Synthesis of New Polydentate Pyrazolyl-ethene Ligands by Interaction of 1*H*-Pyrazole and 1,1,2,2-Tetrabromoethane in a Superbasic Medium

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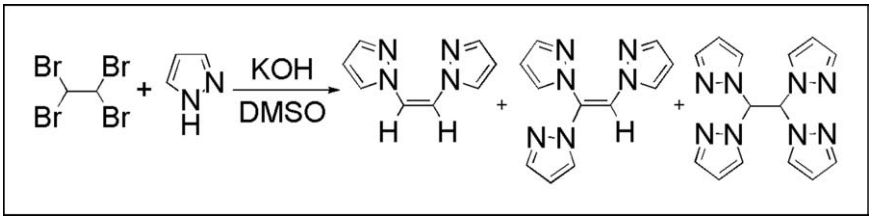

Reaction of pyrazole and 1,1,2,2-tetrabromoethane in a superbasic medium dimethylsulfoxide-potassium hydroxide was investigated, and a number of pyrazolyl- and bromo-substituted ethenes, which are the products of concurrent substitution and elimination reactions, were identified. Carrying out the reaction using different reagent mole ratios allowed to selectively isolate *Z*-1,2-bis(pyrazol-1-yl)ethene, 1,1,2-tris(pyrazol-1-yl)ethane, and 1,1,2,2-tetrakis(pyrazol-1-yl)ethane. Crystal structure of {*Z*-1,2-bis (pyrazol-1-yl)ethene}dichlorozinc was established using X-ray diffraction method.

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INTRODUCTION

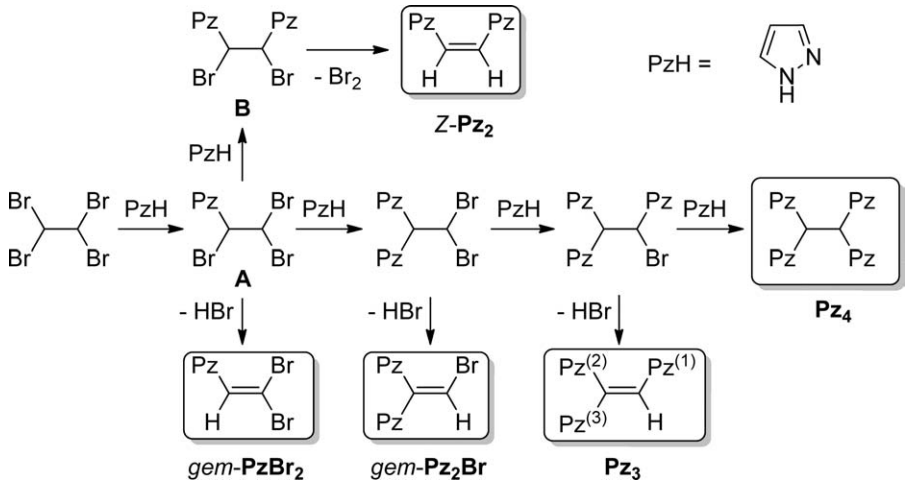
Multitopic pyrazole-containing ligands constitute a third-generation family of scorpionate ligands [1–3]. First-generation scorpionates—poly(pyrazol-1-yl)borates and alkanes containing two or more pyrazole rings joined together by boron of carbon linker into one chelating unit were first prepared by Trofimenko in 1966 [4,5] In the following years, chemistry of scorpionates developed into an independent area of coordination chemistry [6–8]. Modification of the bridging carbon between the pyrazole rings in poly(pyrazol-1-yl)alkanes with additional coordinating functionalities gave rise to the second-generation scorpionate ligands. Starting in 2001, Reger *et al*. [9] first prepared new third-generation ligands containing two, three of four poly(pyrazole) chelating units in one molecule, ligands based on bis(pyrazol-1-yl)methane being the most recent ones [10,11].

We have developed a convenient synthetic procedure for preparing bis(pyrazol-1-yl)alkane ligands by the reaction of pyrazole with dibromoalkanes in a superbasic dimethylsulfoxide (DMSO)-potassium hydroxide (KOH) medium [12,13]. In an attempt to use this synthetic route to prepare a new bitopic ligand 1,1,2,2-tetrakis(pyrazol-1-yl)ethane (**Pz$_4$**, Scheme 1), which contains two bis(pyrazol-1-yl)methane chelating ligands directly linked together without the aid of a spacer, we have carried out the reaction of 1*H*-pyrazole (PzH) with 1,1,2,2-tetrabromoethane (TBE) in 4:1 molar ratio [14]. The new ligand was isolated albeit in a modest yield (20–25%). As a nearly full conversion of starting pyrazole was achieved, it is evident that its reaction with TBE is accompanied by some side reactions that decreased the target product yield. In our previous publication, the overall yield of 57% was mistakenly attributed to **Pz$_4$**, not taking into account the side products [14]. In this article, we report the results of a detailed PzH–TBE reaction investigation that allowed us to improve the yield of the target 1,1,2,2-tetrakis(pyrazol-1-yl)ethane product and isolate, depending on the reaction conditions, some other new polydentate pyrazole-derived ligands.

RESULTS AND DISCUSSION

The reaction of PzH with TBE in 4:1 molar ratio in a superbasic DMSO-KOH medium was carried out for 24 h until the quantity of starting pyrazole ceased to diminish thin layer chromotography (TLC) control. The product 1,1,2,2-tetrakis(pyrazol-1-yl)ethane was isolated by the precipitation of the reaction mixture into the water in 20–25% yield. It is evident that the low yield is associated with some side reactions of TBE, which can also involve

Scheme 1



pyrazole and prevent the formation of **Pz_4** product. To study the nature of these side processes, we have carried out the pyrazole–TBE reactions in a variety of conditions, namely different PzH–TBE molar ratio and PzH concentration in the reaction mixture. The reactions were allowed to run until full conversion of PzH was achieved. After dilution of the reaction mixture with water, **Pz_4** compound was isolated, which turned out to be the only water-insoluble product. The filtrate was extracted with chloroform and the resulting mixtures of products were examined by GC/MS and NMR techniques.

The dependence of product mixture composition on the PzH–TBE ratio was investigated first. The PzH–TBE reaction was carried out using 1:1, 2:1, and 3:1 molar ratios of the reagents. In all the cases, the reactions yielded complex product mixtures, in which pyrazolyl- and bromo-substituted ethenes were the dominating components (Table 1). Formation of unsaturated products reveals that elimination processes take place concurrently with nucleophilic substitution reactions, which is often the case for this class of reactions [15,16].

When pyrazole reacted with TBE in 1:1 ratio, bromoethenes containing one or two pyrazole rings were the major products. The **$PzBr_2$** and **Pz_2Br** products were identified by molecular ions and characteristic fragment peaks in their mass spectra. As NMR spectra of product mixtures were rather complex, density functional theory (DFT) shielding constant calculations were used for assigning signals to specific products. Compound **$PzBr_2$** was the major product in case of 1:1 reaction, while **Pz_2Br** compound dominated in the mixture obtained from 2:1 PzH–TBE reaction. Obviously, the formation of these products is a result of two subsequent reactions—substitution of bromine atoms by pyrazolyl residue and hydrogen bromide elimination from the resulting product (Scheme 1). For 2:1 PzH–TBE reaction, 1,1,2-tris(pyrazol-1-yl)ethane **Pz_3** was detected as a second to the dominating product. Its formation can be attributed to three subsequent bromo-to-pyrazolyl substitutions followed by a hydrogen bromide elimination step (Scheme 1).

In case of 3:1 PzH–TBE ratio, **Pz_3** was obtained as a major product, while only little amount of **Pz_2Br** was formed and no **$PzBr_2$** was detected at all. As for 4:1 PzH–TBE reaction, **Pz_4** compound was isolated as the main product by precipitation of the reaction mixture into water. The extract of the filtrate contained two major components—**Pz_3** compound and 1,2-bis(pyrazol-1-yl)ethene **Pz_2**, the latter being the dominating one (Table 1). The same **Pz_2** compound was detected in 1:1 to 1:3 product mixtures as a minor component. Formation of **Pz_2** compound can be explained by a two-step route involving substitution of vicinal bromine atoms for pyrazolyl residues followed by a debromination of the resulting dibromoderivative (Scheme 1).

It is interesting to note that when the concentration of pyrazole was raised to 1.5*M*, maintaining the PzH–TBE ratio at 2:1, **Pz_2** compound became the main product (51 mol %), while the amount of **Pz_2Br** decreased considerably and that of **Pz_3** remained essentially the same.

It should be noted that several structural isomers are possible for some of the detected compounds—two for **Pz_2** and three for **$PzBr_2$** and **Pz_2Br** (Scheme 2), but according to GC/MS data, one of the isomers always dominated in the product mixture (Table 1). NMR and MS methods alone do not provide enough data for unequivocal structure assignments for compounds **Pz_2**, **Pz_2Br**, and **$PzBr_2$**. We have found that the combination of ^{1}H- and ^{13}C-NMR studies with DFT shielding constants calculations allowed to perform the complete NMR signal assignments and to designate the structure for each of the detected compounds.

The details of computational procedures for shielding constant estimation are given in the Experimental

Table 1

Products of pyrazole–tetrabromoethane reaction at different reagent ratios.

Product	Composition of product mixture (mol % by NMR) at PzH–TBE ratio				
	1:1[a]	2:1[a]	2:1[b]	3:1[a]	4:1[a]
gem-**PzBr$_2$**	48.4	1.76[c]	0.75[c]	–	–
gem-**Pz$_2$Br**	22.8	43.9	17.1	10.7	–
Z-**Pz$_2$**	11.1	24.4	51.0	4.5	77.2
E-**Pz$_2$**	–	–	0.95[c]	–	–
Pz$_3$	17.6	31.7	31.9	84.8	22.3
PzBr$_3$	12.9[c]	–	–	–	–
gem-**Pz$_2$Br$_2$**	8.6[c]	5.2[c]	–	–	–
Tetrabromoethene	8.5[c]	–	–	–	–

[a] $C_{PzH} = 1M$.
[b] $C_{PzH} = 1.5M$.
[c] From GC/MS.

Table 2

Correlation between experimental and calculated NMR shifts.

Compound	r^2 (^{1}H)	r^2 (^{13}C)	$\Delta\delta^{exp}_{(C=C)}/\Delta\delta^{calc}_{(C=C)}$
Pz$_3$	0.951	0.979	7.11/14.96
gem-**Pz$_2$Br**	0.945	0.911	35.9/32.0
Z-**Pz$_2$Br**	0.314	0.734	35.9/9.8
E-**Pz$_2$Br**	0.366	0.722	35.9/12.0
Z-**Pz$_2$**	0.898	0.998	–
E-**Pz$_2$**	0.768	0.925	–

Section. To evaluate the efficiency of chosen model chemistry, calculation of chemical shifts was carried out for **Pz$_3$** compound, structure of which was unequivocally determined from NMR spectra. Calculated and experimental chemical shifts are listed in Supporting Information Tables 1S–3S. As one can see, there is a good correlation between experimental and calculated values for both ^{1}H and ^{13}C chemical shifts, correlation coefficients are given in Table 2. Correlation charts are shown in Supporting Information Figures 1S–3S.

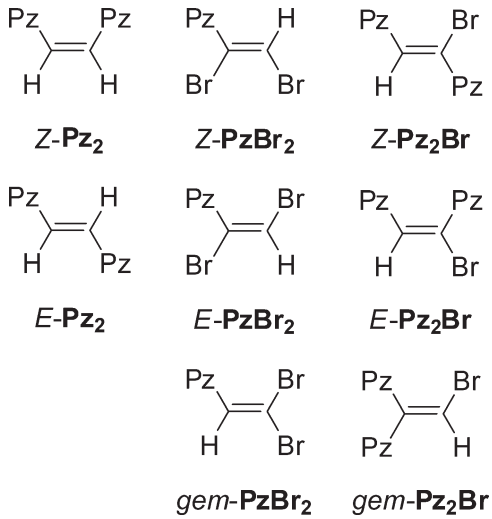
Next, using the described computational strategy, signal assignments were performed for other studied compounds. Thus, for compound **Pz$_2$Br**, the best correlation between experimental and calculated chemical shifts was observed for *gem*-**Pz$_2$Br** structure (Table 2). Moreover, the observed separation between ethene carbon chemical shifts $\Delta\delta^{exp}_{(C=C)}$ of 35.9 ppm differs substantially from the value calculated for *E*- and *Z*-**Pz$_2$Br** isomers and is fairly close to the value for *gem*-**Pz$_2$Br**. Calculated separations between signals of pyrazole carbon atoms are also close to the observed values. Therefore, the structure of 1,1-bis(pyrazol-1-yl)-2-bromoethene (*gem*-**Pz$_2$Br**) should be assigned to **Pz$_2$Br** compound.

In the mass spectrum of this compound, the main peaks are molecular ion peak (doublet $m/z = 238, 240$) and a single peak ($m/z = 159$), assigned to $[M^+ - Br]$ fragmentation pathway. A doublet peak at $m/z = 170, 172$ can be attributed to the elimination of neutral pyrazole (PzH) molecules from the molecular ion, which is probably facilitated by the location of Pz residue and H atom at the same side of the C=C double bond in *gem*-**Pz$_2$Br** compound. The GC analysis of the obtained reaction mixtures shows that certain amounts of one of the isomers of **Pz$_2$Br** was formed. For example, product mixture from 2:1 PzH–TBE reaction contained, according to GC/MS, about 5 mol % of **Pz$_2$Br** (*E*- or *Z*-isomer). In the mass spectrum of this compound, peak at $m/z = 170$ has a very little intensity; therefore, abstraction of PzH molecules from its molecular ion is complicated, which leads to the assignment of *E*-**Pz$_2$Br** structure to this product.

In 2:1 PzH–TBE reaction and C(PzH) = 1.5*M*, **Pz$_2$** compound was the major product, one of the isomers being formed selectively, and only traces of the other isomer was detected by GC/MS (Table 1). The correlation between experimental and calculated NMR ^{1}H and ^{13}C chemical shifts are better for *Z*-**Pz$_2$** compound (Table 2), therefore, this structure should be assigned to the 1,2-bis(pyrazol-1-yl)ethene product.

The structure of *Z*-**Pz$_2$** product was undoubtedly confirmed experimentally by the isolation and X-ray analysis of its complex with zinc chloride. When the product mixture of 2:1 PzH–TBE reaction was treated with $ZnCl_2$ in diethyl ether, white precipitate was formed, which contained only the complex of *Z*-**Pz$_2$** ligand, according to NMR. The NMR signals in the spectra of this complex are shifted compared with the signals of

Scheme 2



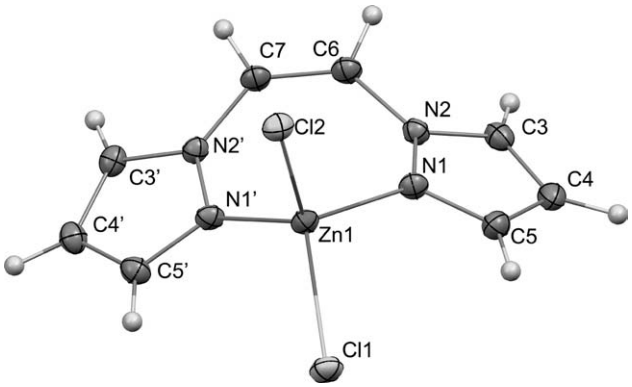


Figure 1. X-ray structure of {Z-1,2-bis(pyrazol-1-yl)ethene}dichlorozinc, [Zn(Z-$\mathbf{Pz_2}$)Cl_2], labels for hydrogen atoms are not shown. Bond lengths (Å): Zn1—N1: 2.020 (1), Zn1—N1′: 2.022 (1), Zn1—Cl1: 2.2311 (3), Zn1—Cl2: 2.2196 (4), C6—C7: 1.335 (2), C6—N2: 1.413 (2), C7—N2′: 1.410 (2); angles (°):N1—Zn—N1′: 97.20 (5), Cl1—Zn1—Cl2: 119.22 (1), Cl1—Zn1—N1: 104.49 (4), Cl1—Zn1—N1′: 105.57 (4), N1—N2—C6: 125.5 (1), N2—C6—C7: 132.2 (1), C6—C7—N2′: 132.8 (1), N1′—N2′—C7: 126.2 (1).

the free ligand, giving evidence that the complexation has actually occurred.

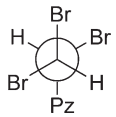
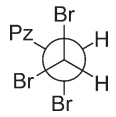
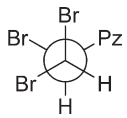
Crystallographic data for complex [Zn(*Z*-$\mathbf{Pz_2}$)Cl_2] and details of diffraction experiment are given in the Experimental Section. The complex crystallizes in a triclinic crystal system, each elementary cell contains two formula units. The *Z*-$\mathbf{Pz_2}$ ligand is coordinated in a bidentate fashion *via* position 2 of pyrazole nitrogen (Fig. 1), the seven-membered metallocycle adopts a boat-shaped form, while the ethene C=C bond retains an essentially planar geometry, the maximum deviation of atom positions from least squares plane being only 0.017 Å. The coordination environment of zinc resembles a distorted tetrahedron, with a somewhat sharp ligand bite angle of 97.20(5)°.

The selective formation of *Z*-$\mathbf{Pz_2}$-$ZnCl_2$ complex on treatment of the product mixture with zinc chloride opens a pathway for isolation of *Z*-$\mathbf{Pz_2}$ compound from a complex product mixture. After filtration, zinc complex was decomposed by dissolving it in DMSO, and after dilution with water, the ligand could be extracted by chloroform.

Having obtained the information on the structure of the products, we can now rationalize on the possible reaction mechanism that leads to the observed set of products. As it was mentioned earlier, pyrazolyl- and bromo-substituted ethenes (*gem*-$\mathbf{PzBr_2}$, *gem*-$\mathbf{Pz_2Br}$, $\mathbf{Pz_3}$) are probably formed by subsequent substitution and elimination steps. The only product not derived from the proposed mechanism is *Z*-$\mathbf{Pz_2}$ compound. It is obvious that this compound is formed as result of the initial substitution of bromine in β-position to the pyrazole ring in compound **A**, leading to intermediate **B** (Scheme 1). Compound **B** undergoes 1,2-debromination to yield *Z*-$\mathbf{Pz_2}$ product (Scheme 1). Compound **B** has two identical stereogenic centers and thus two diastereomers are

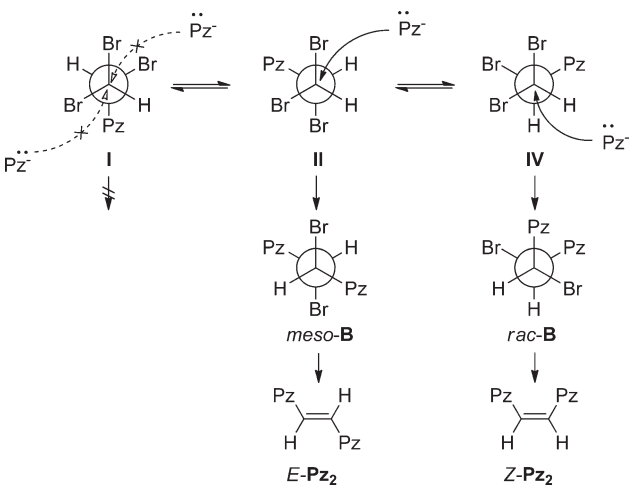
Table 3

Conformers of 1,1,2-tribromo-1-(pyrazol-1-yl)ethane (**A**).

No.	Newman projection	∠(HCCH)	∠(HCNN)	$E_{rel\ (gas)}$, kcal/mol[a]	μ, D	$E_{rel\ (DMSO)}$, kcal/mol[b]
I		−179.11	−168.77	0	2.56	5.31
II		−55.65	9.48	3.05	1.04	6.48
III	Same as **I**	−171.21	5.79	4.38	2.29	10.43
IV		69.02	−15.23	6.66	1.69	0
V	Same as **II**	−53.28	−173.98	12.56	2.84	15.28
VI	Same as **IV**	83.88	−149.13	16.80	3.31	18.22

[a] Computed at RI BP86 QZVPP level of theory in vacuo.
[b] Computed at B3LYP 6–31G(d) level of theory in DMSO using SCRF SCIPCM model.

Scheme 3



possible for this compound. As *Z*-$\mathbf{Pz_2}$ product was formed selectively, it is likely that only one diastereomer of **B** was initially formed. Formation of one or another diastereomer of **B** is determined by the conformational equilibrium of the tribromoderivative **A**. Conformational search was thus performed for this compound taking into account rotation around the ethene backbone C—C bond and rotation of pyrazole ring (C—N bond). The search resulted in six conformers listed in Table 3.

Relative reactivities of chemically unequivalent bromine atoms at β-carbon now have to be considered for each of the conformer. In conformers **I** and **III**, both bromine atoms are shielded from the nucleophilic attack by either bromine atom or pyrazole ring, therefore, these conformers probably do not participate in the S_N2 reaction. In conformers **II** and **IV**, one of the bromine atoms is available for reaction. Substitution of one of them leads to *meso*-diastereomer of intermediate **B**, while that of the other results in racemic mixture of *RR*- and *SS*-enantiomers (Scheme 3). It is known from the literature that 1,2-debromination of 1,2-dibromo-1,2-diphenylethanes is an anti-elimination process and *meso*-diastereomer results in *E*-stylbene, while the racemic dibromide leads to *Z*-isomer [17,18]. Similar behavior should be expected for the heterocyclic stylbene analogs discussed in this article. Conformer **IV** is lowest in energy, therefore, formation of racemic **B** and *Z*-$\mathbf{Pz_2}$ products should be expected. Greater stabilization of conformer **IV** in DMSO compared with conformer **II** can be attributed to its higher polarity (see calculated dipole moment values in Table 3).

Despite the fact that formation of *Z*-$\mathbf{Pz_2}$ is a debromination process, no free bromine was detected in the reaction mixture. The bromine formed as the result of elimination probably participates in further reactions with pyrazolyl-ethenes formed at previous steps. Thus, products derived from *gem*-$\mathbf{PzBr_2}$ and *gem*-$\mathbf{Pz_2Br}$ were detected by GC/MS as minor components of product mixtures (8–12% based on CG/MS, Table 1). Possible mechanism for formation of such products is shown in Scheme 4. The initial step can be represented as an electrophilic attack of bromine cation (or its equivalent formed from bromine in highly basic conditions, such as hypobromite) at the double bond of the alkene. The attack is likely to occur at the sterically least demanding monosubstituted carbon atom of the alkene. The resulting cations then release protons giving rise to $\mathbf{PzBr_3}$ and *gem*-$\mathbf{Pz_2Br_2}$ products. The whole process can thus be considered as electrophilic substitution reaction at alkene sp^2 carbon.

At 1:1 PzH–TBE ratio, tetrabromoethene undergoes similar transformations, first eliminating hydrogen bromide and then giving rise to considerable amount of tetrabromoethene as an electrophilic substitution product, which was detected by GC/MS and ^{13}C-NMR (Scheme 4).

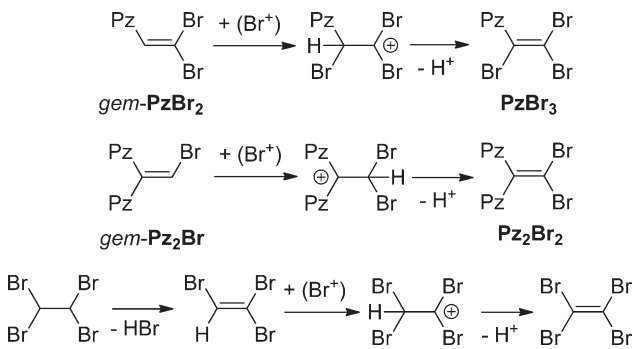
CONCLUSIONS

In summary, detailed study of pyrazole–TBE reaction allowed us to propose facile methods of synthesis of several new poly(pyrazole) compounds—1,1,2,2-tetrakis(pyrazol-1-yl)ethane, *Z*-1,2-bis(pyrazol-1-yl)ethane, and 1,1,2-tris(pyrazol-1-yl)ethene. Bis- and tris(pyrazolyl)-substituted alkenes represent a new class of hetarylalkenes. While *N*-vinylazoles, including *N*-vinylpyrazoles are well investigated [19,20], as far as we know, no alkene derivatives with two or three nitrogen heterocycles were reported so far. Compounds of this type can serve as building blocks for new polydentate scorpionate ligands unavailable by other routes.

EXPERIMENTAL

General methods. Elemental analyses were carried out on a Carlo Erba analyzer. IR spectra of solid samples as KBr pellets and of thin layers (0.1 mm) for liquids were recorded on Nicolet 5700 spectrophotometer. NMR spectra were recorded on Bruker AV300 instrument. GC/MS measurements were carried

Scheme 4



out using TRACE DSQ (Thermo Electron Corporation) instrument.

X-ray crystal structure determination. Intensities of 12,879 reflections were measured on SMART APEX II CCD diffractometer at 100 K [λ(MoKα) = 0.71072 Å, ω-scan technique, $2\theta < 58°$], and 2946 independent reflections (R_{int} = 0.0140) were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. Hydrogen atoms were located from the Fourier density synthesis. All calculations were performed using SHELXTL PLUS 5.0 [21].

Crystal data for [Zn(*Z*-**Pz$_2$**)Cl$_2$]: $C_8H_8Cl_2N_4Zn$, M = 296.45, triclinic, a = 7.1847(3), b = 7.6022(3), c = 11.2242(4) Å, α = 85.4401(7)°, β = 73.8763(6)°, γ = 69.9383(6)°. U = 553.13(4) Å^3, T = 100(2) K, space group P-1 (No. 2), Z = 2, calc. density 1.780 Mg m^{-3}, crystal size 0.45 × 0.29 × 0.22 mm^3, θ_{min} = 1.89°, θ_{max} = 28.99°, 6742 reflections measured, 2946 unique (R_{int} = 0.0140), which were used in all calculations. $R1$ = 0.0199 (refined data) and 0.0210 (all data). The final w$R2$ factors were 0.0523 (refined data) and 0.0530 (all data). Goodness-of-fit 0.992, maximum and minimum electron densities 0.489 and −0.355 e/Å^3, respectively.

Computational chemistry details. Shielding constants were calculated using GIAO methodology [22] at DFT B3LYP [23–25] level of theory and 6-31++G(d,p) basis set [26,27]. This basis set provides fairly good accuracy at an affordable computational cost [28,29]. Conformational search was performed for all of the studied pyrazolyl-ethenes taking into account rotations around all of C(alkene)—N(pyrazole) bonds. Semiempirical PM3 method was used for preliminary scans of the conformational space and DFT B3LYP 6-31G(d) [30] geometry optimizations were performed for all found minima. Frequency calculations were run for all molecules to establish the nature of the stationary points. Lack of imaginary vibration modes for all of the optimized structures indicate that the stationary points found corresponded to minima on the potential energy surface. Minimal energy conformations were used as starting points for further more accurate geometry optimizations at RI DFT BP86 [31] level of theory and TZVPP [32,33] basis set (TZV/J auxiliary basis set [34,35]). Structures obtained in this fashion were used for shielding constant calculations.

Geometry optimizations at PM3 and B3LYP levels of theory as well as shielding constant calculations were carried out using Gaussian 03W package [36], while RI BP86 calculations were performed using the ORCA 2.6.35 package [37].

Solvent effect on the relative energies of conformers for compound **A** were taken into account using SCIPCM [38] reaction field model as implemented in Gaussian 03W package.

Materials. PzH and TBE were obtained from Aldrich. Dimethylsulfoxide was distilled over granulated KOH *in vacuo* (5 torr) prior to use. All other commercially available reagents and solvents were used without further purification.

General procedure for pyrazole–1,1,2,2-tetrabromoethane reaction. A mixture of pyrazole (1 g, 14.7 mmol), finely powdered KOH (1.65 g, 29.4 mmol), and 10 mL of DMSO was heated to 80°C under vigorous stirring. After 30 min, an appropriate amount (based on the desired PzH–TBE ratio) of TBE was added to the resulting suspension, the mixture was heated for 24 h at 80°C and diluted with 200 mL of water, the precipitate of **Pz$_4$** compound was filtered off and dried. The filtrate was extracted with chloroform (5 × 20 mL), the extract was washed with water (2 × 10 mL) and dried over calcium chloride. Removal of the solvent afforded a mixture of pyrazolyl-ethenes that was analyzed by GC/MS and NMR methods.

Z-1,2-Bis(pyrazol-1-yl)ethene (Z-Pz$_2$). A mixture of pyrazole (3 g, 44.12 mmol), finely powdered KOH (4.94 g, 88.24 mmol) in 20 mL of DMSO was heated to 80°C under vigorous stirring. After 30 min, a solution of TBE (7.72 g, 22.06 mmol) in 10 mL of DMSO was added dropwise to the resulting suspension during 30 min. Stirring and heating was continued for 8 h, then the reaction mixture was diluted with 300 mL of water, the precipitate of **Pz$_4$** compound (0.512 g, 16% based on starting pyrazole) was filtered off and dried. The filtrate was extracted with chloroform (5 × 20 mL), the extract was washed with water (2 × 15 mL) and dried over calcium chloride. The residue after removal of chloroform (2.02 g, contains, by NMR, 51 mol % of *Z*-**Pz$_2$**, 30% yield) was dissolved in 5 mL of diethyl ether, insoluble part was filtered, and solution of zinc chloride (2.55 g, 18.75 mmol) in 25 mL of diethyl ether was added to the filtrate. The resulted oily precipitate was crystallized from ethanol, yielding *Z*-**Pz$_2$**-$ZnCl_2$ complex (0.708 g, 45%) as colorless crystals suitable for X-ray analysis. The crystals were dissolved in 3 mL of DMSO and 30 mL of water was added to the solution to achieve the decomposition of the complex. The resulted solution was extracted with chloroform (5 × 5 mL), the extract was washed with water (2 × 5 mL) and dried over calcium chloride. Removal of the solvent and vacuum distillation of the residue gave 0.3 g of pure *Z*-**Pz$_2$** as colorless liquid. Bp 118°C (2 torr). IR (neat): $\tilde{\nu}$ = 1681 ($\nu_{C=C}$), 1521, 1445, 1401 (ν_{Pz}), 1342 (β_{Pz}), 1045 (Pz ring breathing) cm^{-1}. ^{1}H-NMR (MeOD, 300 MHz): δ_H = 6.39 (t, J = 2.1 Hz, 2H, H^4), 6.88 (s, 2H, PzCH), 7.48 (d, J = 2.4 Hz, 2H, H^3), 7.65 (d, J = 2.4 Hz, 2H, H^5) ppm. ^{13}C-NMR (MeOD, 75 MHz): δ_C = 108.6 (Pz-C^4), 119.2 (C=C), 132.2 (Pz-C^3), 142.0 (Pz-C^5) ppm. Anal. Calcd for $C_8H_8N_4$: C, 59.99; H, 5.03; N, 34.98. Found: C, 60.28; H, 5.22; N, 34.90.

1,1,2-Tris(pyrazol-1-yl)ethene (Pz$_3$). Reaction of pyrazole (0.68 g, 10 mmol) and TBE (0.114 g, 3.33 mmol) in 10 mL of DMSO was carried out following the general procedure (vide supra). The yield of **Pz$_4$** product was 0.162 g (22% based on starting pyrazole). Evaporation of the solvent from the extract gave 0.576 g of a solid product mixture, which contains, by NMR, 84.8 mol % (84% yield) of **Pz$_3$** compound. Pure **Pz$_3$** as colorless crystals can be obtained by crystallization from *i*-PrOH, mp 101–102°C. IR(KBr): $\tilde{\nu}$ = 1710 ($\nu_{C=C}$), 1520, 1440, 1390 (ν_{Pz}), 1045 (Pz ring breathing), 1340 (β_{Pz}), cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz, pyrazole ring labeling is shown in Scheme 1): δ_H = 6.23 (t, J = 2.1 Hz, 1H, Pz$^{(3)}$-H^4), 6.38 (t, J = 2.1 Hz, 1H, Pz$^{(1)}$-H^4), 6.53 (d, J = 2.1 Hz, 1H, Pz$^{(3)}$-H^5), 6.54 (t, J = 2.1 Hz, 1H, Pz$^{(2)}$-H^4), 7.19 (d, J = 2.1 Hz, 1H, Pz$^{(1)}$-H^3), 7.58 (d, J = 2.1 Hz, 1H, Pz$^{(1)}$-H^5), 7.61 (d, J = 2.1 Hz, 1H, Pz$^{(3)}$-H^3), 7.70 (d, J = 2.1 Hz, 1H, Pz$^{(2)}$-H^5), 7.90 (d, J = 2.1 Hz, 1H, Pz$^{(2)}$-H^3), 7.95 (s, 1H, C=CH) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ_C = 107.9 (Pz$^{(2)}$-C^4), 108.5 (Pz$^{(3)}$-C^4), 108.8 (Pz$^{(1)}$-C^4), 117.9 (Pz$_2$C=CHPz), 125.1 (Pz$_2$C=CHPz), 128.6 (Pz$^{(3)}$-C^5), 128.9 (Pz$^{(1)}$-C^5), 132.4 (Pz$^{(2)}$-C^5), 141.7 (Pz$^{(3)}$-C^3), 142.2 (Pz$^{(2)}$-C^3), 143.3 (Pz$^{(1)}$-C^3) ppm. Anal. Calcd for $C_{11}H_{10}N_6$: C, 58.40; H, 4.46; N, 37.15. Found: C, 58.20; H, 4.30; N, 37.03.

1,1,2,2-Tetrakis(pyrazol-1-yl)ethane (Pz$_4$). Reaction of pyrazole (0.5 g, 7.35 mmol) and TBE (0.637 g, 1.84 mmol) in 7 mL of DMSO was carried out following the general procedure (vide supra). Yield 0.225 g (47%), colorless crystals. mp 271–

273°C (MeCN). IR(KBr): $\tilde{\nu}$ = 1521, 1437 (ν_{Pz}), 1310 (β_{Pz}), 1051 (Pz ring breathing) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ_H = 6.13 (t, J = 2 Hz, 4H, H^4), 7.47 (d, J = 2 Hz, 4H, H^3), 7.56 (d, J = 2 Hz, 4H, H^5), 7.83 (s, 2H, Pz_2CH) ppm. Anal. Calcd for $C_{14}H_{14}N_8$: C, 57.13; H, 4.79; N, 38.29. Found: C, 56.84; H, 4.48; N, 38.07.

{Z-1,2-Bis(pyrazol-1-yl)ethene}dichlorozinc. Colorless crystals, mp 242–243°C (EtOH). IR(KBr): $\tilde{\nu}$ = 1699 ($\nu_{C=C}$), 1521, 1457, 1407 (ν_{Pz}), 1338 (β_{Pz}), 1040 (Pz ring breathing) cm^{-1}. ^{1}H-NMR (MeOD, 300 MHz): δ_H = 6.46 (t, J = 2.1 Hz, 2H, Pz-H^4), 6.95 (s, 2H, CH=CH), 7.54 (d, J = 2.1 Hz, 2H, Pz-H^3,), 7.72 (d, J = 2.1 Hz, 2H, Pz-H^5) ppm. ^{13}C-NMR (MeOD, 75 MHz): δ_C = 108.8 (Pz-C^4), 119.4 (C=C), 132.8 (Pz-C^3), 142.3 (Pz-C^5) ppm. Anal. Calcd for $C_8H_8N_4Cl_2Zn$: C, 32.41; H, 2.72; N, 18.90. Found: C, 32.71; H, 2.63; N, 18.65.

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