increase in ^{1}J(F,C) coupling (378 Hz compared with 322 Hz in **1**). This effect appears to be characteristic for ^{1}J(F,C) couplings in highly coordinated compounds with linear CF_3-element-CF_3 units.[5]

In the $^{13}C\{^{1}H\}$ NMR spectrum the CF_3 groups were detected as expected as a quartet of quartets (Table 1). The unsymmetrical anion **3** displays a doublet of multiplets at $\delta = -94.0$ in the ^{29}Si NMR spectrum. The above-mentioned by-product was also detected as an additional product. Two signals are detected in the ^{19}F NMR spectrum of **3**, a quartet centered at $\delta = -50.4$ and a doublet at $\delta = -63.9$. The Me_3Si resonance in the ^{13}C NMR spectrum shows an additional doublet splitting (^{2}J(C,F) = 47 Hz).

On the basis of NMR data, anions **2** and **3** are unambiguously identified as the intermediates in reactions of **1** with $[Me_4N]F$ in THF. Attempts to isolate **2** and **3** by condensing off all low-boiling components at a maximum temperature of −20°C failed. After the volume was reduced to approximately one third of the original volume, spontaneous decomposition occurred with formation of a highly viscous brown residue.

It is noteworthy that addition of **1** to a solution of **3** enhances the formation of **2** [Eq. (3)], whereas addition of $[Me_4N]F$ to a solution of **2** does not give any evidence for the formation of **3** [Eq. (4)].

$$\underset{\mathbf{3}}{[Me_4N][Me_3Si(CF_3)F]} + \underset{\mathbf{1}}{Me_3SiCF_3} \longrightarrow \underset{\mathbf{2}}{[Me_4N][Me_3Si(CF_3)_2]} + Me_3SiF \qquad (3)$$

$$\underset{\mathbf{2}}{[Me_4N][Me_3Si(CF_3)_2]} + [Me_4N]F \nrightarrow 2\ \underset{\mathbf{3}}{[Me_4N][Me_3Si(CF_3)F]} \qquad (4)$$

The addition of cyclohexanone either to a solution of **2** or **3** leads spontaneously to 1-trifluoromethylcyclohexan-1-olates, which after treatment with acids are converted into the corresponding alcohol, 1-trifluoromethylcyclohexan-1-ol. The NMR data of the alcohol match well with literature values.[6]

These and further results[4, 5] demonstrate that **2** and **3** are the reactive intermediates in nucleophilic trifluoromethylations.

Experimental Section

2: $[Me_4N]F$ (0.25 g, 2.7 mmol) was suspended in a 10 mm NMR tube in a mixture of THF (4 mL) and $[D_8]$THF (2 mL). At −90°C **1** (0.80 mL, 0.76 g, 5.4 mmol) was added. The mixture was warmed to −60°C and stirred for 1 h. A colorless solution of **2** was obtained which was investigated by NMR spectroscopy at −60°C.

3: $[Me_4N]F$ (0.25 g, 2.7 mmol) was suspended in THF (3 mL) in an 8 mm NMR tube. At −90°C **1** (0.20 mL, 0.19 g, 1.3 mmol) was added. After warming to −60°C and stirring for 1 h, the colorless solution was investigated by NMR spectroscopy (external lock $[D_6]$acetone).

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[1] G. K. S. Prakash, A. K. Yudin, *Chem. Rev.* **1997**, *97*, 757–786.

[2] R. J. Corriu, Y. J. Colin in *Chemistry of Organosilicon Compounds, Vol. 2* (Eds.: S. Patai, Z. Rappoport), Wiley, Chicester, **1989**, pp. 1241–1288.

[3] D. J. Adams, J. H. Clark, L. B. Hansen, V. C. Sanders, S. J. Tavener, *J. Fluorine Chem.* **1998**, *92*, 123–125.

[4] W. Tyrra, D. Naumann, N. V. Kirij, A. A. Kolomeitsev, Yu. L. Yagupolskii, *J. Chem. Soc. Dalton Trans.* **1999**, 657–658.

[5] For comparison: $[I(CF_3)_2]^-$: ^{1}J(F,C) = 442 Hz (CF_3I: ^{1}J(F,C) = 344 Hz); $[Te(CF_3)_3]^-$ (axial): ^{1}J(F,C) = 414 Hz ($Te(CF_3)_2$: ^{1}J(F,C) = 354 Hz); N. Maggiarosa, W. Tyrra, D. Naumann, N. V. Kirij, Yu. L. Yagupolskii, unpublished results.

[6] a) U. Hartkopf, A. de Meijere, *Angew. Chem.* **1982**, *94*, 444–445; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 443–444; *Angew. Chem. Suppl.* **1982**, 1121–1127 (^{13}C); b) S. Sibille, S. Mcharek, J. Perichon, *Tetrahedron* **1989**, *45*, 1423–1428 (^{1}H, ^{19}F).

Rapid Screening of Olefin Polymerization Catalyst Libraries by Electrospray Ionization Tandem Mass Spectrometry**

Christian Hinderling and Peter Chen*

Herein we report the use of electrospray ionization tandem mass spectrometry (ESI-MS/MS) and gas-phase ion–molecule reactions for the rapid screening of Brookhart-type Pd^{II} olefin polymerization catalysts.[1, 2] Whereas the preparation and testing of individual catalysts has long been pursued, the screening of catalyst libraries is a recent phenomenon. Screening of libraries of compounds, either natural products or synthetic molecules which may have been combinatorially prepared, has been extensively applied in biological systems and for the discovery of lead compounds in medicinal chemistry. Attempts to apply the general idea of screening to organometallic catalysts[3] have only recently appeared, with thermographic,[4] fluorescence quenching,[5] conventional microwell parallel reactions,[6] and polymer-supported "bead" methods[7] having been tried. Only the last of these has been attempted for polymerization reactions catalyzed by organometallic complexes, the other methods being inapplicable for a variety of technical reasons. Even the polymer-supported bead method, when applied to polyolefin catalyst screening, suffers from a nonoptimal encoding procedure that limits its usefulness. The experiment reported here has the advantages

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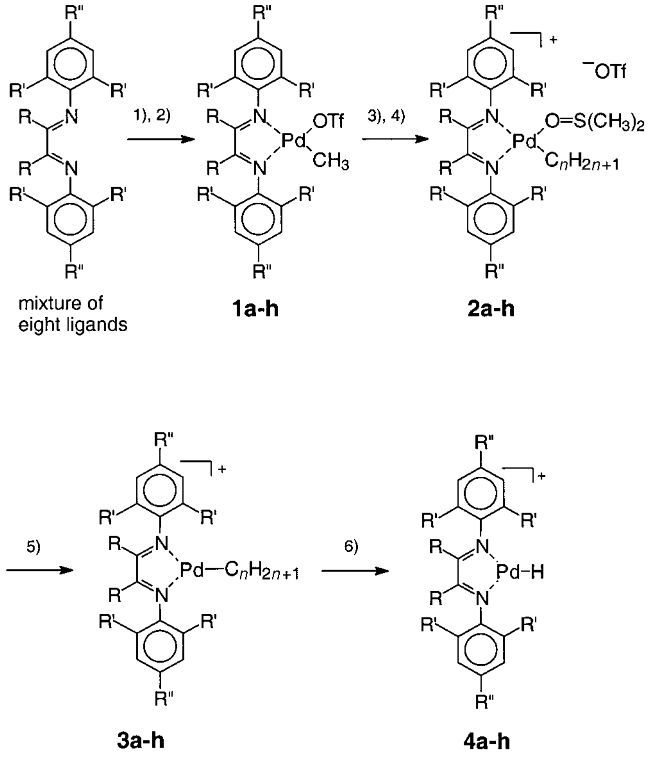
of high sensitivity (milligram quantities), very short assay times (one hour), direct simultaneous competitive screening of multiple catalysts according to their propensity for high polymer formation (rather than a derivative property such as heat release), good prospects for scaling up to large libraries, and implicit encoding of catalyst identity by mass. A novel application of simple ion–molecule reactions drastically simplifies the mass spectrum of complicated mixtures.

The Brookhart-type Pd^{II} complexes[1] were chosen as test molecules for screening because of their ease-of-handling, and also because the ligands could, in principle, be synthesized combinatorially. The eight complexes **1a–h** in the test library were synthesized simultaneously by a modification of the literature procedure starting with an equimolar mixture of the eight individually prepared diimine ligands[8] in diethyl ether, reaction with one equivalent of [(cod)Pd(CH_3)(Cl)][9] at room temperature overnight, evaporation to dryness, washing with hexane, and activation of the solid orange residue in CH_2Cl_2 solution with AgOTf (OTf = trimethanesulfonate, Scheme 1).

A check of the catalyst mixture by ^{1}H nmr spectroscopy prior to activation showed comparable concentrations of each of the eight complexes.[10] An electrospray mass spectrum of the mixture of complexes (activated with AgOTf and then quenched with acetonitrile), showed **1a–h** all to be present, again with comparable peak intensities. The solution comprised of the mixture of complexes, on the order of 10^{-3} M for each catalyst in CH_2Cl_2, was saturated with ethylene and allowed to react at −10 °C for one hour, then quenched by adding to a hundredfold greater volume of 3% DMSO in CH_2Cl_2. The solution was then electrosprayed in a Finnigan MAT TSQ-7000 tandem mass spectrometer, as previously described.[11] The electrospray mass spectrum, recorded by scanning the first quadrupole, was complex, and showed multiple, overlapping series of oligomeric and polymeric ions corresponding to each catalyst species with between zero and approximately one hundred ethylene units added,[12] as seen in Figure 1.



principal *m/z* for **4a-h**

a)	R = Me, R' = H, R" = H	343
b)	R = Me, R' = Me, R" = H	399
c)	R = Me, R' = *i*Pr, R" = H	511
d)	R = Me, R' = Me, R" = Me	427
e)	R = Me, R' = Me, R" = Br	557
f)	R = H, R' = Me, R" = H	371
g)	R = H, R' = *i*Pr, R" = H	483
h)	R = H, R' = Me, R" = Br	529

Scheme 1. 1) [(cod)Pd(CH_3)(Cl)], 20 °C, 10 h; 2) $AgSO_3CF_3$; 3) excess C_2H_4, −10 °C, 1 h; 4) DMSO; 5) electrospray under mild desolvation conditions to give polymeric ions (and loss of DMSO); 6) reject all ions below a certain mass and subject the remaining high-mass ions to collision with Xe.

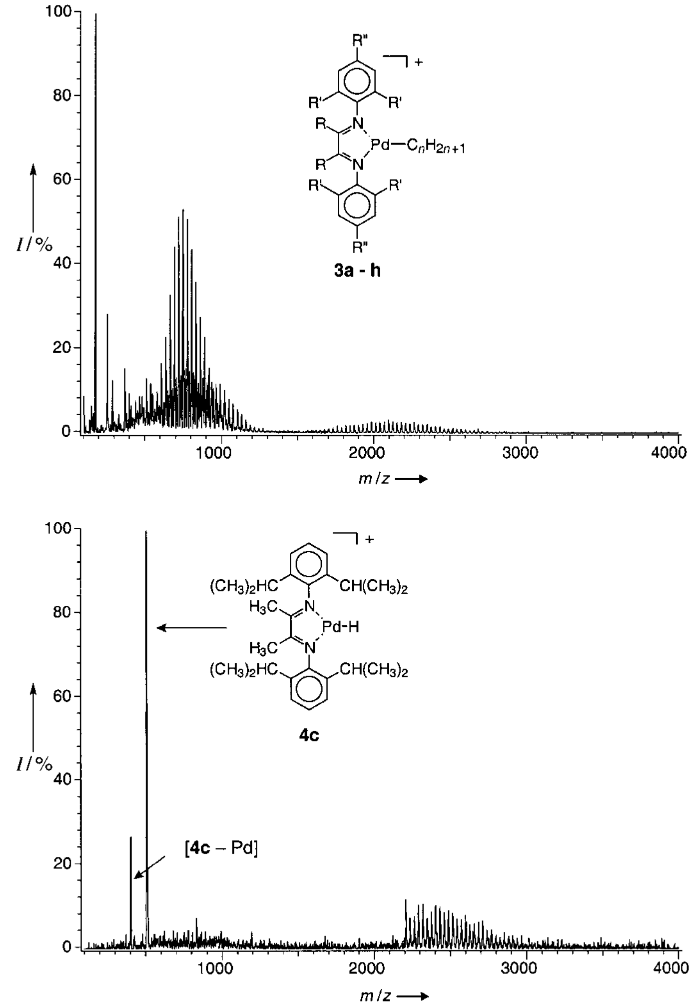


Figure 1. Electrospray ionization mass spectrum (top) of the mixture of oligomeric/polymeric ions **3a–h** after reaction of **1a–h** with ethylene and quenching with DMSO. After selection of ions with *m/z* > 2200 and CID with Xe to induce *β*-hydride elimination (bottom), the daughter ion spectrum shows a predominant peak at *m/z* 511 and a smaller peak at *m/z* 405. The former peak corresponds to **4c** and the latter to a secondary fragment [**4c** – Pd].

Additional complexity or broadening in the mass spectrum comes from the isotopic distribution in palladium,[13] as well as the ^{13}C satellite peaks (which become more prominent as the polymer grows), features that are not resolved in the present mass spectra. The first quadrupole was then set to radiofrequency-only mode, meaning that only ions above a given cutoff *m/z* ratio, in this case either *m/z* 1000 or 2200, would be transmitted. It should be emphasized that high resolution is not needed at this step. The transmitted high-mass ions were collided with xenon (ca. 0.5 mTorr) in an octopole ion guide at nominal ion energies between 30 and 80 eV. Representative daughter ion spectra for the two different cutoffs, recorded by scanning the second quadrupole, are shown in Figure 2.

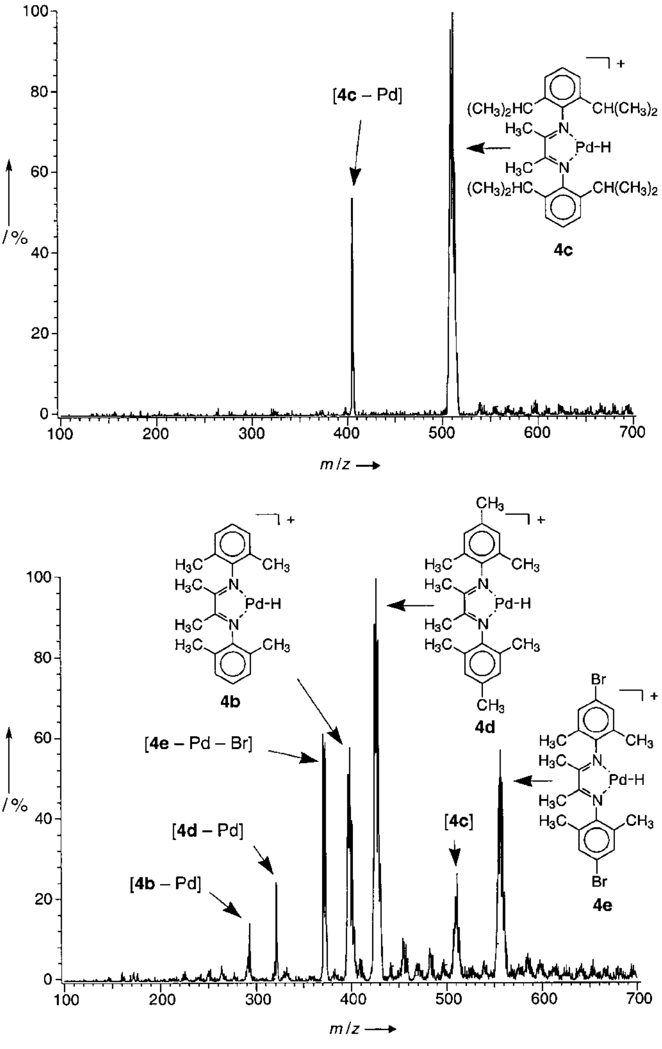


Figure 2. Daughter ion spectra of the low-mass region for mass cutoffs in the first quadrupole of *m/z* 2200 (top) and *m/z* 1000 (bottom).

Clearly indicated in the upper trace of Figure 2 is the predominance of the mass peak(s) at *m/z* 511, which corresponds to ion **4c**, formed by collision-induced β-hydride elimination of the hydrocarbon chain from the ion built from catalyst **1c**. The small "sharp" peak at *m/z* 405 is a secondary fragmentation product corresponding to the diimine ligand without palladium. The secondary fragments [**4** – Pd] (or [**4e** – Pd – Br]) were unambiguously associated with the original ions **4** by performing parent ion scans on both **4** and the secondary fragment masses. The result clearly indicates that, of the eight potential catalysts, **1a**–**h**, complex **1c** is the best actual polymerization catalyst. this result is in agreement with previous reports.[1] Similarly, the daughter ion spectum with a lower mass cutoff shows that the next best catalysts are **1b**, **1d**, and **1e**. The agreement of the mass spectrometric and conventional assays is claimed as evidence for the efficacy of the new method for catalyst screening. The ordering (**1c** $\gg$ **1b** $\approx$ **1d** $\approx$ **1e** $>$ others) matches expectations based on the argument that associative chain transfer is disfavored when steric considerations force the arene moieties to twist out of the N-Pd-N plane. The similarity between **1b**, **1d**, and **1e** also suggests that electronic effects on catalyst efficacy are relatively small. Interestingly, **1g** did not produce high molecular weight polymers in the simultaneous screen, which we then confirmed by assaying it individually. This observation means that the isopropyl groups on the arene have little effect when the backbone of the 1,2-diimine ligand is unsubstituted. Brookhart et al. did report reductions[1] in the mean molecular weight (50-fold) and yield (5-fold) of polymer formed from **1g** relative to that from **1c**.

While electrospray ionization mass spectrometry[14] has been applied extensively to the biopolymers since the introduction of the technique by Fenn and co-workers,[15] applications to organometallic chemistry have come only recently. Straightforward analytical applications were first reported by Chait,[16] Colton[17] and their co-workers. Mechanistic studies of ion–molecule reactions by electrosprayed organometallic ions have been addressed by the present group[11] and by Posey and co-workers.[18] Further applications from a few other groups[19] have also appeared, with two groups[20] investigating polymerization reactions. Neither group attempted, however, to examine more than one catalyst at a time. The mass spectra were furthermore so complicated by the distribution of oligomeric and/or polymeric ions originating from even a single catalyst as to preclude any possibility of screening. The present application is the first instance of ESI-MS/MS as an assay of multiple, competitive, simultaneous, catalyzed reactions in solution. The unique feature of the method, the use of an ion–molecule reaction, simple collision-induced dissociation (CID) in this instance, to simplify the otherwise dauntingly complicated mass spectrum of a mixture of polymers, is a novel development.

The combination of sensitivity, speed, direct assay, and versatility demonstrated in this pilot experiment means that one can already imagine screening large ($n \gg 100$) libraries of combinatorially generated catalysts. The availability of autosamplers for electrospray mass spectrometers suggests furthermore that automation of the screening process might be possible. The applicability of this methodology to other polymerization catalysts,[21, 22, 23] and to nonpolymer-forming reactions is under further investigation.

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[1] a) L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414; b) L. K. Johnson, S.Mecking, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 267.

[2] Much of the basic chemistry of the diimine complexes was explored by: a) M. Svoboda, H. tom Dieck, *J. Organomet. Chem.* **1980**, *191*, 321; b) H. tom Dieck, M. Svoboda, T. Greiser, *Z. Naturforsch. B* **1981**, *36*, 823.

[3] A general review of screening for catalysts has recently appeared: B. Jandeleit, H. W. Turner, T. Uno, J. A. M. van Beck, W. H. Weinberg, *CatTech* **1998**, *2*, 101.

[4] a) S. J. Taylor, J. P. Morken, *Science* **1998**, *280*, 267; b) M. T. Reetz, M. H. Becker, K. M. Kühling, A. Holzwarth, *Angew. Chem.* **1998**, *110*, 2792; *Angew. Chem. Int. Ed.* **1998**, *37*, 2647.

[5] A. C. Cooper, L. H. McAlexander, D. H. Lee, M. T. Torres, R. H. Crabtree, *J. Am. Chem. Soc.* **1998**, *120*, 9971.

[6] a) K. Burgess, H. J. Lim, A. M. Porte, G. A. Sulikowski, *Angew. Chem.* **1996**, *108*, 192; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 220; b) S. M. Senkan, *Nature* **1998**, *394*, 350.

[7] a) B. M. Cole, K. D. Shimizu, C. A. Krueger, J. P. A. Harrity, M. L. Snapper, A. H. Hoveyda, *Angew. Chem.* **1996**, *108*, 1776; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1668; b) T. R. Boussie, C. Coutard, H. Turner, V. Murphy, T. S. Powers, *Angew. Chem.* **1998**, *110*, 3472; *Angew. Chem. Int. Ed.* **1998**, *37*, 3272.

[8] J. M. Kliegman, R. K. Barnes, *J. Org. Chem.* **1970**, *35*, 3140.

[9] R. E. Rülke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. W. N. M. van Leewen, K. Vrieze, *Inorg. Chem.* **1993**, *32*, 5769.

[10] The methyl resonances were sharp singlets, well-separated from each other and from other resonances.

[11] a) C. Hinderling, D. A. Plattner, P. Chen, *Angew. Chem.* **1997**, *109*, 272; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 243; b) C. Hinderling, D. Feichtinger, D. A. Plattner, P. Chen, *J. Am. Chem. Soc.* **1997**, *119*, 10793; c) D. Feichtinger, D. A. Plattner, *Angew. Chem.* **1997**, *109*, 1796; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1718; d) D. Feichtinger, D. A. Plattner, P. Chen, *J. Am. Chem. Soc.* **1998**, *120*, 7175; e) C. Hinderling, C. Adlhart, P. Chen, *Angew. Chem.* **1998**, *110*, 2831; *Angew. Chem. Int. Ed.* **1998**, *37*, 2685.

[12] When **1c** alone is treated with ethylene, quenched, and analyzed by ESI-MS, the envelope of the oligomeric ions parallels the predicted distribution based on the rate constants reported in ref. [1].

[13] Natural abundances are as follows (%): ^{102}Pd 1.02, ^{104}Pd 11.14, ^{105}Pd 22.33, ^{106}Pd 27.33, ^{108}Pd 26.46, ^{110}Pd 11.72.

[14] A complete monograph on the technique is: *Electrospray Ionization Mass Spectrometry* (Ed.: R. D. Cole), Wiley, New York, **1997**.

[15] C. M. Whitehouse, R. N. Dreyer, M. Yamashita, J. B. Fenn, *Anal. Chem.* **1985**, *57*, 675.

[16] V. Katta, S. K. Chowdhury, B. Chait, *J. Am. Chem. Soc.* **1990**, *112*, 5348.

[17] a) R. Colton, J. C. Traeger, *Inorg. Chim. Acta* **1992**, *201*, 153; b) Work from this group has been reviewed: R. Colton, A. D'Agostino, J. C. Traeger, *Mass Spec. Rev.* **1996**, *14*, 79.

[18] a) T. G. Spence, T. D. Burns, L. A. Posey, *J. Phys. Chem. A* **1997**, *101*, 139; b) T. G. Spence, T. D. Burns, G. B. Guckenberger, L. A. Posey, *J. Phys. Chem. A* **1997**, *101*, 1081; c) T. G. Spence, B. T. Trotter, T. D. Burns, L. A. Posey, *J. Phys. Chem. A* **1998**, *102*, 6101.

[19] a) S. R. Wilson, Y. Wu, *Organometallics* **1993**, *12*, 1478; b) A. O. Aliprantis, J. W. Canary, *J. Am. Chem. Soc.* **1994**, *116*, 6985; c) L. A. P. Kane-Maguire, R. Kanitz, M. M. Sheil, *J. Organomet. Chem.* **1995**, *486*, 243; d) B. H. Lipshutz, K. L. Stevens, B. James, J. G. Pavlovich, J. P. Snyder, *J. Am. Chem. Soc.* **1996**, *118*, 6796.

[20] a) Z. M. Dzhabieva, V. P. Kozlovskii, Yu. M. Shul'ga, A. F. Dodonov, G. P. Belov, *Russ. Chem. Bull.* **1996**, *45*, 474; b) R. Saf, R. Schitter, C. Mirtl, F. Stelzer, K. Hummel, *Macromolecules* **1996**, *29*, 7651.

[21] Palladium-based catalysts for olefin–CO copolymerization: a) M. Brookhart, F. C. Rix, J. M. DeSimone, J. C. Barborak, *J. Am. Chem. Soc.* **1992**, *114*, 5894; b) E. Drent, P. H. M. Budzelaar, *Chem. Rev.* **1996**, *96*, 663.

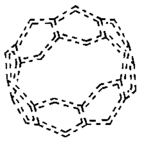
[22] Iron and cobalt-based polyolefin catalysts: B. L. Small, M. Brookhart, A. M. A. Bennett, *J. Am. Chem. Soc.* **1998**, *120*, 4049.

[23] Molybdenum and tungsten-based ROMP catalysts: a) B. L. Goodall, W. J. Kroenke, R. J. Minchak, L. F. Rhodes, *J. Appl. Polymer Sci.* **1993**, *47*, 607; b) M. McCann, D. McDonnell, B. L. Goodall, *J. Mol. Catal. A* **1995**, *96*, 31; c) L. F. Rhodes (B. F. Goodrich, USA), EP-B 0435146 A2, **1990** [*Chem. Abstr.* **1991**, *115*, 184150]; d) A. M. Mazany (B. F. Goodrich, USA), EP-B 0755938 A1, **1995** [*Chem. Abstr.* **1997**, *126*, 200209].

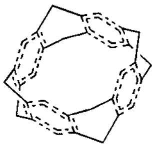
Structures, Magnetic Properties, and Aromaticity of Cyclacenes**

Hyuk Soon Choi and Kwang S. Kim*

The quest to design novel molecular architectures that are intellectually appealing and possess exciting physical and chemical properties has attracted the attention of a number of experimental[1] and theoretical chemists.[2] This has led to the postulation of a number of belt-shaped structures made up of laterally fused benzoid hydrocarbons such as cyclacenes (**1**), collarenes (**2**), and beltenes (**3**). While collarenes have been synthesized, the synthetic approaches to cyclacenes proposed by Vögtle[3] have stalled at the stage of their precursors.[4]



1



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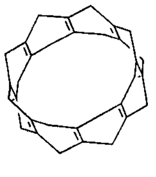

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Cyclacenes are of interest because of their remarkable structural similarity to carbon nanotubes and the possible utility of their cylindrical cavities in host–guest chemistry.[4] Hence, a detailed investigation of their physical and chemical properties could be a useful aid in the broader field of chemistry. The present theoretical study of [*n*]cyclacenes (where *n* refers to the number of fused benzene rings) reveals unusual electronic and magnetic properties, which can be associated with the peripheral rings of the structures being similar to two fused [2*n*]trannulenes (where *n* refers to the number of carbon atoms in the ring). This is in contrast to the original hypothesis of [*n*]cyclacenes having completely aromatic carbon skeletons.

Schleyer and co-workers have recently reported some interesting properties of [*n*]trannulenes (Figure 1a and b).[5] For $n = 4k+2$ ($k =$ integer), [*n*]trannulenes favor aromatic singlet states of D_{nd} symmetry in which all C–C bond lengths are equivalent. On the other hand, for $n = 4k$, singlet states of D_n symmetry are antiaromatic and display C–C bond length alternation. These singlet states are only 5–7 kcal mol^{-1} lower in energy than the corresponding triplet states, which are stabilized by aromaticity. On a similar note, three possible valence isomers of D_{nh}, C_n, and D_n symmetry for [*n*]cyclacenes (Figure 1c–e) existing in either the singlet or triplet state can be considered.

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