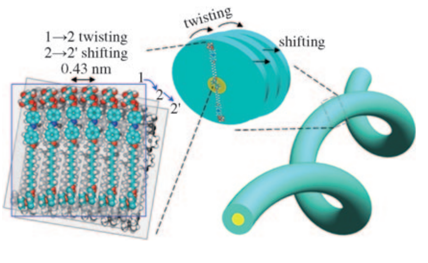
Put a(n) (y)lid(e) on it! The one-pot palladium-catalyzed allylic alkylation and Wittig reaction of phosphorus ylides with various aldehydes and ketenes has been realized, which produce skipped dienes, including trisubstituted alkenes and tetrasubstituted allenes, respectively (see scheme), in moderate to good overall yields.

Alkene/Allene Synthesis



Narcissism of molecules! Configurationally restricted chiral perylene bisimide dyes show a very strong preference for the formation of homochiral dimers (self-recognition) (red pair) upon π stacking in solution. Minor amounts of heterochiral dimers (red–yellow pair) enable the determination of *P*/*M* enantiomeric ratios by ^{1}H NMR spectroscopy without using any chiral auxiliary.

Chiral Recognition



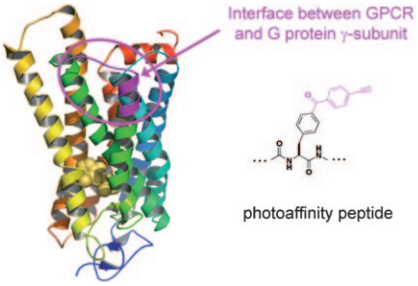
Let's twist again! A chiral rod–coil organometallic material, FC11, has been synthesized and shows liquid-crystalline behavior. By taking advantage of the self-assembly of the chiral Schiff based rod–coil molecule that is end-capped with ferrocene, the self-assembled superstructure can serve as a template to form iron-rich spiral superstructures (see graphic).

Self-Assembly

Proteins

Y. Chen, Y. Wu, P. Henklein, X. Li, K. P. Hofmann, K. Nakanishi, O. P. Ernst** .... 7389 – 7394

A Photo-Cross-Linking Strategy to Map Sites of Protein–Protein Interactions

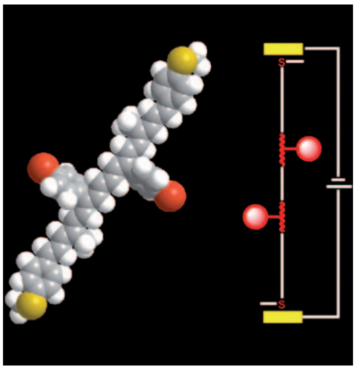


Clicked! Exemplified on a G-protein-coupled receptor (GPCR; see figure)/G-protein model system, a specific protein–peptide interaction was analyzed by using a G-protein-derived peptide containing *p*-ethynylbenzoyl-modified phenylalanine. Click chemistry with a biotin propyl azide probe enabled isolation of photo-cross-linked products and facilitated mass spectrometric analysis of the protein–peptide interaction sites.

Nanotechnology

*J. Maeng, S. B. Kim, N. J. Lee, E. Choi, S.-Y. Jung, I. Hong, S.-H. Bae, J. T. Oh, B. Lim, J. W. Kim, C. J. Kang, S. Koo** .... 7395 – 7399

Conductance Control in Stabilized Carotenoid Wires

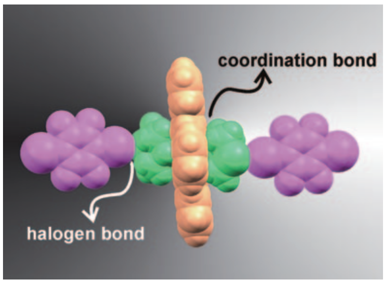


Tunable carots: Construction of the stable carotenoid wires with a specific conductance value is possible by the attachment of phenyl groups to the polyene chain to overcome the in vitro instability of natural carotenoids, the perfect molecular wires utilized in various biological processes. Diverse electronic natures of the substituents on the phenyl groups provide the carotenoids with tunable conductance (see figure).

Supramolecular Chemistry

G. Lapadula, N. Judaš, T. Friščić, W. Jones** .... 7400 – 7403

A Three-Component Modular Strategy to Extend and Link Coordination Complexes by Using Halogen Bonds to O, S and π Acceptors



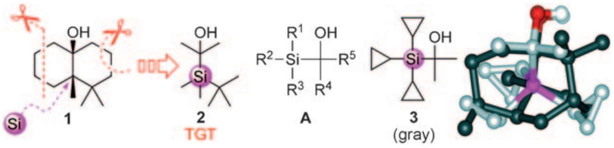
Strategic extension! A modular strategy, involving the recognition and assembly of three molecular components, was used to decorate complexes of Ni^{II} and Co^{II} with halogen bonds of I···S and I···O type. In addition to this rational implementation of halogen bonding to extend coordination structures, the resulting materials also demonstrate the self-assembly through I···π interactions as a means to form polymers based on coordination and halogen bonds (see graphic).

FULL PAPERS

Silanes

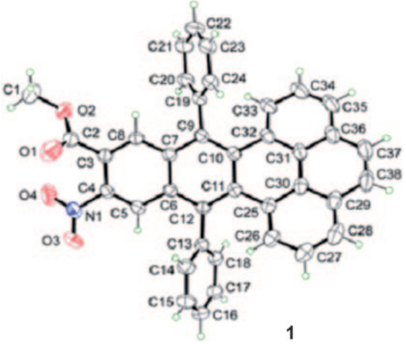
A. Sunderkötter, S. Lorenzen, R. Tacke, P. Kraft** .... 7404 – 7421

Novel Silicon-Based Patchouli Odorants of the Trialkyl(1-hydroxy-1-methylethyl)silane Type: Design, Synthesis, and Olfactory Properties

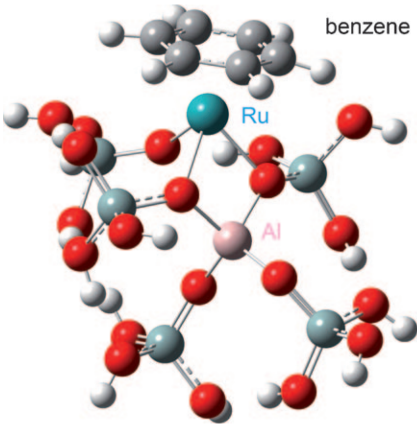


Silicon-enhanced "patchoulies": Silane **2**, designed as a sila-*seco* structure of the *cis*-decalol **1**, as well as several silanes of type **A** (R = organyl) were synthesized and studied for their olfactory properties, which were often closely reminiscent of natural patchouli oil. Silane **3** is the most attractive and is more powerful than the natural lead (−)-patchoulol.

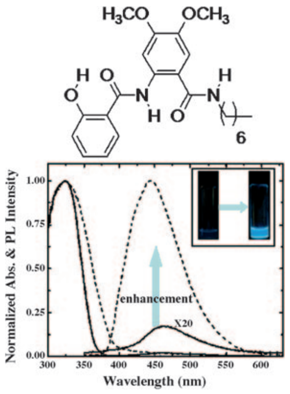
An asymmetric twistacene, 1′,4′-diphenyl-naphtho-(2′.3′:1.2)-pyrene-6′-nitro-7′-methyl carboxylate (tetracene **1**, see graphic), was synthesized by using benzyne-trapping chemistry. Its structure confirmed that this material has a twisted topology with torsion angles as high as 23.8(3)°. Organic light-emitting devices with tetracene **1** as either charge-transporting materials or emitters have been fabricated.



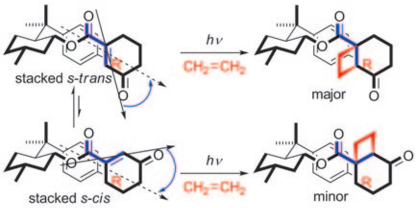
Look below the surface: A highly uniform mononuclear ruthenium–benzene complex supported on zeolite (see figure) has been synthesized and characterized by using IR, ^{13}C NMR, and EXAFS spectroscopies complemented by density functional theory calculations.



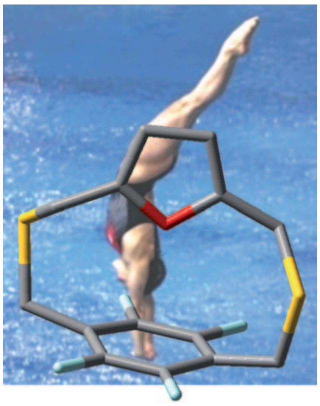
Gelation-enhanced fluorescence: The fluorescence emission intensity of the organogel formed by a salicylanilide-containing organogelator is 10–50 times higher than that of the corresponding solution phase (see picture). The fluorescence enhancement is due to restricted intramolecular rotation in the gel state, which prevents access to the twisted intramolecular charge-transfer state after excited-state intramolecular proton transfer.



Stacking the odds! The diastereoselectivity of the [2+2] photocycloaddition of ethylene to cyclohexenones can be enhanced by using a chiral *p*-substituted arylmenthyl auxiliary. The stacked *s-trans* conformer of substrates is more populated at lower temperatures to give the major photocycloadduct in higher diastereoselectivities (up to 90 % *de*; see scheme).

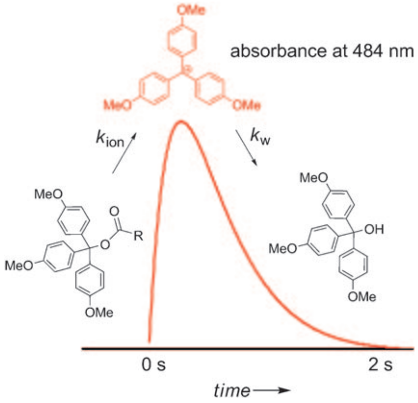


Conformational Analysis



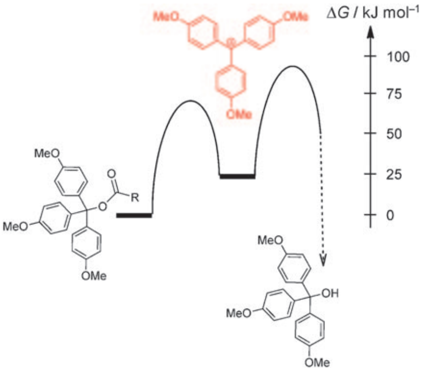
A dive into an electron sea! Four thiophene- and furan-containing [3.3]meta(heterocyclo)paracyclophanes were designed and synthesized to study the intramolecular interaction between standard heteroaromatic rings and tetra-H- or tetra-F-substituted benzenes. The furan-derived adducts were shown by calculations and NMR spectroscopy to adopt a perpendicular edge-to-face disposition of the rings with the oxygen atom pointing toward the benzene platform (see figure).

Protecting Groups



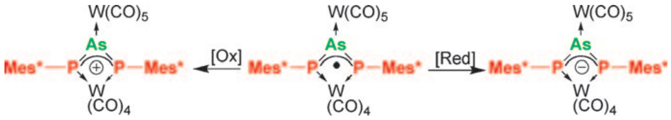
Detritylation quantified: The appearance and disappearance of the red trimethoxytritylium ion can be followed with the naked eye when water is added to colorless solutions of the trimethoxytrityl carboxylates in acetonitrile (see figure). Trityl carboxylates with weaker electron donors hydrolyze according to the ordinary S_N1 mechanism, whereas hydrolyses of trityl carboxylates with stronger electron donors give persistent carbocations.

Protecting Groups



Tritylation quantified: Relationships between the electrophilic reactivities of tritylium ions and their thermodynamic stabilities in the gas phase and in solution have been investigated. The ionization rate constants of trityl carboxylates reported in the preceding article are linked with the rate constants for the reactions of tritylium ions with water to construct complete free-energy profiles for the hydrolyses of trityl esters (see figure).

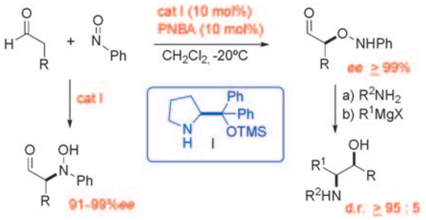
Radicals



Radically complex: The photolytic reaction of $[Cp^*As\{W(CO)_5\}_2]$ ($Cp^* = C_5Me_5$) with a diphosphene produces an air-stable complexed diphospha-monoarsa-allyl radical. Oxidation of the radical leads to a cationic complex, which is only stable at low temperatures, whereas a stable anion is formed by reduction (see scheme).

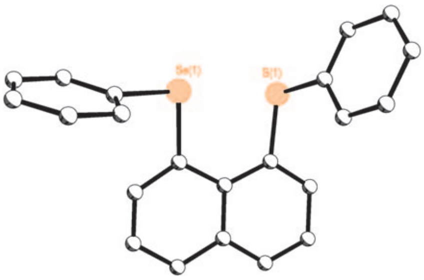
Synthetic Methods

All change! Catalyst **I** (see scheme) is able to promote the oxyamination reaction between aldehydes and nitrosobenzene and, in the presence of *p*-nitrobenzoic acid (PNBA), it catalyses the aminoxylation reaction with essentially complete regio- and enantioselectivity. This method provides a fast entry to 1,2-amino alcohols with predefined configuration.



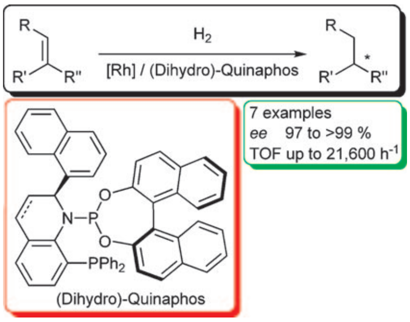
Intramolecular Interactions

Close enough to bond? Are atoms bonded when they are closer than the sum of their Van der Waals radii? *peri*-Substituted systems allow us the opportunity to test weak interactions between chalcogens (see figure).



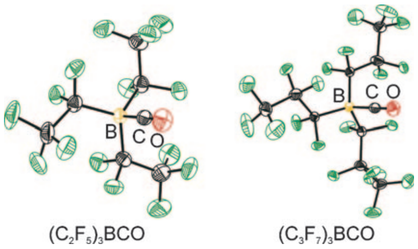
Asymmetric Synthesis

It's fast, it's selective, it's Quinaphos! Efficient and highly enantioselective Rh-catalysed hydrogenation of various functionalised olefins was achieved by using the readily available phosphine–phosphoramidite ligands of the Quinaphos family (see graphic).

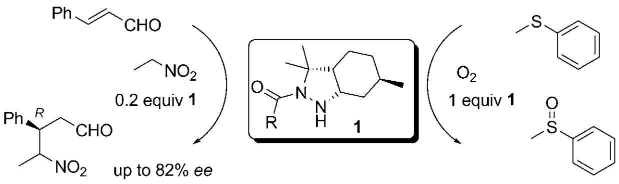


Boron Chemistry

σ-Bonded carbonyls: The two new tris(perfluoroalkyl)borane carbonyls, $(C_2F_5)_3BCO$ and $(C_3F_7)_3BCO$ (see picture), are synthesized and, together with their precursors, characterized by NMR, IR, and Raman spectroscopy, as well as X-ray crystallography. The carbonyls exhibit essentially pure σ-bonded B–CO moieties.



Organocatalysis

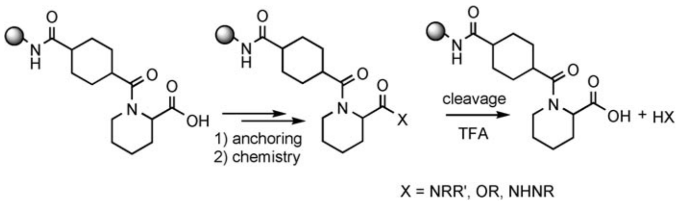


Abundant pulegone served as the starting material for a two-step synthesis of octahydroindazoles **1**. The compounds were evaluated for their potential to be used as iminium ion catalysts in a Michael-type reaction. In addition, they turned out to be good reducing agents for atmospheric oxygen capable of promoting the sulfoxidation of methyl phenyl sulfide.

Solid-Phase Synthesis

*P. Zajdel, G. Nomezine, N. Masurier, M. Amblard, M. Pawłowski, J. Martinez, G. Subra** ...... 7547 – 7553

A New Highly Versatile Handle for Chemistry on a Solid Support: The Pipecolic Linker

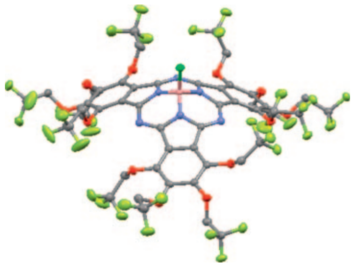


Firm grip: A pipecolic linker can immobilize primary, secondary, and aromatic amines, as well as alcohols, phenols, and hydrazides, on a solid support. Compared with other linkers, the anchoring step is easy and efficient. The release of final products from the resin proceeds upon acidic treatment with high purities (see scheme).

Subphthalocyanines

N. Shibata, B. Das, E. Tokunaga, M. Shiro, N. Kobayashi** . . . 7554 – 7562

Trifluoroethoxy-Coating Improves the Axial Ligand Substitution of Subphthalocyanine

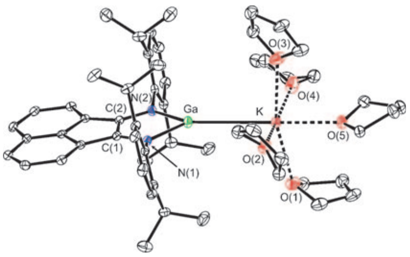


Fluorine effect: Coating of subphthalocyanine with trifluoroethoxy groups has been shown to have clear beneficial effects. Trifluoroethoxy-coated subphthalocyanine has been synthesised for the first time; this has proven to be a very efficient precursor for diverse syntheses of axially substituted subphthalocyanine derivatives (such as that depicted).

Main Group Chemistry

I. L. Fedushkin, A. N. Lukoyanov, A. N. Tishkina, G. K. Fukin, K. A. Lyssenko, M. Hummert* .... 7563 – 7571

Reduction of Digallane [(dpp-bian)Ga−Ga(dpp-bian)] with Group 1 and 2 Metals

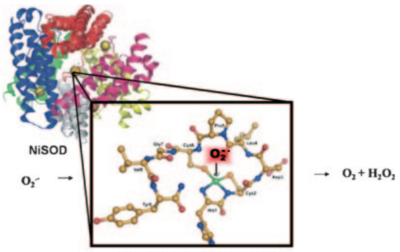


Gallium dreams: [(dpp-bian)Ga−Ga(dpp-bian)] (**1**; dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene), a compound with a gallium–gallium bond, has been prepared in one step starting from gallium metal. Reduction of **1** with Group 1 and 2 metals results in cleavage of the Ga−Ga bond and formation of monomeric compounds with alkali metal–gallium and alkaline earth metal–gallium bonds (see picture).

Biomimetics

*D. Tietze, M. Tischler, S. Voigt, D. Imhof, O. Ohlenschläger, M. Görlach, G. Buntkowsky** .... 7572 – 7578

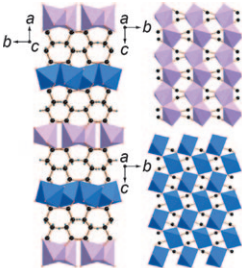
Development of a Functional *cis*-Prolyl Bond Biomimetic and Mechanistic Implications for Nickel Superoxide Dismutase



cis prolyl NiSOD biomimetic

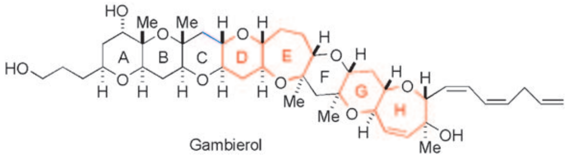
Is *cis* important? Peptide-based Ni superoxide dismutase (NiSOD) models show an important structural difference compared to the native NiSOD enzyme, which could cause a completely different mechanism of superoxide dismutation. To shed light on how the configuration of a single peptide bond influences the activity of the NiSOD model peptides, a new *cis* prolyl bond surrogate was developed (see graphic).

Inorganic–Organic Frameworks



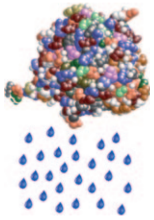
Manganese succinate framework: $Mn(C_4H_4O_4)$ has a unique structure with alternating sheets of edge-sharing MnO_6 octahedral chains and corner-sharing MnO_6 octahedra (see graphic). It has a rich and complex magnetic behaviour, sequentially adopting two antiferromagnetic phases at low temperature. The lowest temperature antiferromagnetic phase undergoes two further transitions with applied magnetic field.

Natural Products



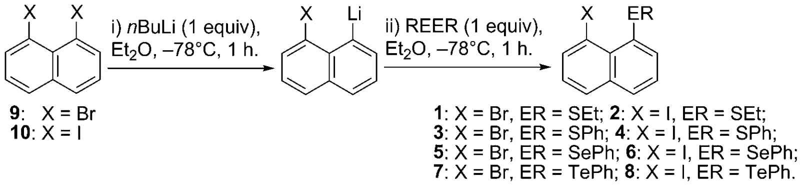
Epoxide alchemy: The total synthesis of gambierol has been achieved by utilizing an oxiranyl anion strategy in an iterative manner. Synthetic highlights of this route include direct carbon–carbon bond formation on epoxides, sulfonyl-assisted 6-*endo* cyclization, and an expansion reaction of tetrahydropyranyl rings to oxepanes to forge the polycyclic architecture of the target molecule.

Enzyme Catalysis



Water is key: The influence of water concentration on the activity and enantioselectivity of enzymes in dry organic media has been investigated by using the hydrocyanation of benzaldehyde catalyzed by hydroxynitrile lyase cross-linked enzyme aggregate (*Me*HNL-CLEA, see figure) as a model reaction. Higher enantioselectivity was seen at higher water concentrations, thus suggesting a positive effect of enzyme flexibility on selectivity.

Intramolecular Interactions



A strained relationship? In *peri*-substituted naphthalenes, the non-bonded distance between the halogen and chalcogen (see scheme) is shorter than the sum of the van der Waals radii for the two *peri* atoms by 12–18%. Is this a bonding or a strained repulsive interaction?

peri-Substitution

*F. R. Knight, A. L. Fuller, M. Bühl, A. M. Z. Slawin, J. D. Woollins** .... 7617 – 7634

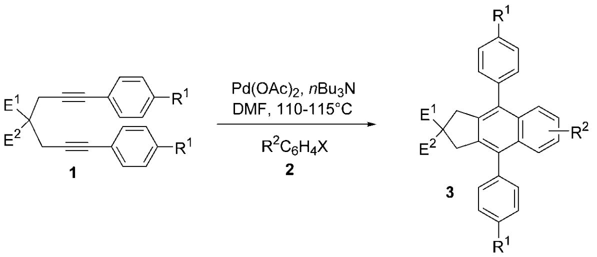
Sterically Crowded *peri*-Substituted Naphthalene Phosphines and their P^V Derivatives

Crowd control: Steric crowding that gives quasi-linear E···P–C fragments (see figure) does not result in three-centre–four-electron (3c–4e) bonds, but calculations suggest that these molecules are ideal radical precursors.

C–H Activation

Y. Hu, H. Yao, Y. Sun, J. Wan, X. Lin, T. Zhu* .... 7635 – 7641

Efficient Activation of Aromatic C–H Bonds for Fused Polyaromatic Hydrocarbon Construction



Domino sequence: An extraordinary domino reaction for the construction of polycyclic aromatic hydrocarbons has been established. Various 4,9-diphenyl-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalene derivatives are constructed by palladium-catalyzed reaction of diynes with aryl halides through C–C coupling and C–H bond activation of the incorporated aryl group (see scheme), which provides an effective π-system synthesis.

---

* Author to whom correspondence should be addressed

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

VIP Full Papers labeled with this symbol have been judged by two referees as being "very important papers".

A video clip is available as Supporting Information on the WWW (see article for access details).

SERVICE