with A to give the same sandwich cluster as the reaction of A with magnesium does.

Recently Sykes and colleagues reported the following reaction to give mixed-metal aqua complexes with Mo_3MS_4 cores:[11]

$$Mo_3S_4(aq)^{4+} + M^{2+} + 2e \rightarrow Mo_3MS_4^{4+}$$

Generation of $[Mo_4S_4(H_2O)_{12}]^{5+}$ from A and $[Mo(H_2O)_6]^{3+}$ in the presence of $NaBH_4$ is also described.

By the addition of $SbCl_3$ or CuI to incomplete cubane-type clusters $[Mo_3S_4(dtp)_4(L)]$ (L = H_2O, C_3H_3ON), new mixed-metal clusters with Mo_3MS_4 cores (M = Sb, Cu) have been synthesized: Lu et al.[12] and Huang et al.[13] reported the syntheses, characterization and structures of $[Mo_3SbS_4(dtp)_4(Cl_3)(L)]$ (L = EtOH, oxazole); Wu et al.[14] described the synthesis and structure of $[Mo_3CuS_4(dtp)_3(CH_3COO)(I)(dmf)]$; the structure of $[Mo_3CuS_4(dtp)_3(CH_3COO)(I)(H_2O)]$ has also been determined.[13]

Kuchen and co-workers synthesized $[Mo_3WS_4(Et_2PS_2)_6]$ by the reaction of equimolar quantities of $[Mo_3S_4(Et_2PS_2)_4]$, $[W(CO)_3(CH_3CN)_3]$, and $(Et_2P(S))_2S_2$.[15]

Except for compound **7** (Table VII), the formal charges of the cores of the mixed-metal compounds are addition of the formal charges of the Mo_3S_4 core (=+4) and the metals or metal ions: 4 + 0 for **1**–**4**; 4 + 1 for **5** and **6**; 4 + 3 for **8** and **9**; 2 × 4 + 2 × 0 for **10** and **11**; 2 × 4 + 0 for **12** and **13**; 4 + 2 for **14**. In compound **7**, oxidative addition of the ligand $(Et_2P(S))_2S_2$ occurs: 4 + 0 (from $[W(CO)_3(CH_3CN)_3]$) + 2 (from the ligand).

Acknowledgment. We thank Miss Riyoko Yoshihara for her help in the preparative work. This work was supported by Grants-in-Aid for Scientific Research (62470043, 02453043) from the Ministry of Education, Science, and Culture of Japan.

Supplementary Material Available: Listings of crystallographic and machine parameters, thermal parameters, bond distances and angles, and short contacts (Tables SI–SVIII) and plots of absorption changes by the addition of Fe^{3+} to B′ (Figure S1), absorption at 700 nm vs Fe^{3+}/B′ (Figure S2), and determination of the formation constant (Figure S3) (25 pages); tables of F_o and F_c values for compounds B and C (27 pages). Ordering information is given on any current masthead page.

Notes

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Reactions of Polycyano Compounds with Chlorine Fluoride

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Introduction

N,N-Dihaloperfluoroalkylamines continue to be of interest as isolable intermediates. Straightforward, high-yield syntheses of chlorofluoroamines have made these compounds readily available in useful quantities. *N,N*-Dichloroperfluoroalkylamines are commonly used for generation of perfluoroalkyldiazenes via photolytic or thermal processes.[3,4]

We have sought to produce new *N,N*-dichloroperfluoro(polyfluoro)alkylamines by the reaction of ClF with compounds possessing two or more cyano groups. In this way, new compounds with multiple $-NCl_2$ functionalities should result that could lead to new heterocycles or possibly azo polymers. Compounds that contain two $-NCl_2$ groups are known; e.g., with ClF, cyanogen gives $Cl_2NCF_2CF_2NCl_2$. However, H_2NCN was observed to lose NCl_3 upon reaction with an excess of ClF, which suggests that $Cl_2NCF_2NCl_2$ was an intermediate.[5] Perfluoromalononitrile, also gives a bis-NCl_2 derivative.[6]

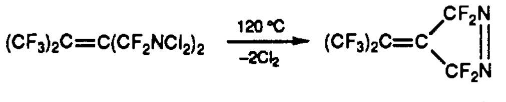
Compounds with two or more cyano groups undergo rapid reaction to produce the respective derivatives in nearly quantitative yields. Reactants that contain carbon–carbon double bonds give products that are also unsaturated. In this paper, we report the reactions of $(NC)_2C{=}C(CN)_2$ (TCNE), $H_2C(CN)_2$, $KC(CN)_3$, and $(CF_3)_2C{=}C(CN)_2$ with ClF and the subsequent attempts to prepare diazenes. In addition, an improved, one-step synthesis of CF_3NCl_2, a precursor of hexafluoroazomethane, from ClCN and ClF over CsF is given.

Results and Discussion

In general, the controlled addition of ClF to polycyano compounds leads to interesting new products. The product obtained from the reaction of $(CF_3)_2C{=}C(CN)_2$ with ClF (1:5) exhibits a weak carbon–carbon double bond at 1635 cm^{-1} in the infrared spectrum. Only 80% of the chlorine fluoride is consumed, which also indicates that the reaction is one of saturation of the cyano groups only

$$(CF_3)_2C{=}C(CN)_2 + ClF(excess) \rightarrow \underset{95\%}{(CF_3)_2C{=}C(CF_2NCl_2)_2}$$

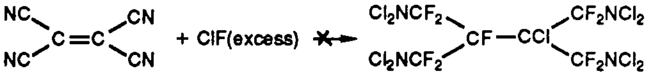
Although a molecule ion is not observed in the mass spectrum, with ($M^+ - Cl_2F$) being the highest *m/e* seen, when $(CF_3)_2C{=}C(CF_2NCl_2)_2$ is thermolyzed at 120 °C, loss of chlorine occurs to give the cyclic diazene



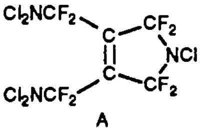
No molecule ion is observed in the mass spectrum, where the highest *m/e* seen is at *m/e* 262 ($M^+ - N_2$), but excellent elemental analyses support the proposed structure.

Because of the low thermal stability of $H_2C(CF_2NCl_2)_2$ [$H_2C(CN)_2$ + ClF], dimerization via thermolysis or photolysis was not attempted. However, since HF elimination was observed, several attempts were made in order to isolate a new olefin. With KF or CsF, there was a violent reaction but no new compounds were isolated.

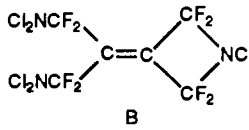
When study of these systems was initiated, it was supposed that an excess of ClF would saturate all of the multiple bonds in TCNE



Because stoichiometric elimination of N_2 and Cl_2 was observed and only two groups of structurally equivalent fluorine atoms were found in the ^{19}F NMR spectrum, two structures seem likely



A



B

Because of the ease of formation and subsequent greater stability of a five-membered ring, structure A is more likely. The intensity of the C=C bond stretching frequency at 1685 cm^{-1} in the infrared spectrum is very weak, but the band is definitely present. This suggests little polarization in the molecule. Structure B would be expected to have a much more intense C=C stretching band

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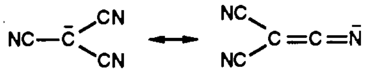
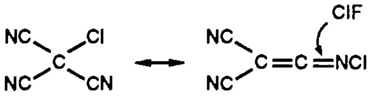
in the infrared spectrum. The elimination of [NCl_3] has been seen for at least one other compound, but it appears to be rare.[6] The evidence points to the formation of a heterocyclic compound with structure A.

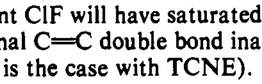
The structure of the $KC(CN)_3$/ClF product was only tentatively identified. The same dense liquid was always isolated from the reaction, and KF was the sole byproduct. By analogy with the expected product from the TCNE/ClF reaction, a saturated molecule was expected: $KC(CN)_3 + 7ClF \rightarrow ClC(CF_2NCl_2)_3 + KF$. Again, the data indicate a much different end result. The presence of a C=C bond at 1633 cm^{-1} is evident in the infrared spectrum. The elemental analysis proved consistent with a 5:1 $ClF/KC(CN)_3$ reaction. It is known that, for the $C(CN)_3^-$ anion and covalent derivatives such as $HC(CN)_3$, two resonance forms predominate[7]



where the latter form is statistically 3 times more prevalent. On the basis of this assumption, one can postulate how the $C(CN)_3^-$ anion reacts with ClF. When Cl(I) replaces K^+ of $KC(CN)_3$, it should make little difference whether the chlorine resides on the central carbon or on the nitrogen, since $ClC(CN)_3$ would be subject to the analogous tautomerization, and ClF would then add to the most reactive site:



Eventually, sufficient ClF will have saturated the cyano groups and rendered the final C=C double bond inactive toward electrophilic attack (as is the case with TCNE). This explains the presence of the carbon–carbon double bond observed in the IR spectrum, but it does not explain the NMR data or elemental analyses. A 5:1 observed ratio of ClF addition indicates an empirical formula of $C_4Cl_5F_4N_3$. One possible structure would be



which may exist in *Z* and *E* forms. Such a structure necessitates a 32-line ^{19}F spectrum, assuming no accidental degeneracy of peaks. The fact that no C=N bond was seen in the IR spectrum and that ^{19}F NMR the spectrum contained only 22 lines led us to believe that the compound may be dimerized or that a total rearrangement has occurred. A definitive structure, however, remains to be established for this product. Thermolysis at ≥160 °C gave small amounts of chlorine and CF_2=NCl.

The resistance of the C=C bond to saturation in all but the product from the malononitrile/ClF reaction suggests that these compounds are surprisingly stable. Treatment of these new materials with excess ClF in the presence of CsF failed to saturate the double bond. TCNE and $(CF_3)_2C$=$C(CN)_2$ are two olefins that are deactivated with respect to electrophilic attack, yet their polarities are quite different. In both cases, ClF did not attack the original carbon–carbon double bond. For $KC(CN)_3$, the tautomerization postulated above would also result in the formation of an intermediate with a C=C double bond and, thus, explain the presence and retention of a C=C bond in the final product. For the reaction between malononitrile and ClF, the product is certainly saturated, but it also tends to lose HF and form an unsaturated species that apparently polymerizes.

The synthesis of CF_3NCl_2 has been previously described.[8,9] With cyanogen chloride, ClF forms $ClCF_2NCl_2$ in high yields.[10] However, in the presence of CsF, an additional equivalent of ClF gives rise to a nearly complete conversion to CF_3NCl_2. No $ClCF_2NCl_2$ was found during separation of the products although undoubtedly $ClCF_2NCl_2$ is formed initially, since when the mixture reaction was examined shortly after reaching 22 °C, it was found to contain mainly $ClCF_2NCl_2$ with a significant amount of CF_3NCl_2. After 2 h at 22 °C, almost all $ClCF_2NCl_2$ was converted to CF_3NCl_2; after 6 h, not a trace of $ClCF_2NCl_2$ remained.

Experimental Section

General Methods. All the compounds were handled in a Pyrex vacuum system equipped with both glass and glass–Teflon valves. Quantities of volatile compounds were determined by *PVT* measurements assuming ideal gas behavior. Pressures were measured with a Heise Bourdon tube gauge. Infrared spectra were recorded on a Perkin-Elmer 599B spectrometer by using a 10-cm gas cell equipped with KBr windows. Mass spectra were obtained from a Perkin-Elmer Hitachi RMU-6E spectrometer at an ionization potential of 15 eV. ^{19}F NMR spectra were obtained on a JEOL FX-90Q spectrometer using $CDCl_3$ as solvent and $CFCl_3$ as reference.

Reagents. Malononitrile (Kay-Fries) was distilled from P_4O_{10} before use. Tetracyanoethene (Aldrich) was resublimed twice before use. The compounds $KC(CN)_3$[7] and $(CF_3)_2C$=$C(CN)_2$[11] were prepared by literature methods. Chlorine fluoride (Ozark-Mahoning) and cyanogen chloride (K&K) were used without purification. Cesium fluoride (Aldrich) was finely ground prior to drying at 140 °C. Treatment of CsF with ClF in the stainless steel vessel before use greatly improved its activity.

Reaction of Tetracyanoethane with ClF. A 150-mL stainless steel Hoke vessel was passivated with ~10 mmol of ClF for 1 h and then evacuated. Tetracyanoethane (TCNE) (0.44 g, 3.44 mmol) was added, and the vessel was reevacuated and cooled to −196 °C. A 9:1 molar excess of ClF and ~5 mL of dry CCl_3F were introduced. The system was warmed to 22 °C and allowed to remain for 2 h with occasional agitation. Examination of the reactor contents at −196 °C showed that 1.70 mmol of N_2 had been eliminated. Other materials volatile at this temperature were Cl_2, excess ClF, and $CFCl_3$. The involatile liquid remaining at 22 °C was extracted with pentane. Subsequent evaporation and vacuum distillation in a simple glass apparatus attached to the vacuum line afforded the pure compound. An infrared spectrum indicated that a C=C bond was present and that no C≡N bond remained. Subsequent experiments showed that each mole of TCNE eliminated 1 mol of [NCl_3] during reaction. Elemental analysis confirmed the empirical formula of $C_6Cl_5F_8N_3$. The compound is a glass at −85 °C and is extremely viscous at temperatures below 0 °C. Anal. Calcd for $C_6Cl_5F_8N_3$: Cl, 39.98; F, 34.28; N, 9.48. Found: Cl, 39.32; F, 33.6; N, 9.44. IR (neat film, AgCl windows): 1685 w, 1340 m, 1267 vs, 1216 s, 1126 vs, 1000 m, 984 m, 863 s, 837 m, 804 m, 767 m, 755 m, 722 s, 706 m, 695 m, 678 m, 646 w, 616 m, 560 m, 522 w cm^{-1}. ^{19}F NMR ($CDCl_3$): two pentetlike resonances of equal intensity with fine splitting centered at ϕ −81.8 and −86.9, respectively. Major peaks in the mass spectrum (all spectra will consider ^{35}Cl isotope only for sake of simplicity), *m/e*: 441, M^+; 387, $C_6F_7N_3Cl_4^+$; 333, $C_6F_6N_3Cl_3^+$; 298 $C_6F_6N_3Cl_2^+$ (base peak); 244, $C_6F_5N_3Cl^+$; 190, $C_6F_4N_3^+$; 171 $C_6F_3N_3$.

Reaction of Malononitrile with ClF. In a typical experiment, 1.17 g of $H_2C(CN)_2$ (17.7 mmol) was placed in a passivated 150-mL stainless steel Hoke vessel. A 5-fold molar excess of ClF was condensed onto the $H_2C(CN)_2$ at −196 °C. The mixture was allowed to warm from −116 °C in an ethanol slush bath. After reaching 22 °C (~12 h), the materials that are volatile at this temperature (mainly excess ClF) were examined and found to contain no other species of significance. A nonvolatile liquid remained in the vessel. It was extracted with pentane, and the extract was distilled. The yield of $H_2C(CF_2NCl_2)_2$ was greater than 95% on the basis of subsequent experiments to determine the amount of unreacted ClF. Characterization was based mainly on the ^{19}F NMR and IR spectra. Experimental data for $H_2C(CF_2NCl_2)_2$ are as follows. IR (neat, NaCl windows): 3009 w, 2975 w, 1423 m, 1372 s, 1250 vs, 1195 vs, 1126 vs, 1045 s, 1028 s, 904 s, 876 m, 853 s, 785 m, 728 m, 695 w, 682 w, 654 m, 611 s cm^{-1}. ^{19}F NMR: ϕ −87.05 (t). ^1H NMR: δ 3.19 (p); $^3J_{HF}$ = 13 Hz. Anal. Calcd for $C_3Cl_4F_4H_2N_2$: Cl, 49.96; F, 26.77; N, 9.87. Found: Cl, 50.60; F, 24.80; N, 10.34. The error in the elemental analysis resulted from a slow loss of HF from the compound during shipment to Germany for analysis. Similar behavior was eventually observed in subsequent reactions. The instability of this compound at higher temperatures prohibited us from obtaining an interpretable mass spectrum.

Reaction of $(CF_3)_2C$=$C(CN)_2$ with ClF. 1,1-Dicyano-2,2-bis(trifluoromethyl)ethane (4.39 g, 20.5 mmol) and ClF (103 mmol) were condensed into a 150-mL stainless steel Hoke vessel and cooled to −196 °C. The system was allowed to warm directly to 22 °C over 2 h. Excess

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ClF was recovered in a quantity indicating that a quantitative conversion had taken place. The isolated product amounted to 94% yield after distillation. The compound is a glass at −85 °C with a vapor pressure of 0.5−1 Torr at 22 °C. IR (neat liquid, KBr windows): 1635 w, 1300 s, 1215 vs, 1125 vs, 1056 s, 990 m, 902 m, 863 m, 818 m, 777 w, 742 w, 724 s, 696 s, 669 w, 647 m, 613 m, 597 w, 540 m, 515 w $\mathrm{cm^{-1}}$. ^{19}F NMR: ϕ −58.24 (t-t), $\mathrm{CF_3}$; ϕ −80.59 (m), $\mathrm{CF_2}$. Major peaks in the mass spectrum, *m/e*: 341, $\mathrm{C_6F_9N_2Cl_2^+}$; 287, $\mathrm{C_6F_8N_2Cl^+}$; 268, $\mathrm{C_6F_7N_2Cl^+}$; 262, $\mathrm{C_6F_{10}^+}$; 243, $\mathrm{C_6F_9^+}$; 212, $\mathrm{C_5F_8^+}$; 193, $\mathrm{C_5F_7^+}$; 145, $\mathrm{C_5F_3N_2^+}$; 69, $\mathrm{CF_3^+}$.

Preparation of $\mathrm{CF_3NCl_2}$. Into a dry 300-mL Monel Hoke vessel were placed 25 g of CsF and three steel balls. The vessel was evacuated and cooled to −196 °C. Next, 50 mmol of ClCN was condensed into the bomb, followed by 155 mmol of ClF. The system was warmed directly to 22 °C and, with intermittent shaking, was allowed to stand for 6−12 h. At the end of this time, the only detectable volatile compound at 50 Torr by IR analysis was $\mathrm{CF_3NCl_2}$. By repeated separation through traps at −125, −100, and −78 °C, pure $\mathrm{CF_3NCl_2}$ was collected as a liquid in the trap at −78 °C. Only $\mathrm{Cl_2}$ passed through −100 °C and was discarded. The trap at −100 °C contained mostly $\mathrm{CF_3NCl_2}$ with some dissolved $\mathrm{Cl_2}$. The material in this trap was repeatedly run through the system until all of the chlorine was separated from the $\mathrm{CF_3NCl_2}$. In this way, 48 mmol of $\mathrm{CF_3NCl_2}$ was collected. The compound was identified by its IR spectrum. The stoichiometry of the reaction obeys the chemical equation $\mathrm{ClCN + 3ClF \xrightarrow{CsF} CF_3NCl_2 + Cl_2}$. The role of CsF appears to be catalytic, since all ClF is consumed in the reaction. Furthermore, a single 10-g charge of CsF was used for 35-, 50-, and 60-mmol batches in succession with no loss of activity or yield.

Thermal Decomposition of $\mathrm{(CF_3)_2C{=}C(CF_2NCl_2)_2}$. This thermal decomposition reaction was the only case in which a pure diazene derivative resulted via loss of $\mathrm{Cl_2}$. Typically, 1.58 g (3.66 mmol) $\mathrm{(CF_3)_2C{=}C(CF_2NCl_2)_2}$ was injected into a Pyrex tube reactor, which was quickly evacuated and flame-sealed. The system was placed in an oven at 90 °C, and the temperature was then set at 120 °C. Upon this further warming, the chlorine was readily evident, and heating was continued until no more of the dense starting material was seen to reflux on the walls of the tube. When the reaction was over, the tube was connected to the vacuum line, frozen to −196 °C, and cracked open. There were no noncondensable materials at −196 °C, which indicates that dinitrogen was not formed. All the volatile materials were condensed onto Hg, and the amount of $\mathrm{Cl_2}$ taken up was measured. The $\mathrm{Cl_2}$ (6.91 mmol) eliminated corresponded to a 94.4% conversion to a diazene that was subsequently identified by its IR, NMR, and mass spectra and elemental analysis. IR (vapor): 1705 m, 1590 m, 1352 m, 1280–1200 vs, 1116 s, 1058 vs, 1018 m, 955 w, 908 s, 851 s, 827 w, 770 w, 748 s, 710 s, 682 m, 625 s, 547 w, 468 s, 426 m $\mathrm{cm^{-1}}$. ^{19}F NMR: ϕ −61.27 m, $\mathrm{CF_3}$; ϕ −80.69 m, $\mathrm{CF_2}$. Anal. Calcd for $\mathrm{C_6F_{10}N_2}$: C, 24.85; F, 65.50; N, 9.66. Found: C, 24.75; F, 65.60; N, 9.73. Major peaks in the mass spectrum, *m/e*: 262, $\mathrm{M^+ - N_2}$ ($\mathrm{C_6F_{10}^+}$); 243, $\mathrm{C_6F_9^+}$; 212, $\mathrm{C_5F_8^+}$; 193, $\mathrm{C_5F_7^+}$; 143, $\mathrm{C_4F_5^+}$; 69, $\mathrm{CF_3^+}$.

Reaction of $\mathrm{KC(CN)_3}$ with ClF. In a 150-mL stainless steel Hoke bomb, 0.47 g (3.64 mmol) of previously dried $\mathrm{KC(CN)_3}$ was mixed with ~3 mL of dry $\mathrm{CCl_3F}$. The contents were frozen to −196 °C, and an 8:1 mole ratio of ClF was condensed inside. After the contents were warmed from −116 to +22 °C over 12 h, excess ClF and $\mathrm{CCl_3F}$ were removed, leaving a nonvolatile dense liquid. During the extraction with pentane, the insoluble KF byproduct was evident. A yield of 90% or higher was obtained under optimum conditions. In cases where $\mathrm{KC(CN)_3}$ was not predried or the reaction was scaled to greater than 0.65 g of $\mathrm{KC(CN)_3}$, complete degradation of the contents was observed ($\mathrm{N_2}$, $\mathrm{CF_4}$, $\mathrm{CF_3Cl}$). This occurred even when the reactor was allowed to warm slowly from −116 °C. Also, the product must be isolated shortly after the reactor reaches 22 °C or partial decomposition occurs. The impurities that result in this case attack the glass distillation vessel. The pure product was tentatively identified on the basis of its IR and NMR spectra and elemental analysis. The elemental analysis indicated an empirical formula of $\mathrm{C_4Cl_5F_4N_3}$. Anal. Calcd for $\mathrm{C_4Cl_5F_4N_3}$: Cl, 51.63; F, 22.13; N, 12.24. Found: Cl, 51.17; F, 22.60; N, 12.05. A complex, but symmetric, pattern of 22 resolvable lines was observed in the ^{19}F NMR spectrum centered at ϕ −86.76. No combination of *J* values corresponded to a quartet, indicating that only doublets and triplets comprised the pattern. IR (liquid, NaCl windows): 1633 m, 1238 vs, 1200–1090 vs, 1065 s, 1041 m, 995 m, 965 m, 922, 898 s, 827 s, 735 s, 715 s, 694 s, 631 s, 596 s $\mathrm{cm^{-1}}$.

Conclusion

Our investigation has shown that certain nonfluorinated cyano compounds can now be reacted cleanly with ClF on a relatively large scale. It is likely that the reaction could be applied to many other polycyano compounds, including aromatics. These new *N,N*-dichloro compounds, despite their general resistance to being easily converted to azo derivatives, still show promise as starting materials for further reactions. Work continues in the development of these compounds with respect to their syntheses and uses.

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Crystal Structure and Magnetic Properties of $\mathrm{[Fe(pyz)_2(NCS)_2]_n}$ (pyz = Pyrazine), a 2D Sheetlike Polymer

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M. Carmen Muñoz,[1a,c] and Miguel Julve[1a]

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A lot of work has been devoted to the study of exchange interactions between transition-metal ions through extended bridging groups in the last two decades,[2] the fundamental understanding of the long-range magnetic interactions being one of the main reasons. Pyrazine (1,4-diazine), hereafter noted as pyz, has been one of such multiatom bridges that has been widely used because of its ability to yield one-dimensional linear chains or two-dimensional layer compounds.[3] This ligand coordinates to metal ions in a bis-monodentate fashion through its two nitrogen lone pairs leading to intramolecular metal–metal separations of about 6.7 Å.[3b] Thorough discussions of the exchange pathway for pyrazine-containing copper(II) complexes have been carried out in the light of the structural data revealing that an effective d(metal)−π(pyz) overlap is operative in some cases.[3b,c,4,5] In a theoretical paper about orbital interactions in dinuclear complexes[6] the extended Hückel molecular orbital approach was used to predict that pyz would be a very effective ligand to transmit exchange interactions through a σ-type exchange pathway. In general, the interaction through this ligand is weak, and this discrepancy with the theoretical prediction is attributed to the fact that these calculations overemphasize the intermolecular overlap.[5e,6]

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