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Synthesis of the silver(I) complex of $CH_2[CH(pz^{4Et})_2]_2$ containing the unprecedented $[Ag(NO_3)_4]^{3-}$ anion: A general method for the preparation of 4-(alkyl)pyrazoles†

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A general two-step method for the syntheses of 4-(alkyl)pyrazoles has been developed. The first step involves the reaction between organyl diethylacetals and the Vilsmeier reagent to give a mixture of ethoxy- and dimethylamino- acroleins. This mixture reacts directly with hydrazine monohydrogenchloride to yield the desired (4-substituted)pyrazoles. The 4-(phenyl)pyrazole derivative exhibited a markedly lower solubility in common organic solvents. In the solid state structure the phenyl and pyrazolyl groups are nearly coplanar and extensive intermolecular CH–π interactions organize the molecules in two-dimensional sheets that are held in a three dimensional arrangement by NH···N hydrogen bonds. Tetrakis[(4-ethyl)pyrazolyl]propane, $CH_2[CH(pz^{4Et})_2]_2$, was prepared by a transamination reaction and reacts with $Ag(NO_3)$ to yield a compound with a 4 : 3 metal : ligand mole ratio that when crystallized by diffusion of Et_2O into an acetone solution produced $[Ag_2\{\mu\text{-}CH_2[CH(pz^{4Et})_2]_2\}_2][Ag(NO_3)_4]_2$ (**1**). This complex contains dimeric units in which two silver cations are sandwiched between two $CH_2[CH(pz^{4Et})]_2$ ligands and the counterion is the unprecedented tetra(nitrato)argentate anion. ESI mass spectral data support the existence of both the cationic dimeric units and the $[Ag(NO_3)_4]^-$ anion in solution.

Introduction

As part of our ongoing interest in developing next-generation scorpionate ligands, we have recently been exploring the chemistry of poly(pyrazolyl)methane ligands, the charge-neutral analogues of the more familiar poly(pyrazolyl)borates initially developed by Trofimenko.[1] We are particularly interested in the development of multitopic derivatives where poly(pyrazolyl)methane units are joined by a variety of organic spacers (Fig. 1), such as in $CH_2[CH(pz)_2]_2$[2] and in $C_6H_{6-n}[CH_2OCH_2C(pz)_3]_n$, ($n$ = 2, 4, pz = pyrazolyl ring),[3] for the development of coordination polymers and discrete complexes with unusual supramolecular structures. Research into these types of complexes is driven by the fact that they can play a role in catalysis, molecular recognition or can act as molecular containers, molecular sensors and sieves.[4,5] In an effort to more fully develop this chemistry, the efficient syntheses of a variety of 4-substituted pyrazoles was needed to improve the solubility characteristics and to provide a vehicle for controlling the factors that dominate the supramolecular structures of the new complexes while minimizing both steric and electronic effects associated with replacing substituents on the pyrazolyl group on their coordination behavior toward metal centers.[6] While a few 4-substituted pyrazoles, $H(pz^{4R})$ (R = Me, Br, I) are commercially available, the capability for the methyl and halide groups to participate in non-covalent interactions and our additional long term goal of improving the solubility characteristics of poly(pyrazolyl)methane coordination complexes and coordination polymers prompted us to explore other groups, such as long chain alkyls, as substituents.

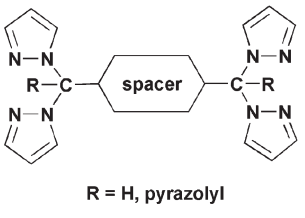

Fig. 1 Multitopic poly(pyrazolyl)methane ligands.

It was initially surprising that there are only sporadic reports concerning the synthesis of pyrazoles substituted by simple organyl groups solely at the 4-position.[7–10] A series of 4-(cycloalkyl)pyrazoles[9e] along with a 4-(2-pyrazinyl)pyrazole[11] have been prepared from malonaldehyde precursors, Fig. 2a. The inherent difficulty encountered in preparing and isolating the logical 2-substituted malonaldehyde precursors has likely hindered further research into this area. For instance, we (and undoubtedly many others) have found that the Claisen reaction between alkanals and ethyl formate affords the self-condensation compounds (*i.e.*, $HC(O)CH(R)C(O)CH_2R$) rather than the desired dialdehyde as the major product. Therefore, the preparation of the desired malonaldehydes requires indirect multi-step syntheses. Alternatively, malonaldehyde analogues have been used for pyrazole synthesis.

† Electronic supplementary information (ESI) available: Crystal packing diagram of the unit cell of $[Ag_2\{\mu\text{-}CH_2[CH(pz^{4Et})_2]_2\}_2][Ag(NO_3)_4]_2(acetone_x/Et_2O_y)$. See http://www.rsc.org/suppdata/nj/b3/b307306h/

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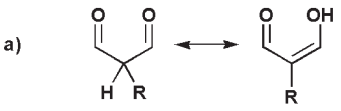
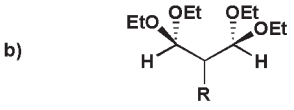


R = cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, 2-pyrazinyl



R = alkyl

X = Cl, R = Et; X = OMe, R = ^{n}Bu; X = NMe_2, R = Ph; X = NH_2, R = ^{sec}Bu

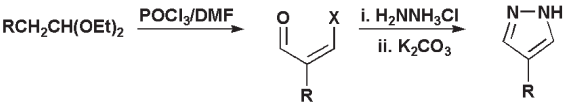
Fig. 2 Precursors to 4-(organyl)pyrazoles.

A series of 4-(alkyl)pyrazoles (and 2-malonaldehydes) have been prepared by the reaction between hydrazine and either 2-substituted 1,1,3,3-tetraethoxypropanes[8c] (Fig. 2b) or acrolein derivatives[7e,8a,9a,10f] (Fig. 2c). It is noteworthy that the 2-substituted malonaldehydes depicted in Fig. 2a are prepared by hydrolyzing either tetraalkoxypropanes or acroleins by first basification with OH^- followed by acidification.[9e,11]

A feature common to the synthesis of most of the malonaldehydes analogues described above is the use of vinyl ethers as starting materials. The vinyl ethers are typically prepared by acid-catalyzed alcoholysis of alkanal diethylacetals.[8c,12] In our hands this seemingly simple reaction failed to provide useful quantities of vinyl ethers, regardlesss of the acid catalyst used. Therefore, we sought alternative routes for the synthesis of either 4-substituted pyrazoles or their malonaldehyde analogues.

One alternative approach to 4-substituted pyrazoles described heating a $POCl_3$-pyrazolinone mixture to above 200 °C in a sealed glass vessel in one step and a sodium reduction of the resulting chloropyrazole in liquid ammonia in a subsequent step.[8c] Both of these steps were deemed to be unnecessarily dangerous for the large quantity of pyrazole needed for the preparation of useful quantities of poly(pyrazolyl)-methane ligands. Therefore, we refocused our attention to the preparation of acroleins as potential intermediates to 4-(organyl)pyrazoles.

It has long been known that the reaction between alkanal diacetals and the Vilsmeier reagent, $[Me_2N{=}CHCl^+][PO_2Cl_2^-]$ (derived from the stoichiometric reaction between DMF and $POCl_3$) or its chloride analogue (DMF and either phosgene or oxalyl chloride) affords a mixture of acroleins of the type HC(O)C(R)CH(X) (X = NMe_2, OEt, Cl) where the dimethylamino and ethoxy derivatives are usually the major products.[13] We reasoned that it should be possible to use the acrolein mixture directly for the preparation of 4-substituted pyrazoles without the need for separation or conversion to malonaldehydes prior to their reaction with hydrazine. This report will document our successful endeavors in using this simple, two-step approach for the preparation of a variety of (4-organyl)pyrazoles as depicted in Scheme 1. In addition, the derivatization of one 4-(alkyl)pyrazole, namely H(pz^{4Et}), to its tetrakis(pyrazolyl)propane derivative, and the subsequent coordination chemistry with silver nitrate will be reported.



X = OEt, NMe_2; R = alkyl, aryl

Scheme 1

Results and discussion

Syntheses and characterization of 4-pyrazoles

The reaction between organyl diethylacetals and the Vilsmeier reagent occurred smoothly at or below 80 °C to give a mixture of ethoxy- and dimethylamino- acroleins. A number of factors were found to contribute to improving the overall yield of the mixture and, hence, the desired pyrazole (Table 1) by the current route. The temperature at which the Vilsmeier reaction was carried out was found to be critical to the success of the reactions; when the reactions were performed above 80 °C extensive decomposition occurred. Also, as can be expected from the hydrolytic susceptibility of the acroleins and as was indicated from the original report,[13a] after hydrolysis, the extraction of the product mixture from the aqueous layer of the Vilsmeier reaction is tedious since the partition coefficient between the organic and aqueous phases slightly favors the latter. The difficulty in separating the product mixture from aqueous solution was partially alleviated by performing the extraction from solutions that were either slightly acidic or near neutral pH. The use of alkali metal carbonates or bicarbonates as bases was helpful toward providing a visual indication of neutralization (effervescence ceases). The extraction process also varied in difficulty depending on the substituents to be incorporated into the desired pyrazole and, consequently, the nature of the organic substituent has a significant impact on the overall yield of 4-(organyl)pyrazole (Table 1). It was found that in the case of an ethyl substituent, the ethoxy acrolein is preferentially extracted with either diethyl ether or benzene whereas the dimethylamino acrolein is preferentially extracted with methylene chloride, so both solvents were used. With longer chain alkyl derivatives (butyl or longer) the partition coefficient is increasingly in favor of the organic phase. Furthermore, after extraction, it is necessary to remove any DMF (reaction solvent) by vacuum distillation prior to reaction with hydrazine. The dark residue that remains after removal of the DMF is sufficiently pure to be used directly for the preparation of the desired pyrazoles; significant improvements in yield were not encountered by removing the traces of highly-colored decomposition products from the residues. This beneficial feature eliminated the need for separation of acroleins by vacuum distillation, a step that works well in the case of the ethyl derivative but is more challenging for the remaining derivatives owing to their relatively low volatility and high melting points. Finally, the conversion of the acrolein mixture to (4-substituted)pyrazoles is relatively straightforward, but it should be noted that hydrazine monohydrogenchloride was necessary for complete conversion

Table 1 Overall yields of 4-substituted pyrazoles from $RCH_2CH(OEt)_2$

R group	Yield
ethyl	44%
butyl	65%
pentyl	58%
rac-4-(α-ethyl)pentyl	51%
cyclohexyl	47%
phenyl	36%

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since the dimethylamino acroleins remained unreacted when hydrazine monohydrate was used.

The noncyclic alkyl substituted pyrazoles are either liquids or low-melting solids (mp: *ca.* 23–25 °C) that can be purified by vacuum distillation at *ca.* 130 °C/1 mm Hg while the cyclohexyl and phenyl derivatives are solids that are best purified by recrystallization. The phenyl derivative exhibited a markedly lower solubility in common organic solvents when compared to the remaining derivatives and prompted an investigation into its solid-state structure (Fig. 3). It was found that the phenyl and pyrazolyl groups are nearly coplanar with a dihedral angle of 2.3°. This geometry favors extensive intermolecular CH–π interactions such that two-dimensional sheets assemble along the crystallographic *bc* plane as in Fig. 4. The assembly occurs by tandem CH–π interactions between pyrazolyl and phenyl groups in concurrence with edge-to-face (CH–π) interactions between phenyl groups. Specifically, H_3 of a hydrogen-donating pyrazole interacts with the centroid of the hydrogen-accepting phenyl group of an adjacent pyrazole [C(3)H(3)···cent. 2.516 Å, 150.8°] while the H(5) and H(6) edge of the mean plane of one phenyl group is directed toward the normal axis of the mean plane of an adjacent phenyl group [C(5)H(5)···cent.(Ph) 3.204 Å, 125.7°; C(6)H(6)···cent. 3.204 Å, 125.7°]. The sheets are stacked along the *a*-axis by NH···N hydrogen bonds (Fig. 5). The equal population of the acidic hydrogen over both nitrogens results in crystallographic disorder. The hydrogen bonding interaction of each component of the disorder is unsymmetrical with NH···N distances and angles of 2.02(2)Å, 157(2)°; 1.98(2)Å, 175(2)°. The geometries of all of the above non-covalent interactions are within typical values.[2,5,14] The solid state structures of two forms of 4-(pentyl)pyrazole monohydrogen chloride are provided in the ESI‡ and further reveal the importance of hydrogen bonding interactions in the solid state organization of pyrazole-based compounds.

Synthesis and characterization of $[Ag_2\{\mu\text{-}CH_2[CH(pz^{4Et})_2]_2\}_2]_3[Ag(NO_3)_4]_2$ (1)

Tetrakis[(4-ethyl)pyrazolyl]propane, $CH_2[CH(pz^{4Et})_2]_2$, was prepared by a transamination reaction (eqn. 1) similar to that reported for the unsubstituted derivative $CH_2[CH(pz)_2]_2$.[2] The reaction between $Ag(NO_3)$ and $CH_2[CH(pz^{4Et})_2]_2$ (L) in a 1 : 1 mol ratio in CH_3CN afforded a compound with a 4 : 3 metal : ligand mole ratio as indicated from its analytical data. The compound exhibited excellent solubility in chlorinated solvents, acetone, and acetonitrile in contrast to the silver nitrate

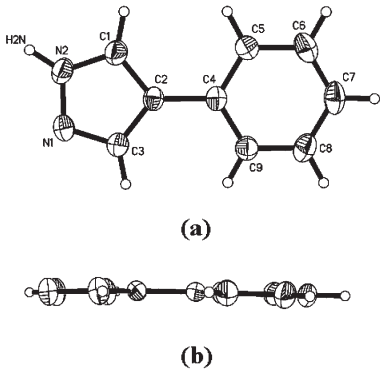


Fig. 3 Two views of the molecular structure of (4-phenyl)pyrazole emphasizing (a) atom labeling scheme and (b) the coplanarity of phenyl and pyrazolyl groups.

‡ CCDC reference numbers 216925–216928. See http://www.rsc.org/suppdata/nj/b3/b307306h/ for crystallographic data in .cif or other electronic format.

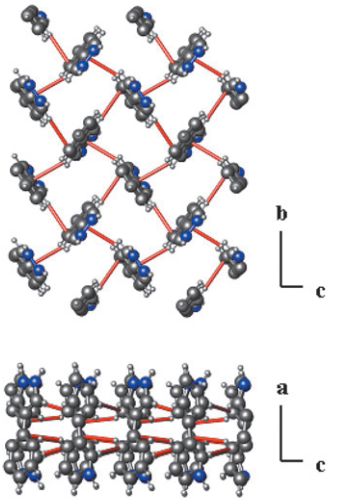
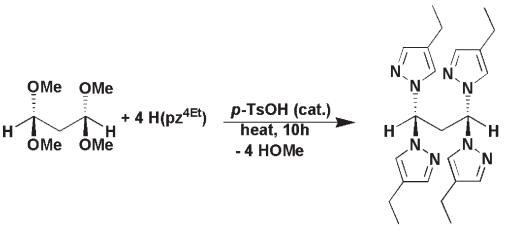


Fig. 4 Two-dimensional sheets formed by CH–π interactions in the crystal of 4-(phenyl)pyrazole.

complex of the $CH_2[CH(pz)_2]_2$ ligand reported earlier, which was insoluble in chloroform and only partially soluble in acetone. The NMR spectrum of the silver compound in either $CDCl_3$ or acetone shows equivalent pyrazolyl rings, as we have observed previously with analogous complexes.



(1)

Slow diffusion of Et_2O into an acetone solution of the $Ag_4L_3(NO_3)_4$ compound, afforded exceedingly fragile but well-formed crystals of a solvate that were subjected to X-ray structural studies. The results of the study are shown in Fig. 6. While the crystallographic data are of low quality, several notable features can be clearly identified. First, in contrast to the silver nitrate complex of its tetrakis(pyrazolyl)propane counterpart derivative but similar to $[Ag_2\{CH_2[CH(pz)_2]\}_2](SO_3CF_3)_2$, the two tetrakis[4-(ethyl)pyrazolyl]propane ligands sandwich two silver cations forming a dimeric unit. In the current case there are three distinguishable dications within

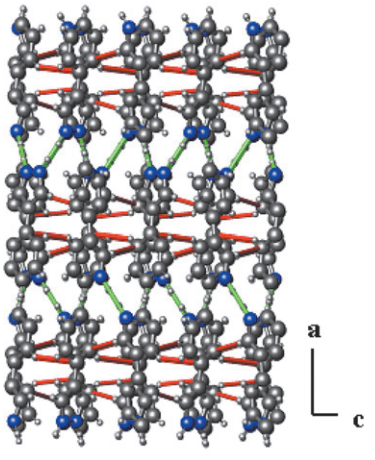


Fig. 5 Stacking of sheets by N–H···N hydrogen bonding in the structure of 4-(phenyl)pyrazole.

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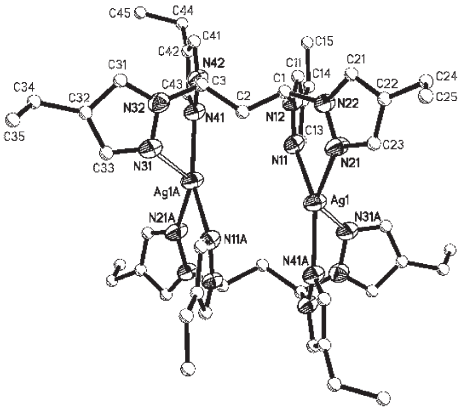

Fig. 6 View of cation in $[Ag_2\{\mu\text{-}CH_2[CH(pz^{4Et})_2]_2\}_2]_3[Ag(NO_3)_4]_2$ (**1**).

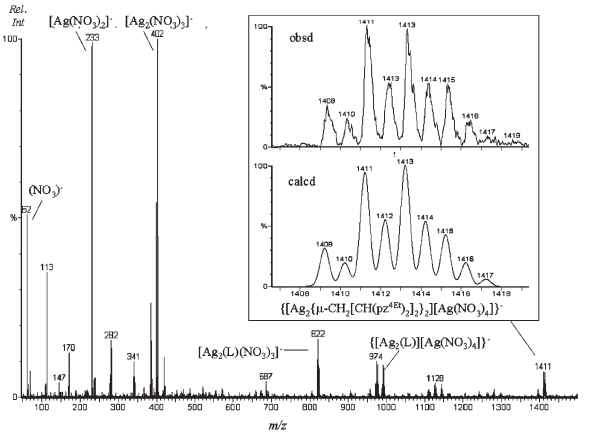

Fig. 8 ESI(−) Mass spectrum of $[Ag_2\{\mu\text{-}CH_2[CH(pz^{4Et})_2]_2\}_2]_3[Ag(NO_3)_4]_2$ (**1**) after crystallization and removal of solvent by vacuum distillation. Inset shows the observed (top) and calculated (bottom) isotope pattern for the $\{[Ag_2\{\mu\text{-}CH_2[CH(pz^{4Et})_2]_2\}_2][Ag(NO_3)_4]\}^-$ anion.

the unit cell where the interatomic separations between silver centers in the dicationic units range between 3.75–4.03 Å. These distances are comparable to that found in $[Ag_2\{CH_2[CH(pz)_2]\}_2](SO_3CF_3)_2$ of 4.32 Å and are longer than the upper limit of 3.25 Å usually attributed to significant Ag···Ag interactions.[15] Second, in agreement with charge balance and the composition indicated by elemental analyses, two [tetra(nitrato)argentate(3−)] anions are found in the unit cell and the geometry of these anions are found in Fig. 7. While the tetra(nitrato)metallate anions of the group 12 elements are known and have been structurally characterized,[16] those of the group 11 series are limited to derivatives in the divalent state, Cu(II)[16a] and the unstable Ag(II) derivative[17] but the latter has not been structurally characterized. This report provides the first synthesis and characterization of a group 11 tetra(nitrato)metallate trianion. Examination of the extended structure of $[Ag_2L_2]_3[Ag(NO_3)_4]_2\cdot(Et_2O_x/acetone_y)$ (See ESI†) reveals a highly porous framework where a mixture of disordered diethylether and acetone solvent molecules of unknown stoichiometry comprise *ca.* 45% of the total unit cell volume as calculated by PLATON.[23] The rapid gaseous diffusion of solvent molecules from the highly porous solid framework is thought to be responsible for the immediate cracking of the crystals upon removal from the mother liquor, the crystal instability with respect to thermal gradients, and the lack of appreciable X-ray scattering above *ca.* $2\theta = 40°$.

ESI-mass spectral studies

The ESI(−) mass spectral data (Fig. 8) show peaks of weak intensity at $m/z = 1411$ and 990 corresponding to the $\{[Ag_2L_2{}^{2+}][Ag(NO_3)_4{}^{3-}]\}^-$ and $\{[Ag_2L^{2+}][Ag(NO_3)_4{}^{3-}]\}^-$ anions supporting the existence of the tetra(nitrato)argentate trianion in solution. The peak at $m/z = 1411$ also supports the existence of the dimeric cation in solution. The fragmentation of the $Ag(NO_3)_4{}^{3-}$ trianion was indicated by peaks of weak intensity for $[Ag_2L(NO_3)_3]^-$, and of strong intensity for the $[Ag_2(NO_3)_3]^-$, $[Ag(NO_3)_2]^-$, and $(NO_3)^-$ anions. The ESI(+) mass spectral data show peaks of very weak intensity for $[Ag_3L_2(NO_3)_2]^+$ and $[Ag_3L_2(NO_3)_2\cdot(H_2O)]^+$, peaks of strong intensity for the monometallic $[Ag(L)]^+$, $[Ag(L)(CH_3CN)]^+$ and $[Ag(L)_2]^+$ species, and peaks for $[Ag_2L_2(NO_3)]^+$. The peaks for $[Ag_3L_2(NO_3)_2]^+$ and $[Ag_3L_2(NO_3)_2(H_2O)]^+$ can be ascribed to be due to the $\{[Ag_2L_2{}^{2+}][Ag(NO_3)_2{}^-]\}^+$ ion pair and its water solvate where the tetra(nitrato)argentate trianion fragments in the electrospray process, as also indicated in the ESI(−) experiments. These peaks in the ESI(+) support that the binuclear cations in **1** are retained under the conditions of this experiment also indicating that the same dimeric species exist in solution.

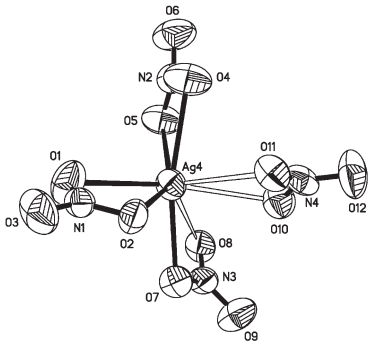

Fig. 7 View of the tetranitratoargentate(3−) anion.

Conclusions

A simple two-step preparation of 4-(organyl)pyrazoles has been developed, carefully detailed, and found to be general for a variety of substituents. The first crystal structures of the mono 4-substituted pyrazoles have also been reported. The supramolecular organization of 4-(phenyl)pyrazole by intermolecular CH–π and by NH···N hydrogen bonding interactions was observed in the solid state and accounts for the low solubility of this derivative in common organic solvents. The 4-(ethyl)pyrazole was successfully derivatized to the corresponding tetrakis(pyrazolyl)propane ligand. The reaction of $CH_2[CH(pz^{4R})_2]_2$ and $Ag(NO_3)$ yields $[Ag_2\{\mu\text{-}CH_2[CH(pz^{4Et})_2]_2\}_2]_3[Ag(NO_3)_4]_2$ (**1**), a complex that contains dimeric units in which two tetrakis[4-(ethyl)pyrazolyl]propane ligands sandwich two silver cations and contains the unprecedented tetra(nitrato)argentate trianion. ESI mass spectrometric experiments indicate that the binuclear cations and $[Ag(NO_3)_4]^{3-}$ trianion in **1** are retained in solution, but the $[Ag(NO_3)_4]^{3-}$ trianion was prone to fragmentation. The low quality of the crystal structure data and the different anions did not permit a meaningful comparison of the aggregation behavior of the $[Ag_2\{CH_2[CH(pz^{4R})_2]_2\}_2]^{2+}$ (R = H and R = Et) dications, but the increased solubility of **1** indicates that this substitution pattern will solve solubility problems encountered in our development of the coordination chemistry of multitopic ligands based on poly(pyrazolyl)methane units. The general route to 4-substituted pyrazoles reported here is of general use for the development of future poly(pyrazolyl)-borate and poly(pyrazolyl)methane ligands designed for specific characteristics.

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Experimental

General comments

All reagents were used as purchased from Aldrich. Solvents were commercially available, purified by conventional means, and distilled immediately prior to use. Diethyl acetals $RCH_2CH(OEt)_2$ were prepared according to standard methodology either by *p*-TsOH-catalyzed rearrangements of alkanals[18] (R = ethyl, butyl, pentyl) or by reactions of RCH_2MgBr with $HC(OEt)_3$ (R = pentyl, Et(Bu)CH, Ph, Cy).[19] Silica gel (230–400 mesh, 40–63 μm) was purchased from Fisher Scientific. Robertson Microlit Laboratories, Inc. (Madison, NJ) performed the elemental analyses. Samples for melting point determinations were contained in flame sealed capillaries and the reported temperatures are uncorrected. The NMR spectra were recorded by using a Varian Mercury 300 or 400 MHz instrument. Chemical shifts are reported in ppm and were referenced to the solvent resonances as internal standards. Mass spectrometric measurements recorded in ESI mode were obtained on a Micromass Q-Tof spectrometer whereas those performed by using direct probe analyses were made on a VG 70S instrument.

Since the procedure used for the Vilsmeier formylation of the following alkanal diethylacetals essentially followed that described by Nair, Vietti, and Cooper[20] for the formylation of propionaldehyde diethylacetal, only the preparation of the ethyl derivative will be detailed and only the quantities of reagents used in this step of the preparation of the remaining pyrazoles will be reported. The methods of extraction and purification were unique to each system under study, so these procedures will be more detailed.

Syntheses

(4-Ethyl)pyrazole. A 500 mL three-necked flask fitted with a magnetic stir bar was connected to a pressure-equalizing addition funnel, a nitrogen inlet valve, the system was sealed with rubber septa, and was purged by three alternating evacuations and nitrogen backfills. A 45.6 mL (74.6 g, 486 mmol) portion of $POCl_3$ was added to the 500 mL flask by syringe and was cooled to 0 °C by an external ice water bath. Freshly distilled (dry) DMF (50.1 mL, 47.1 g, 644 mmol) was added to the addition funnel by syringe, then dropwise over the course of 30 min to the vigorously stirred $POCl_3$. During the addition, the Vilsmeier reagent, $[Me_2N{=}CHCl^+][PO_2Cl_2^-]$, precipitated as a colorless solid. Next, 32.5 g (222 mmol) of butyraldehyde diethylacetal was added by syringe to the addition funnel, then dropwise over the course of 30 min, to the suspension of the Vilsmeier reagent. After the reaction mixture was warmed to room temperature with an external water bath, the flask was placed in a preheated oil bath (that was maintained between 70–80 °C) for 2 h where the reaction mixture gradually changed color from yellow to orange to brown. The resulting brown mixture was poured into 600 g crushed ice and was allowed to stand overnight. Anhydrous potassium carbonate (*ca.* 100 g) was carefully added in 5 g portions (to prevent overflow from effervescence) until the solution became basic and 370 mL of water was added to dissolve the precipitated salts. The aqueous solution was sequentially extracted with CH_2Cl_2 (5 × 150 mL), benzene (5 × 150 mL), Et_2O (3 × 100 mL), THF (4 × 150 mL) and finally $CHCl_3$ (3 × 150 mL) (see text), the organic fractions combined and dried over $MgSO_4$, filtered, and solvent was removed by rotary evaporation to leave a red-brown oil. The red-brown oil was transferred to a distillation apparatus and the portion that distilled below *ca.* 55 °C/1 mmHg (DMF) was discarded. The portion that distilled between 65–70 °C/1 mmHg (4.32 g, 33.7 mmol) was identified as 3-ethoxy-2-ethyl-prop-2-enal by NMR ^{1}H NMR (300 MHz, $CDCl_3$) 9.18 (s, 1H, HC=O), 6.89 (s, 1H, HC(OEt)), 4.16 (q, J = 7.2 Hz, 2 H, OCH_2CH_3), 2.22 (q, J = 7.5 Hz, 2 H, CCH_2CH_3), 1.39 (t, J = 7.2 Hz, 3 H, OCH_2CH_3), 0.98 (t, J = 7.5 Hz, 3 H, OCH_2CH_3). The residue (11.31 g, 88.9 mmol) was 3-(dimethylamino)-2-ethyl-prop-2-enal ^{1}H NMR (300 MHz, $CDCl_3$) 8.83 (s, 1H, HC=O), 6.46 (s, 1H, $HC(NMe_2)$), 3.13 (s, 6 H, NMe_2), 2.42 (q, J = 7.5 Hz, 2 H, CCH_2CH_3), 1.02 (t, J = 7.5 Hz, 3 H, OCH_2CH_3). The combined yield (123 mmol) was 55% based on butyraldehyde diethyl acetal. This mixture was dissolved in 100 mL MeOH, and 8.91 g of $NH_2NH_2{\cdot}HCl$ in 200 mL H_2O was added in one portion. The mixture was heated at reflux 1 h, was cooled to room temperature and neutralized with anhydrous $NaHCO_3$. After 200 mL CH_2Cl_2 had been added and the layers separated, the aqueous portion was extracted with three 100 mL portions of CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered and solvent was removed by rotary evaporation to leave a red-brown oil. The red–brown oil was transferred to a distillation apparatus fitted with a vigreaux column. The 9.42 g (44% yield based on butyraldehyde diethylacetal) of colorless to pale yellow liquid that distilled between 73–74 °C/1 mmHg (Lit bp's, 87–89 °C/2 mmHg;[7c] 82–85 °C/3 mmHg[7d] 104–105 °C/3 mmHg;[7e] 98–100 °C/5 mmHg;[7f] 122 °C/16 mmHg[7b]) was pure $H(pz^{4Et})$ as indicated by ^{1}H NMR spectroscopy. HRMS-Direct probe (m/z): calcd for $C_5H_8N_2$, 96.0687 found, 96.0682. ^{1}H NMR (300 MHz, $CDCl_3$) 9.86 (br s, 1H, NH), 7.42 (s, 2H, $H_{3,5}$-pz), 2.54 (q, J = 7.8 Hz, 2 H, CH_2CH_3), 1.22 (t, J = 7.8 Hz, 3 H, CH_2CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$) 132.4 (br s, C=N), 123.1 (C_4-pz), 17.5 (CH_2), 15.4 (CH_3)

4-(Butyl)pyrazole. The product mixture from the Vilsmeier formylation of 40.6 g (233 mmol) hexanaldehyde diethylacetal with 46.9 mL $POCl_3$ (78.6 g, 513 mmol) and 43.0 mL (40.9 g, 560 mmol) DMF, after hydrolysis and neutralization, was extracted with four 100 mL portions of CH_2Cl_2 followed by four 100 mL portions of Et_2O. The combined organics were dried over $MgSO_4$, filtered, and solvent was removed to leave a red–brown oil. DMF was removed by vacuum distillation and the distillation residue (31.3 g) was found to be a mixture of 3-ethoxy-2-butyl-prop-2-enal and 3-(dimethylamino)-2-butyl-prop-2-enal)] in a 1.21 : 1 mol ratio (201 mmol total, 86% based on hexanaldehyde diethylacetal). [Note: these products were separated in a repeated experiment; ethoxy derivative ^{1}H NMR (300 MHz, $CDCl_3$) 9.18 (s, HC=O), 6.92 [s, HC(OEt)], 4.16 (q, J = 7.2 Hz, OCH_2), 2.70 (t, J = 5.4 Hz, 2H, CCH_2), 2.20 (t, J = 7.2 Hz, OCH_2CH_3), 1.40–1.27 (br m, 2H), 0.88 (t, J = 8 Hz, CH_3); dimethylamino derivative ^{1}H NMR (300 MHz, $CDCl_3$) 8.75 (s, HC=O), 6.76 [s, $HC(NMe_2)$], 3.18 (s, 6H, NMe_2), 2.37 (m, 2H, CCH_2), 1.36–1.25 (br m, 4H, Bu), 0.90 (t, 3H, CH_3).] The residue was allowed to react with 14.4 g (210 mmol) $NH_2NH_2{\cdot}HCl$, as above, neutralized, and extracted with four 150 mL portions of CH_2Cl_2. Fractional distillation at 97–99 °C/1 mmHg (Lit[8c] bp, 95–98 °C/1.5 mmHg) afforded 18.8 g (65% based on hexanaldehyde diethylacetal) of (4-butyl)pyrazole as a colorless to pale yellow liquid. HRMS- Direct probe (m/z): calcd for $C_7H_{12}N_2$, 124.1000 found, 124.0996. ^{1}H NMR (300 MHz, $CDCl_3$) 9.86 (br s, 1H, NH), 7.41 (s, 2H, $H_{3,5}$-pz), 2.50 (t, J = 7.8 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 1.56 (m, 2 H, $CH_2CH_2CH_2CH_3$), 1.37 (m, 2 H, $CH_2CH_2CH_2CH_3$), 0.93 (m, 3 H, $CH_2CH_2CH_2CH_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$) 132.9 (br s, C=N), 121.5 (C_4-pz), 33.3 (CH_2), 23.9 (CH_2), 22.5 (CH_2), 14.1 (CH_3).

4-(Pentyl)pyrazole. The product mixture from the Vilsmeier formylation of 43.1 g (229 mmol) heptanaldehyde diethylacetal, 46.0 mL (77.1 g, 503 mmol) $POCl_3$, and 42.0 mL (40.1 g, 0.55 mol) DMF after hydrolysis was extracted with four 150 mL portions CH_2Cl_2 and two 150 mL portions of diethyl

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ether. The aqueous fraction was neutralized by adding 140 g (1.01 mol) anhydrous K_2CO_3 in 5 g portions to prevent overflow from effervescence, then was extracted with an additional two 100 mL portions of CH_2Cl_2 followed by two 100 mL portions of Et_2O. After drying the combined organics over $MgSO_4$, filtering, and removing solvents by rotary evaporation, 9.62 g (132 mmol) of DMF was removed by vacuum distillation at 35–45 °C/1 mmHg. The residue 32.0 g was a mixture of 3-ethoxy-2-pentylprop-2-enal and 3-(dimethylamino)-2-pentylprop-2-enal in a 2 : 3 mol ratio as indicated by NMR (188 mmol total, 82% based on heptanaldehyde diethylacetal). [Note: these products were separated in a repeated experiment; ethoxy derivative ^{1}H NMR (300 MHz, $CDCl_3$) 9.16 (s, HC=O), 6.92 [s, HC(OEt)], 4.14 (q, $J = 7.2$ Hz, OCH_2), 2.67 (t, $J = 5.4$ Hz, 2H, CCH_2), 2.17 (t, $J = 7.2$ Hz, OCH_2CH_3), 1.43–1.30 (br m, 6H), 0.88 (t, $J = 8$ Hz, 3H, CH_3); dimethylamino derivative ^{1}H NMR (300 MHz, $CDCl_3$) 8.53 (s, HC=O), 7.63 [s, HC(NMe_2)], 3.33 (s, 6 H, NMe_2), 2.38 (m, 2H, CCH_2), 1.43–1.30 (br m, 4H), 0.88 (t, $J = 8$ Hz, CH_3)]. The distillation residue was allowed to react with 15.6 g (228 mmol) NH_2NH_2·HCl as above. The red–brown oil obtained after neutralization and extraction was transferred to a short path distillation apparatus. The yellow liquid that distilled between 125–127 °C/1 mmHg was pure (4-pentyl)pyrazole as indicated by NMR (18.5 g, 133.7 mmol, 58.4% based on heptanaldehyde diethylacetal). This compound crystallized on standing overnight in a refrigerator. Mp, *ca.* 21–23 °C. HRMS- Direct probe (m/z): calcd for $C_8H_{14}N_2$, 138.1157 found, 138.1155. ^{1}H NMR (400 MHz, $CDCl_3$) 8.02 (br s, 1H, NH), 7.41 (s 2H, $H_{3,5}$-pz), 2.49 (t, $J = 8$ Hz, 2H, CH_2), 1.58 (pseudoquint, 2H, CH_2), 1.33 (m, 4H, CH_2), 0.90 (t, $J = 8$ Hz, CH_3). ^{13}C NMR ($CDCl_3$) 132.9 (br s, -C=N), 121.6 (C_4-pz), 31.7 (CH_2), 30.8 (CH_2), 24.2 (CH_2), 22.7 (CH_2), 14.3 (CH_3).

Alternatively, 4-pentylpyrazole may be more easily handled as its hydrogen chloride salt (prepared independently with aqueous HCl solution and Et_2O in the above preparation). Colorless crystals of [H_2pz][Cl] in two morphologies (needles as the major form and blocks as the minor component) are produced by layering an Et_2O solution with hexanes and by allowing the layers to diffuse. See ESI‡ for crystal structures. Mp: 127–128 °C. (Lit.[8b] mp 127–128.5 °C) Anal. Calcd. (Obs.) For $C_8H_{15}N_2Cl$: C, 55.01 (55.40); H, 8.66 (8.28); N, 16.04 (16.21). ^{1}H NMR (400 MHz, $CDCl_3$) δ. 13.98 (br s, 2H, NH), 7.73 (s 2H, $H_{3,5}$-pz), 2.56 (t, $J = 8$ Hz, 2H, CH_2), 1.60 (pseudoquint, 2H, CH_2), 1.31 (m, 4H, CH_2), 0.89 (t, $J = 8$ Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ 130.8 (br s, -C=N), 123.5 (C_4-pz), 31.2 (CH_2), 30.0 (CH_2), 23.7 (CH_2), 22.5 (CH_2), 14.1 (CH_3).

***rac*-4-[(α-Ethyl)pentyl]pyrazole.** The product mixture from the Vilsmeier formylation of 9.00 g (41.6 mmol) (3-ethyl)heptanaldehyde diethylacetal with 8.40 mL $POCl_3$ (14.1 g, 91.8 mmol) and 7.80 mL (7.36 g, 101 mmol) DMF after hydrolysis and extraction with six portions of CH_2Cl_2 followed by three 100 mL portions Et_2O, afforded 4.71 g of a mixture of the ethoxy acrolein and dimethylamino acrolein in a 1.7 : 1 mol ratio (23.8 mmol, 57.1% based on (3-ethyl)heptanaldehyde diethylacetal). [^{1}H NMR (400 MHz, $CDCl_3$) of unseparated mixture had resonances for ethoxy derivative at δ_H 9.16 (s, HC=O), 6.89 [s, HC(OEt)], 4.14 (q, $J = 7.2$ Hz, OCH_2), 2.58 (m, 1H, CH), 1.62 (m 2H), 1.50 (m, 2H), 1.38 (t, $J = 7.2$ Hz, 3H OCH_2CH_3) 1.29–1.12 (br m, 2H), 0.92–0.77 (br m, CH_3) along with resonances for the dimethylamino derivative at δ_H 8.23 (s, HC=O), 6.76 [s, HC(NMe_2)], 3.11 (s, NMe_2).] After dissolving the mixture in 10 mL MeOH and allowing the mixture to react with 1.7 g (25 mmol) N_2H_4·HCl in 25 mL H_2O, followed by standard workup, a 3.5 g (51% based on (3-ethyl)-heptanaldehyde diethylacetal) of *rac*-[4-(α-ethyl)pentyl]pyrazole as a pale yellow liquid was isolated by collecting the fractions that distilled between 120–140 °C under vacuum (1 mmHg). HRMS-Direct probe (m/z): calcd for $C_{10}H_{18}N_2$, 166.1470 found, 166.1472. ^{1}H NMR (300 MHz, $CDCl_3$) 7.39 (s 2H, $H_{3,5}$-pz), 7.10 (br s, 1H, NH), 2.45 (m, 1H, CH(Et)Bu), 1.62 (m, 2H, CH_2), 1.49 (m, 2H, CH_2), 1.35–1.15 (br, m, 4H, CH_2), 0.86 (t, $J = 7$ Hz, 3H, CH_3), 0.82 (t, $J = 8$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) 132.4 (br s, -C=N), 125.6 (C_4-pz), 37.3, 36.2, 29.8, 29.7, 23.0, 14.3, 12.0.

4-(Cyclohexyl)pyrazole. The product mixture from the Vilsmeier formylation of 8.07 g (44.4 mmol) 2,2′-diethoxyethylcyclohexane, 8.10 mL $POCl_3$ (13.6 g, 88.5 mmol) and 6.88 mL (6.49 g, 88.8 mmol) DMF, after hydrolysis, neutralization, and extraction with three 100 mL portions CH_2Cl_2, one 100 mL portion C_6H_6, one 100 mL portion Et_2O followed by another two 100 mL portions CH_2Cl_2 afforded 6.20 g of a mixture of the ethoxy acrolein and dimethylamino acrolein in a 4.26:1 mol ratio (34.1 mmol, 78% based on 2,2′-diethoxyethylcyclohexane). [^{1}H NMR (400 MHz, $CDCl_3$) of unseparated mixture had resonances for ethoxy derivative at δ_H 9.27, 9.09 (s, HC=O), 6.89 [s, HC(OEt)], 4.48, 4.14 (q, $J = 7.2$ Hz, 2H, OCH_2CH_3), 2.56 (m, 1H, CH), 1.80–1.60 (m 2H), 1.50–1.35 (m, 2H), 1.37 (t, $J = 7.2$ Hz, 3H OCH_2CH_3) 1.31–1.12 (br m, CH_2), 0.90–0.77 (br m, CH_2) along with resonances for the dimethylamino derivative at δ_H 8.62, 7.88 (s, HC=O), 7.00 [s, HC(NMe_2)], 3.88, 3.47, 3.14 (s, NMe_2).] After dissolving the mixture in 10 mL MeOH and allowing the mixture to react with 2.33 g (25 mmol) N_2H_4·HCl in 25 mL H_2O, followed by standard workup, the crude red oil (3.98 g) was transferred to a 100 mL Schlenk flask which was subsequently connected to another 100 mL Schlenk flask by a glass elbow, the flask containing the residue was evacuated (0.1 mmHg) and heated to *ca.* 230 °C. The crude pyrazole sublimed into the glass elbow and was washed with hexanes to remove trace highly-colored impurities. The washings were cooled to −20 °C overnight to give 0.52 g of the desired pyrazole as pale yellow needles after filtering from the mother liquor and drying under vacuum. The combined yield of (4-cyclohexyl)-pyrazole as a colorless powder (the original hexane insoluble solid) and as the recovered crystalline solid was 2.90 g (47% based on 2,2′-diethoxyethylcyclohexane). Mp: 128–130 °C (Lit.[9e] 130 °C). Anal. Calcd. For $C_9H_{14}N_2$: C, 71.96 (71.64) H, 9.39 (9.04) N, 18.65 (18.42). ^{1}H NMR (300 MHz, $CDCl_3$) 7.56 (br s, 1H, NH), 7.42 (s 2H, $H_{3,5}$-pz), 2.53 (m, 1H, C_1H-cy), 1.92 (m, 2H, CH_2), 1.81–1.70 (br, m, 3H), 1.44–1.17 (br m, 5H). ^{13}C NMR (75.4 MHz, $CDCl_3$) 131.5 (br s, -C=N), 127.9 (-C=), 34.7, 34.1 (C_1), 26.6, 26.3.

4-(Phenyl)pyrazole. The product mixture of the Vilsmeier reaction between 5.20 mL $POCl_3$ (8.71 g, 56.8 mmol), 4.60 mL (4.34 g, 59.4 mmol) DMF, and 5.04 g (25.9 mmol) phenylacetaldehyde diethylacetal was hydrolyzed and neutralized as described for the ethyl derivative. Extraction with six 100 mL portions of CH_2Cl_2 and removal of solvents (including DMF) left 2.00 g of a solid residue thought to be the dimethylamino acrolein (11.4 mmol, 44.0% based on phenylacetaldehyde diethylacetal) due to the lack of ethoxy resonances in its complicated NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$) 10.5, 9.78, 9.66, 9.06, 8.66, 8.01, 7.80, 7.56–7.17 (br m), 6.93 (br m), 3.86–2.60 (br). The residue was dissolved in 10 mL MeOH and was treated with 0.78 (11.4 mmol) N_2H_4·HCl in 25 mL H_2O. Following workup, a red black solid remained and was subjected to purification as described for (4-cyclohexyl)pyrazole affording 1.36 g of (4-phenyl)pyrazole as a colorless solid (36.4% based on phenylacetaldehyde diethylacetal). Mp: 234–235 °C (Lit mp's; 236–237 °C,[10b] and others between 228–232 °C.[7d,10a,10d–h]) Anal. Calcd. for $C_9H_8N_2$: C, 74.98 (74.98) H, 5.59 (5.50) N, 19.43 (19.36). ^{1}H NMR (300 MHz, acetone-d_6) 12.21 (br, s, 1H, NH), 8.01 (s, 2H, $H_{3,5}$-pz), 7.61 (d, $J = 7.5$ Hz, 2H, o-Ph), 7.35 (dd, $J = 7.5$, 1 Hz, 2H, m-Ph),

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(dt, $J = 7.5$, 1 Hz, 1 H, p-Ph). ^{13}C NMR (75.4 MHz $CDCl_3$) 136.5, 134.2, 129.6, 126.8, 126.2, 125.9, 122.8.

1,1′,3,3′-Tetrakis[(4-ethyl)pyrazol-1-yl]propane, $CH_2[CH(pz^{4Et})_2]_2$. A 10 mL Schlenk tube fitted with a magnetic stirbar was charged with 0.43 mL (0.43 g, 0.026 mol) malonaldehyde dimethylacetal, 1.0 g (0.10 mol) of (4-ethyl)pyrazole, and 0.050 g (0.26 mmol) *p*-toluenesulfonic acid monohydrate. The flask was attached to a reflux condenser and heated 10 h with an oil bath maintained at 180° (*caution*, an oil bath at this temperature must be located in a hood and can ignite). The sample was periodically cooled and the progress of the reaction was monitored by ^{1}H NMR spectroscopy which indicated 90% conversion during the heating period. After that time, the reaction mixture was worked up by transferring the contents of the Schlenk tube to a separatory funnel with CH_2Cl_2, the organic layer was washed with water and was separated. The aqueous portion was then extracted with three 50 mL portions of CH_2Cl_2, the combined organic fractions were dried over $MgSO_4$, filtered and solvent was removed to leave a brown oil. Column chromatography on silica gel with Et_2O as the eluent afforded 0.66 g (60% yield based on malonaldehyde dimethylacetal) of $CH_2[CH(pz^{4Et})_2]_2$ as a pale yellow-brown viscous liquid in the first yellow band. HRMS-direct probe (m/z): calcd for $C_{23}H_{32}N_8$: 420.2750 found, 420.2740. Direct probe MS m/z (Rel. Int.%) [assgn]: 420 (9) $[M]^+$, 325 (26) $[M\text{-}pz^{4Et}]^+$, 229 (77) [M-2 pz^{4Et} -H]$^+$, 204 (100) $[HC(pz^{4Et})_2]^+$, 133 (42) [M-3H pz^{4Et}]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$) 7.39 (s, 4H, H_5-pz), 7.30 (s, 4H, H_3-pz), 6.00 (t, $J = 8$ Hz, 2H, $CH(pz)_2$), 3.80 (t, $J = 8$ Hz, 2H, CH_2), 2.44 (q, $J = 8$ Hz, 8H, CH_2CH_3), 1.16 (t, $J = 8$ Hz, 12 H, -CH_3). ^{1}H NMR (400 MHz, acetone-d_6) 7.55 (s, 4 H, H_3-pz), 7.37 (s 4H, H_5-pz), 6.08 (t, $J = 8$ Hz, 2H, $CH(pz)_2$), 3.86 (t, $J = 8$ Hz, 2H, CH_2), 2.44 (q, $J = 8$ Hz, 8H, CH_2CH_3), 1.14 (t, $J = 8$ Hz, 12 H, -CH_3). ^{13}C NMR (101.62 MHz, $CDCl_3$) 140.1 (C_5-pz), 126.1 (C_3-pz), 124.8 (C_4-pz), 72.0 (CH-pz), 38.1 (CH_2), 17.6 (–CH_2CH_3), 15.0 (CH_3). ^{13}C NMR (101.62 MHz, acetone-d_6) 140.0 (C_5-pz), 127.3 (C_3-pz), 125.0 (C_4-pz), 72.6 (CH-pz), 38.1 (CH_2), 17.9 (–CH_2CH_3), 15.3 (CH_3).

$[Ag_2\{\mu\text{-}CH_2[CH(pz^{4Et})_2]_2\}_2]_3[Ag(NO_3)_4]_2$ (1). A solution of 0.11 g (0.62 mmol) $Ag(NO_3)$ in 10 mL CH_3CN was added by cannula to a foil-covered 50 mL Schlenk flask that contained a solution of 0.26 g (0.62 mmol) $CH_2[CH(pz^{4Et})_2]_2$ in 10 mL CH_3CN. After the resulting tea-colored solution had been magnetically stirred for 2 h at room temperature, the solvent was removed by vacuum distillation, the residue was washed with two 5 mL portions of Et_2O, dried under vacuum to leave a pale tan solid. The solid was then dissolved in a minimal amount (5 mL) of acetone, filtered into a vial for crystallization, and layered with Et_2O. Colorless crystals formed while allowing the solvents to diffuse overnight. The mother liquor was removed by pipette and the resulting crystals were dried under vacuum for 1 h to leave 0.25 g of analytically pure **1** (84% based on $CH_2[CH(pz^{4Et})_2]_2$) as opaque blocks. Mp 125–130 °C decomp. pale yellow glass; 145–150 °C apparent gas evolution, 160 °C liquifies. Anal. Calcd. (found) for $C_{138}H_{192}N_{56}O_{24}Ag_8$: C, 42.69 (42.22); H, 4.98 (4.72); N, 20.20 (19.84). ESI(+) MS m/z (Rel. Int.%) [assgn]: 1305 (0.3) $[Ag_2L_2(NO_3)_2(H_2O)]^+$, 1287 (0.5) $[Ag_3L_2(NO_3)_2]^+$, 1118 (10) $[Ag_3L_2(NO_3)]^+$, 949 (87) $[AgL_2]^+$, 568 (40) $[AgL(CH_3CN)]^+$, 527 (40) $[AgL]^+$, 421 (22) $[L]^+$, 325 (100) $[L\text{-}pz^{4Et}]^+$. ESI(−) MS m/z (Rel. Int.%) [assgn]: 1411 (9) $\{[Ag_2L_2][Ag(NO_3)_4]\}^-$, 991 (8) $\{[Ag_2L][Ag(NO_3)_4]\}^-$, 822 (15) $[Ag_2L(NO_3)_3]^-$, 402 (100) $[Ag_2(NO_3)_3]^-$, 231 (70) $[Ag(NO_3)_2]^-$. ^{1}H NMR (400 MHz, acetone-d_6) 7.92 (s, 4H, H_3-pz), 7.63 (t, $J = 8$ Hz, 2H, $CH(pz)_2$), 7.53 (s, 4H, H_5-pz), 4.48 (t, $J = 8$ Hz, 2H, CH_2), 2.46 (q, $J = 8$ Hz, 8H, CH_2CH_3), 1.16 (t, $J = 8$ Hz, 12 H, -CH_3). ^{13}C NMR (101.62 MHz, acetone-d_6) 143.0 (C_5-pz), 131.1 (C_3-pz), 124.6 (C_4-pz), 71.6 (CHpz), 38.5 (CH_2), 17.7 (-CH_2CH_3), 15.1 (CH_3). Samples for X-ray structural studies were grown similarly, however, since the crystals decompose readily in the absence of solvent, the mother liquor was retained and the crystals were mounted as described below.

Crystal structure determinations

$H(pz^{4Ph})$. A brown needle bar crystal of $H(pz^{4Ph})$ was mounted onto the end of a thin glass fiber using inert oil. X-ray intensity data were measured at 150.0(2) K on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å).[21] The raw data frames were integrated with SAINT+,[21] which also applied corrections for Lorentz and polarization effects. The final unit cell parameters are based on the least-squares refinement of 4205 reflections from the data set with $I > 5\sigma(I)$. Analysis of the data showed negligible crystal decay during data collection. No correction for absorption was applied.

Systematic absences in the intensity data uniquely determined the space group Pbcn. The structure was solved by a combination of direct methods and difference Fourier syntheses, and refined against F^2 by full-matrix least-squares, using SHELXTL.[22] After identification and anisotropic refinement of all non-hydrogen atoms, hydrogen atoms attached to appropriate carbon atoms were clearly located in the difference map and freely refined with isotropic displacement parameters. At this point apparent hydrogen positions (H1N and H2N) for both nitrogens were observed, in violation of electroneutrality. This corresponds to equal disorder of one hydrogen over both nitrogens. Refinement of the occupancies of H1N and H2N resulted in reasonable U_{eq} values and occupancies close to $\frac{1}{2}$ for each H atom. For the final refinement cycles the occupancies of H1N and H2N were fixed at $\frac{1}{2}$, and their xyz coordinates and U_{eq} was allowed to refine freely.

Crystal data for $C_9H_8N_2$, $M = 144.17$, orthorhombic, Pbcn, $a = 17.2047(11)$ Å, $b = 11.8608(8)$ Å, $c = 7.3253(5)$ Å, $U = 1494.81(17)$ Å^3, $Z = 8$, μ(Mo-Kα) = 0.079 mm^{-1}, $T = 150(2)$. 8275 reflections measured, 1191 unique ($R_{int} = 0.0525$), 137 parameters. Final $R1$ [$I > 2(I)$] = 0.0354, $wR2$ [all data] = 0.0860, GoF = 1.055.

$[Ag_2\{\mu\text{-}CH_2[CH(pz^{4Et})_2]_2\}_2]_3[Ag(NO_3)_4]_2$ (1). Large well-formed colorless block crystals of $[Ag_2\{\mu\text{-}CH_2[CH(pz^{4Et})_2]_2\}_2]_3[Ag(NO_3)_4]_2$ (**1**) are stable when left undisturbed in the mother liquor, but are extremely sensitive to temperature changes and mechanical manipulation. Crystals survive for several seconds in paratone-N oil, long enough for quick mounting and flash-freezing on the diffractometer, but crack immediately when placed in the diffractometer cold stream. After a series of unsuccessful attempts at temperatures ranging from 240 K to 100 K, low-temperature data collection was abandoned and crystals were mounted in the mother liquor inside thin-walled capillary tubes. Complete (sphere) data sets for three crystals were collected (Bruker SMART APEX diffractometer, Mo Kα, $\lambda = 0.71073$ Å; raw data frame integration with SAINT+).[21] All three crystals showed significant cracking during the <8 h data collections, and only the best of these data sets is reported here. Due to the crystal stability problems, only general features of the connectivity and molecular geometry will be reported; bond lengths and angles should be considered imprecise and unreliable. The crystal instability is most likely due to the high disordered solvent content (*ca.* 45% of the total unit cell volume, calculated by PLATON[23]), which is also responsible for the lack of appreciable X-ray scattering above *ca.* $2\theta = 40°$.

Compound **1** crystallizes in the triclinic system, in the space group $P\bar{1}$. The asymmetric unit contains half each of three $[Ag_2(\mu\text{-}C_{23}H_{32}N_8)_2]^{2+}$ cations and one $[Ag(NO_3)_4]^{3-}$ anion. All ethyl groups of the cations show inflated displacement ellipsoids, a symptom of disorder. Two terminal –CH_3 groups

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of the ethyl substituents could not be located due to disorder [the affected ethyl groups are associated with pz rings N(61)–C(63) (Ag2) and N(111)–C(113) (Ag3)]. All located species were refined anisotropically with hydrogens in idealized positions. Multiple diffusely distributed electron density peaks are also present in voids between the identifiable species, assumed to be disordered solvent. These were modeled as variable occupancy carbon atoms with a common fixed isotropic displacement parameter. Solvent peaks were assigned until the largest residual electron density was located near an Ag atom. SHELXTL[22] and PLATON[23] were used to perform the calculations.

Crystal data for $C_{138}H_{192}Ag_8N_{56}O_{24}$, $M = 3882.44$, triclinic, $P\bar{1}$, $a = 12.2524(7)$ Å, $b = 21.8178(13)$ Å, $c = 27.0779(16)$ Å, $\alpha = 68.5730(10)°$, $\beta = 80.9340(10)°$, $\gamma = 87.3490(10)°$, $U = 6653.5(7)$ Å^3, $Z = 1$, μ(Mo-Kα) = 0.626 mm^{-1}, $T = 293(2)$. 31 940 reflections measured, 14 793 unique ($R_{int} = 0.0387$), 1079 parameters. Final $R1$ [$I > 2(I)$] = 0.0727, $wR2$ [all data] = 0.2481, GoF = 1.037.

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