uration in the formation of the unsupported metal–metal bond. Furthermore, the steric bulk of the pyridonate rings does not hinder the formation the unsupported metal–metal bond. Therefore, one could envisage the accessibility of a hypothetical tetrametallic chain made of two HT units.

With the experimental confirmation of the intervention of HT dimers in tetrametallic chains, it seems likely that the lack of HT-pyridonate dimers in the platinum blues complexes should be attributed mainly to thermodynamic reasons rather than to steric factors.

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[5] Selected analytical and spectroscopic data for the new complexes: Complex **1**: elemental analysis (%) calcd for $C_{14}H_8N_2O_6Ir_2$: C 24.56, H 1.18, N 4.09; found: C 24.95, H 1.47, N 4.18; IR (toluene): $\tilde{\nu}=\nu(CO)=$ 2079 (s), 2048 (m), 2002 (s) cm^{-1}; ^1H NMR (C_6D_6, 333 K): HH isomer: $\delta=7.64$ (d, $J=6.9$ Hz, 2H), 6.60 (ddd, $J=8.7$, 6.9, 1.8 Hz, 2H), 6.36 (d, $J=8.7$ Hz, 2H), 5.77 (t, $J=6.9$ Hz, 2H); HT isomer $\delta=7.53$ (d, $J=$ 6.9 Hz, 2H), 6.60 (ddd, $J=8.7$, 6.9, 1.8 Hz, 2H), 6.31 (d, $J=8.7$ Hz, 2H), 5.77 (t, $J=6.9$ Hz, 2H). Complex **2**: elemental analysis (%) calcd for $C_{28}H_{16}N_4O_{12}Ir_4I_2$: C 20.72, H 0.99, N 3.45; found: C 20.94, H 1.18, N 3.25; IR (toluene): $\tilde{\nu}=\nu(CO)=2110$ (w), 2093 (s), 2066 (m), 2052 (s), 2027 (w) cm^{-1}; ^1H NMR (C_6D_6, 295 K): $\delta=9.52$ (dd, 4H), 6.47 (ddd, 4H), 6.26 (dd, 4H), 5.73 (td); $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): $\delta=175.3$, 167.2 (CO), 165.5 (CO), 152.7, 139.8, 116.7, 115.7. Complex **3**: elemental analysis (%) calcd for $C_{28}H_{16}N_4O_{12}Ir_4I_2$: C 20.72, H 0.99, N 3.45; found: C 20.52, H 0.78, N 3.44; IR (nujol): $\tilde{\nu}=\nu(CO)=2087$ (s), 2071 (m) 2050 (sh), 2041 (s) 2006 (m) cm^{-1}; ^1H NMR: $\delta=9.65$ (dd, 1H), 9.52 (dd (1H), 9.48 (dd, 1H), 9.21 (dd, 1H), 6.56 (m, 2H), 6.53 (m (1H), 6.45 (m, 1H), 6.38 (dd, 1H), 6.33 (dd, 1H), 6.20 (dd, 1H), 6.10 (dd, 1H), 5.90 (td, 1H), 5.86 (td, 1H), 5.74 (m, 2H).

[6] a) Crystallographically imposed twofold symmetry was observed relating the two halves of the tetranuclear complex. Crystal data for **2**: $C_{28}H_{16}I_2Ir_4N_4O_{12}$, $M_r=1623.04$, laminar crystal ($0.14\times0.11\times$ 0.06 mm), monoclinic, space group $C2/c$, $a=27.709(3)$, $b=9.2163(10)$, $c=16.9592(17)$ Å, $\beta=124.274(2)^\circ$, $V=3578.9(6)$ Å^{-3}, $Z=4$, $\rho_{calcd}=$ 3.012 g cm^{-3}, $F(000)=2888$, $T=150(2)$ K, $Mo_{K\alpha}$ radiation ($\lambda=$ 0.71073 Å, $\mu=16.615$ mm^{-1}). Data collected with a Bruker SMART APEX CCD diffractometer. Of 5545 measured reflections (2θ: 5–50°, ω scans 0.3°), 2662 were unique ($R_{int}=0.0808$); a multiscan absorption correction was applied (PLATON program) with min./max. transmission factors of 0.204/0.436. Structure solved by Patterson and difference-Fourier maps; refined using SHELXTL. Final agreement factors were $R1=0.0808$ (1965 observed reflections, $F^2>4\sigma(F^2)$) and $wR2=0.2264$; data/restrains/parameters 2662/72/227; GOF = 1.039. Largest peak and hole in the final difference map 6.084 and -3.483 e Å^{-3}. The limited quality of the structural data (also the merging and agreement factors, and the high residuals) should be necessarily associated to the diffracting weakness, to the anisotropic morphology, and to the high absorption of the crystals. b) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-165456 (**2**) and CCDC-165457 ($\mathbf{3}\cdot2CH_4O$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[7] Crystal data for $\mathbf{3}\cdot2CH_4O$: $C_{28}H_{16}I_2Ir_4N_4O_{12}\cdot2CH_4O$, $M_r=1687.13$, triclinic, space group $P\bar{1}$, $a=10.2440(8)$, $b=13.4751(10)$, $c=15.2437$ (11) Å, $\alpha=75.8696(15)$, $\beta=71.2963(13)$, $\gamma=78.1790(15)^\circ$, $V=$ 1914.4(2) Å^{-3}, $Z=2$, $\rho_{calcd}=2.927$ g cm^{-3}, $F(000)=1516$, $T=150(2)$ K, $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å, $\mu=15.541$ mm^{-1}). Data collected as described for **3** with an elongated block ($0.20\times0.06\times0.04$ mm). Of 10303 measured reflections (2θ: 5–50°, ω scans 0.3°), 6555 were unique; a multiscan absorption correction was performed (SADABS program) with min./max. transmission factors of 0.119/0.583. Structure solution and refinement as described for **2**. Final agreement factors were $R1=0.0656$ (4735 observed reflections) and $wR2=0.1606$. Data/restrains/parameters 6555/61/487; GOF = 1.049. Largest peak and hole in the final difference map 3.638 and -2.464 e Å^{-3}.[6b]

Enantiomeric Discrimination in a Reiterative Domino Coupling Process: Cu^I-mediated *Syn* Cyclotrimerization of Racemic Polycyclic Trimethylstannyl Bromonorbornadienes**

Sergio Cossu,* Chiara Cimenti, Paola Peluso, Antonio Paulon, and Ottorino De Lucchi

The fundamental concept of molecular discrimination considers the ability of a chemical object to identify, in the presence of alternative possibilities, a defined chemical counterpart through specific interactions.[1] When discrimination depends on the chiral properties of the chemical partners, only one of the events that derive from the possible stereochemical combinations can be realized.[1] In this context, a peculiar discrimination was observed during the self-coupling of racemic ketones that possess the bicyclo[2.2.1]heptene skeleton, either by means of aldol reactions or via organocuprate derivatives. The main feature of the reported

[*] Dr. S. Cossu, Dr. C. Cimenti, Dr. P. Peluso, Dr. A. Paulon, Prof. Dr. O. De Lucchi
Dipartimento di Chimica, Università Ca' Foscari di Venezia
Dorsoduro 2137, 30123 Venezia (Italy)
Fax: (+39) 041-257-8517
E-mail: cossu@unive.it

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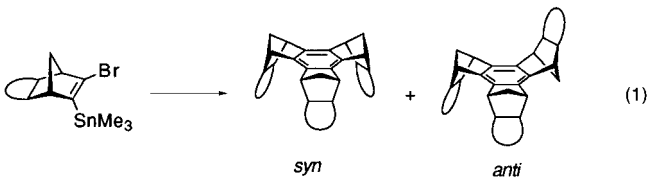
examples is that these enolate anions prefer to react with the reaction partner with the same absolute configuration.[2]

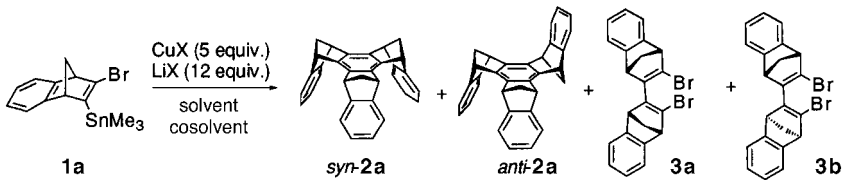
Herein we report a new Cu^{I}-mediated cyclotrimerization of racemic 3-bromo-2-trimethylstannylalkenes which affords *syn* cyclotrimers through a reiterative enantiomeric discrimination process. Previously, these compounds were obtained as mixtures with the corresponding *anti* isomers, through cyclotrimerization processes of substituted polycyclic alkenes [Eq. (1)].[3, 4] The reaction of polycyclic bromotrimethylstannyl alkenes in the presence of copper(II) nitrate in THF was



(1)

reported to afford a statistical 1:3 mixture of *syn* and *anti* isomers. On the other hand, only the Pd^{0}-catalyzed *anti*-selective synthesis of the cyclotrimer has been achieved efficiently.[3] Cyclotrimers with *syn* geometry have peculiar concave architectures and electronic potential surface (EPS) values,[3d, 5] similar to those reported for a variety of nonplanar complexing molecules such as cycloveratrylene,[6] molecular tweezers,[5] and others[7] which also present interesting applications in the field of liquid crystals.[8]

The benzonorbornadiene derivative **1a** was chosen as the model compound for the preliminary screening. The main results of the reaction depicted in Scheme 1 are summarized in Table 1. Under the reaction conditions of Piers et al.[9] (Table 1, entry 2), which are known to promote the coupling of vinylstannanes by using CuCl as the sole catalyst, and also



1a *syn*-**2a** *anti*-**2a** **3a** **3b**

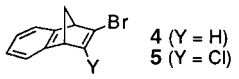
Scheme 1. General synthesis of coupled products from benzonorbornadiene **1a**.

Table 1. Reagents, solvents, reaction conditions, products, and yields for the reaction of **1a**.

Entry	CuX	Solvent	Co-solvent	LiX	*T*	*t* [h]	*syn*/*anti*-**2a** (% yield)	**3a**,**b** [%]
1	Cl	DMF	–	–	RT	1	1:2 (75)	traces
2	Cl	THF	–	Cl	RT	4	1:2 (5)	5
3	Cl	DMF	–	Cl	RT	19	1:1 (50)	50
4	Cl	DMF	DME	Cl	60 °C	4	2:1 (80)	–
5	Cl	DMF	DMDPE	Cl	RT	2	2:1 (70)	20
6	I	DMF	DME	Cl	RT	24	4.5:1 (80)	3
7	I	DMF	DME	Br	RT	360	3:1 (15)	35
8	Cl	DMF	DME	I	RT	168	1:1.5 (25)	25
9	I	DMF	DME	I	RT	12	–	–
10	I	NMP	DME	NO_3	RT	24	9:1 (80)	–

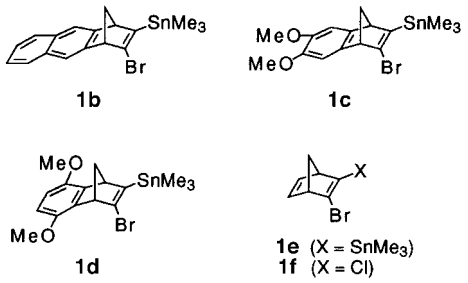
DMF = *N*,*N*-dimethylformamide; DME = 1,2-dimethoxyethane; DMDPE = *rac* 1,2-dimethoxy-1,2-diphenylethane; NMP = *N*-methylpyrrolidone. All compounds were separated, purified, and characterized by using NMR spectroscopy, GC-MS, and in some instances X-ray techniques.

in the reaction carried out in presence of LiCl as co-catalyst (Table 1, entry 2), a 1:2 mixture of stereoisomeric *syn* and *anti* trimers **2** is obtained. These results already seemed significant to us because this was the first time that we observed a preferential formation of the *syn* isomer (rather than the statistical 1:3 ratio). The reaction gave a 1:1 *syn*/*anti* ratio in DMF (Table 1, entry 3), without the formation of protodestannylated or chlorodestannylated compounds **4** and **5**, respectively.



A further improvement in the yields of the trimers resulted from the use of dimethoxyethane as cosolvent, which led to a reaction mixture composed exclusively of the cyclotrimers, in a 2:1 *syn*/*anti* ratio (Table 1, entry 4). We reasoned that the diether formed a complex with the copper intermediates and therefore tested the effect of the chiral enantiopure diether (*R*,*R*)-1,2-dimethoxy-1,2-diphenylethane (Table 1, entry 5), but no significant variation in the *syn*/*anti* selectivity was observed. A final definite improvement was found when CuCl was replaced with CuI (Table 1, entry 6), which led to a reaction mixture enriched with the *syn* cyclotrimer (4.5:1) in 80% yield. Other combination of salts (X = Cl, Br, I either in the copper or in the added lithium salt) did not improve the reaction further (Table 1, entries 7–9); instead, the reactivity of the system decreased, in agreement with the literature.[9, 10, 11] An exception proved to be lithium nitrate in NMP (Table 1, entry 10), which gave a result comparable with that in entry 5, with the extra advantage that it required milder reaction conditions and that it complete suppressed the formation of halogenated derivatives **5**.

The 3-bromo-2-trimethylstannyl-substituted naphthonorbornadiene **1b**, 6,7-dimethoxybenzonorbornadiene **1c**, 5,8-dimethoxybenzonorbornadiene **1d**, and norbornadiene **1e** were tested under the reaction conditions of entries 6 and 10 of Table 1. Naphthobenzonorbornadiene derivative **1b** exhibited the same selectivity as **1a**. The reaction of 6,7-dimethoxybenzonorbornadiene derivative **1c** proved to be totally stereoselective and afforded only the *syn* cyclotrimer **2c**. However, 5,8-dimethoxybenzonorbornadiene derivative **1d** was much less reactive, probably as a result of the steric interactions between the methoxy groups. The norbornadiene derivative **1e** was subjected to the reaction conditions of entry 5 and predominantly afforded the chlorodestannylated product **1f** as well as



1b **1c** **1d**

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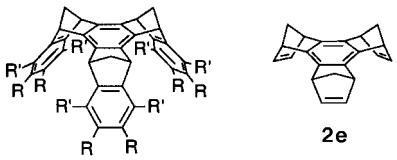
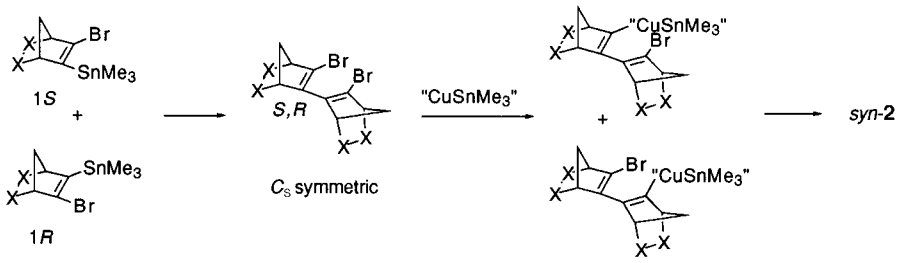
small amounts of cyclotrimers, with a preference for **2e** in a 3:1 *syn*/*anti* ratio.

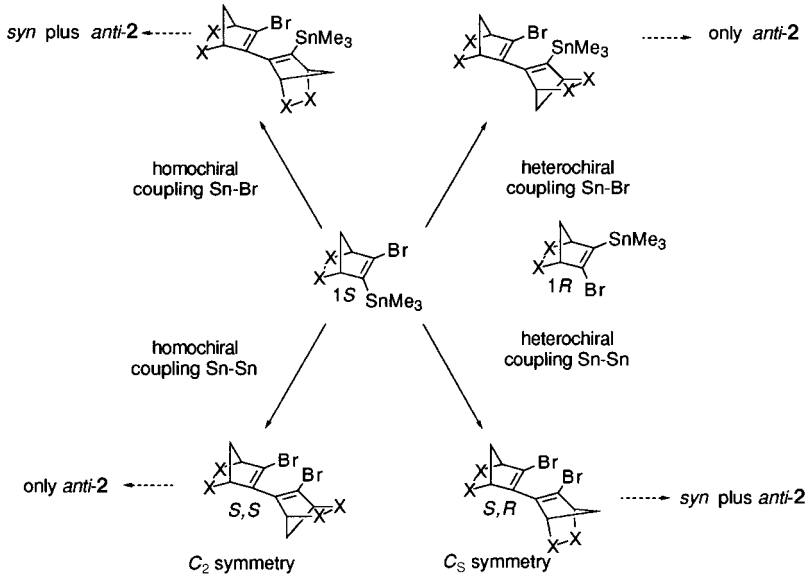


2b ($\widehat{R\,R}$ = -(CH=CH)$_2$ -; R' = H)
2c (R = OMe; R' = H)
2d (R = H; R' = OMe)



Scheme 3. Stereoselective formation of *syn*-**2**.

The predominant formation of the *syn* cyclotrimer requires an explanation, because the reaction of a racemic mixture of bromotrimethylstannyl alkenes **1** should afford a statistical 1:3 isomeric mixture. Taking into account that the coupling of **1** may occur between enantiomers of the same (homochiral) or opposite (heterochiral) configuration, and to establish if the mechanism proceeds through a Sn–Br or a Sn–Sn coupling process (Scheme 2), the reaction was carried out with the enantiomerically pure **1a**.[12] The reaction was dramatically



Scheme 2. Dimerization of bromotrimethylstannyl alkenes **1**.

slower than that of racemic **1a** and afforded only a small amount of dibromo dimer **3b** with C_2 symmetry and traces of *anti* cyclotrimer **2a**. This result suggests an Sn–Sn coupling process and an intrinsic reluctance of homochiral monomers to couple between themselves; it also suggests that the reaction cannot proceed *via* a symmetric alkyne metal complex in which the chiral information would be lost.[13] Hence the mechanism has to proceed with a total selectivity of each enantiomer in choosing the reaction partner of opposite configuration, not only in the formation of the dimer but also in the further coupling to the trimer (Scheme 3).

The described methodology represents the first highly selective direct access to *syn* cyclotrimers: starting from a racemic mixture of reagents, *via* racemic reactive species generated in situ, the final product is obtained after a domino regio- and chemoselective enantiomeric discrimination process, which involves the formation of diastereoisomeric intermediates, as a final result of a reiterative recognition between opposite enantiomers.[14] From a conceptual point of view, the ability of a reagent to discriminate between the *Re* and *Si* faces, which in the present case are defined by the trimethylstannyl-substituted sp^2 carbon atoms of two different molecules (the enantiomers), is virtually equivalent to an enantiotopic discrimination between the sp^2 carbon atoms of "*meso*" compounds, which are typical substrates for stereoselective desymmetrization processes.[15]

Experimental Section

General cyclotrimerization: A 25-mL, two-necked, flame-dried flask, equipped with a magnetic stirring bar, was charged with lithium salt (6 equiv) and further dried (110 °C, vacuum/argon) for 30 min. After cooling to room temperature, freshly dried DME (10 equiv), DMF (2 mL), and Cu^I salt (5 equiv) were added sequentially. After 15 min, the mixture was treated with a solution of **1a** (0.5 mmol) in dry DMF (1 mL) and stirred under argon at room temperature. The reaction was monitored by means of NMR spectroscopy. The crude reaction mixture was diluted with Et_2O (60 mL), washed with H_2O (3 × 40 mL), aqueous NH_4OH (10%, 4 × 30 mL), and brine (3 × 30 mL). The organic layer was separated and dried (Na_2SO_4). The residue was purified by flash chromatography (silica gel, eluant: gradient of *n*-hexane/ethyl acetate). Products were identified by comparison of their spectral data with those of the authentic samples.[3] Selected data for **3a, 3b**:[3d] ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ = 7.58–7.53, 7.41–7.37, 7.20–7.13 (series of m, 16H; Ar, both isomers), 4.69 (br s, 2H; **3a**), 4.46 (br s, 2H; **3b**), 3.86 (br s, 4H; both isomers), 2.57 (dt, J = 7.7 and 1.7 Hz, 1/2 AB system, 1H; **3b**), 2.45 (dt, J = 7.7 and 1.7 Hz, 1/2 AB system, 1H; **3a**), 2.26 (dt, J = 7.7 and 1.7 Hz, 1/2 AB system, 1H; **3b**), 2.19 (dt, J = 7.7 and 1.7 Hz, 1/2 AB system, 1H; **3a**); ^{13}C NMR ($CDCl_3$, 100 MHz): (both isomers) δ = 149.4, 149.2, 149.0, 148.7, 145.2, 144.1, 132.3, 131.1, 125.2, 125.1, 124.8, 124.5, 122.8, 122.2, 121.8, 121.7; (**3a**): 65.8, 60.1, 52.7; (**3b**): 66.7, 59.7, 53.0.

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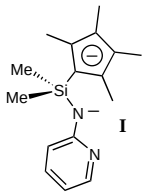
Yttrate Metathesis: Ligand Design for the Controlled Synthesis of f-Block Heterobimetallic Compounds**

Michael S. Hill* and Peter B. Hitchcock

Heterobinuclear derivatives in which one of the constituent metals is a member of Group 3 or the lanthanide series display unusual cooperative properties for a variety of diverse applications.[1] Approaches to bimetallic rare earth complexes that comprise metals other than those of Group 1 are however uncommon and usually inflexible with regard to the identity and coordination requirements of the second metal.[2] We describe here a simple and readily modified ligand design that permits the synthesis of molecules containing a trivalent rare earth element with a defined and proximal disposition to a second metal center. Our adopted strategy exploits the tendency of these large cations to form uninegative "ate" complexes, through the attachment of two amido-cyclopentadienyl dianions, **I**. Further bimetallic systems may then be synthesized by metathesis of the initial alkali metal derivative with a metal halide.



I

For this approach to succeed, the ligand design must suppress fragmentation of the lanthanide ate anion. Kempe et al. have shown that metathesis of a variety of early and late transition metal halides with aminopyridinato-based lanthanide ate complexes results in complete ligand transfer (albeit via unstable bimetallic intermediates).[3] This reactivity may be perturbed, however, permitting the synthesis of Nd/Rh and Nd/Pd bimetallic compounds, through the use of chelating bis-aminopyridinato ligands.[2d]

Dianion **I** is based upon the ligand framework applied by Bercaw et al. to the synthesis of "constrained geometry" olefin polymerization catalysts.[4] Our ligand constitution is determined by the demonstrated ability of Bercaw's and similar ligands to saturate the coordination sphere of Group 3 metals.[5] The amido functionality of **I** results from the deprotonation of a 2-aminopyridine substituent, selected for the capacity of 2-aminopyridinato ligands to bind a wide variety of metal centers.[6] For the initial investigation of the ligating properties of **I**, we chose to study the chemistry of trivalent yttrium derivatives, mindful of the diagnostic solution-state NMR data derived from observation of the ^{89}Y nucleus and its attendant internuclear couplings.

Reaction of YCl_3 and two equivalents of the dilithium derivative of **I** in THF afforded the colorless complex **1** [Eq. (1)]. Complex **1** is very soluble in THF and aromatic solvents but poorly soluble in aliphatic hydrocarbons. The

[*] Dr. M. S. Hill, Dr. P. B. Hitchcock
School of Chemistry, Physics and Environmental Science
University of Sussex
Brighton BN1 9QJ (UK)
Fax: (+44) 1273-677196
E-mail: m.s.hill@sussex.ac.uk

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