

# Synthesis of copper(I) bis(3,5-dimethylpyrazolyl)methane olefin complexes and their reactivity towards carbon monoxide

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## Abstract

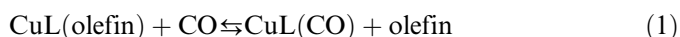
The chemistry of bis(3,5-dimethylpyrazolyl)methane complexes of copper(I) has been investigated and a dinuclear copper(I) derivative of formula  $\{\text{Cu}_2[\mu\text{-CH}_2(3,5\text{-Me}_2\text{Pz})_2]_2\}(\text{TfO})_2$  [TfO = trifluoromethanesulphonate anion,  $\text{CF}_3\text{SO}_3^-$ ], characterized by an uncommon bridging coordination of the bis(pyrazolyl)methane ligands, has been isolated and characterized by X-ray diffraction methods. Moreover, new olefin derivatives of general formula  $[\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{olefin})]\text{TfO}$  have been prepared (olefin: coe = cyclooctene, van = 4-vinylanisole, nbe = norbornene), their carbonylation reactions,  $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{olefin})\}\text{TfO} + \text{CO} \rightleftharpoons \{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{CO})\}\text{TfO} + \text{olefin}$ , have been studied gas volumetrically and the thermodynamical parameters of the equilibria for the displacement of the coordinated olefin by carbon monoxide have been determined.

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**Keywords:** Structure; Copper; Olefin; Exchange; Carbon monoxide; Equilibrium

## 1. Introduction

In the framework of our research on the CO/olefin exchange reactions in transition metal complexes, we have recently reported on the synthesis and the reactivity of a variety of copper(I) olefin complexes containing trifluoroacetato- [1], hexafluoroacetylacetonato- [2], and poly(pyrazolyl)borato [3] anions as ancillary ligands. The CO/olefin exchange data obtained from these studies suggest that the stability of the olefin complexes with respect to the corresponding carbonyl derivatives, depends on the anionic ligand, i.e., the enthalpy variation of the reaction reported in Eq. (1) is higher for trifluoroacetates and bis(3,5-trifluoromethyl)pyrazolyl borates than for the corresponding hexafluoroacetylacetonates.



Aiming to investigate the role played by the ancillary ligand in determining the stability of the olefin derivative with respect to the carbonyl one, we have employed the neutral bis(3,5-dimethylpyrazolyl)methane ligand to synthesize compounds of general formula  $\{\text{Cu}[(3,5\text{-dimethylpyrazolyl})\text{methane}](\text{olefin})\}\text{TfO}$ . This study was expected to be interesting because of the cationic nature of the resulting complexes and due to the fact that the coordination chemistry of the poly(pyrazolyl)methane complexes has been less investigated than that of the poly(pyrazolyl)borate analogues as clearly stated in recent reviews [4,5].

In this paper, we report the synthesis and the characterization of the first examples of olefin bis(3,5-dimethylpyrazolyl)methane complexes  $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{olefin})\}\text{TfO}$  and of the copper(I) cationic dinuclear complex  $\{\text{Cu}_2[\mu\text{-CH}_2(3,5\text{-Me}_2\text{Pz})_2]_2\}(\text{TfO})_2$ , characterized by the uncommon bridging coordination of the two bis(3,5-dimethylpyrazolyl)methane ligands. The equilibrium constants for the exchange reaction shown in

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Eq. (1) have been also determined and compared with those of analogous compounds containing, when possible, the same type of olefin.

## 2. Results and discussion

### 2.1. Synthesis and characterization

The steric hindrance of the ancillary ligand on the stability of poly(pyrazolyl)borate olefin derivatives of copper(I) has been recently emphasized [3]; as a matter of fact, all of the attempts to prepare  $\text{Cu}[\text{BH}(3,5\text{-Me}_2\text{Pz})_3](\text{olefin})$  complexes were unsuccessful and only derivatives containing the less bulky  $[\text{BH}_2(3,5\text{-(CF}_3)_2\text{Pz})_2]^-$  anion were reported. In the light of these observations, the use of bis(3,5-dimethylpyrazolyl)methane,  $\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2$ , as a neutral analogue of a bis(pyrazolyl)borato anion, was expected to be a good choice in order to prepare stable olefin derivatives of copper(I). Furthermore, to the best of our knowledge, only few examples of bis(pyrazolyl)methane derivatives of copper(I) have been reported until now [6].

When  $\text{Cu}(\text{TfO})(\text{toluene})_{0.5}$  was added to a dichloromethane solution of  $\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2$ , a fast reaction was observed. Work up of the reaction mixture afforded high yields of a compound formulated as  $\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2]\text{TfO}$  (83% yield) which was characterized by IR, NMR and analytical methods. By crystallization from  $\text{CH}_2\text{Cl}_2/\text{heptane}$ , the dichloromethane solvate  $\{\text{Cu}_2[\mu\text{-CH}_2(3,5\text{-Me}_2\text{Pz})_2]_2\}(\text{TfO})_2 \cdot \text{CH}_2\text{Cl}_2$  was obtained, whose X-ray structure revealed the presence of a dimeric  $\{\text{Cu}_2[\mu\text{-CH}_2(3,5\text{-Me}_2\text{Pz})_2]_2\}^{2+}$  fragment, in which two bis(3,5-dimethylpyrazolyl)methane ligands bridge two copper atoms and the two metal atoms interact weakly with one of the two triflate anions. It is noteworthy that this coordination mode is rather unusual in pyrazolylmethane chemistry: as a matter of fact, only two examples have been reported: the mixed sodium/chromium derivative  $\{[\text{NaCr}(2,2'\text{-bipy})(\text{oxalate})_2]_2[\text{bis}(\text{pyrazolyl})\text{methane}] \cdot 2\text{H}_2\text{O}\}_n$  [7] and the silver aquo complex  $\{\text{Ag}_2[\mu\text{-CH}_2(3,5\text{-Me}_2\text{Pz})_2]_2(\text{OH}_2)_2\}(\text{OTf})_2$  [8].

An ORTEP view of  $\{\text{Cu}_2[\mu\text{-CH}_2(3,5\text{-Me}_2\text{Pz})_2]_2\}^{2+}$  cation is shown in Fig. 1. The most important bond distances and angles are collected in the caption of the figure. Two copper atoms ( $\text{Cu1} \cdots \text{Cu2}$  separation:  $2.7278(8) \text{ \AA}$ ) are bridged by two bis(pyrazolyl)methane ligands through the nitrogen atoms (the Cu–N bond lengths span from  $1.882(2)$  to  $1.893(3) \text{ \AA}$ ). The coordination of the two nitrogen atoms to each copper atom is nearly linear, the N–Cu–N angles being  $165.50(11)^\circ$  and  $167.11(11)^\circ$  at Cu1 and Cu2, respectively.

It is interesting to notice that one of the two triflate anions shows some interaction with the copper atoms ( $\text{O1} \cdots \text{Cu1} = 2.666(2)$ ,  $\text{O1} \cdots \text{Cu2} = 2.745(2) \text{ \AA}$ ). As a matter of fact, an interaction between a second triflate anion and the cation is prevented by the conformation adopted by the pyrazolylmethane ligands which provide a large steric hindrance on one side of the cation as shown in Fig. 2.

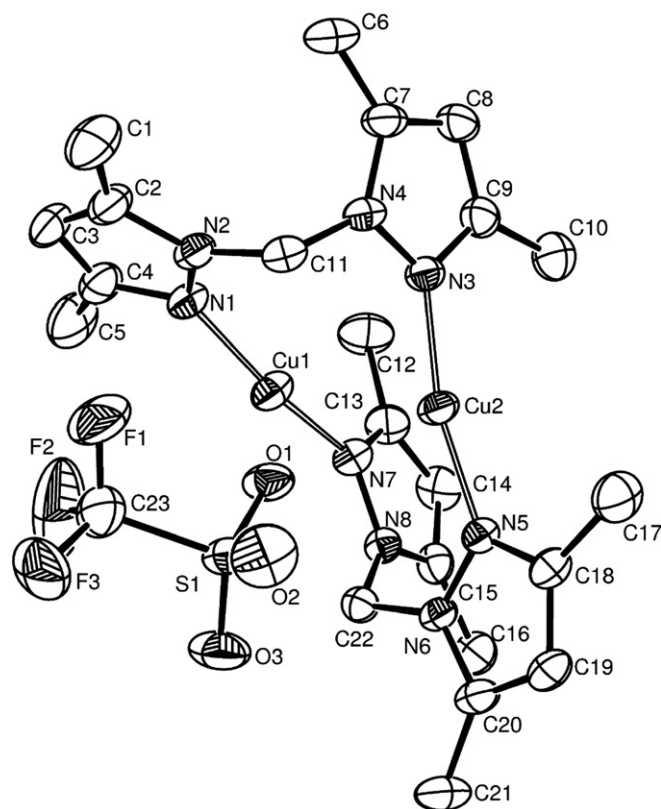


Fig. 1. ORTEP [9] view of the  $\{\text{Cu}_2[\mu\text{-CH}_2(3,5\text{-Me}_2\text{Pz})_2]_2\}^{2+}$  cation together with the closer triflate anion. Hydrogen atoms have been omitted for clarity. Non hydrogen atoms are represented by their 30% probability ellipsoids. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): Cu1–N1  $1.891(3)$ , Cu1–N7  $1.893(3)$ , Cu2–N5  $1.882(2)$ , Cu2–N3  $1.882(2)$ , Cu1  $\cdots$  Cu2  $2.7278(8)$ , O1  $\cdots$  Cu1  $2.666(2)$ , O1  $\cdots$  Cu2  $2.745(2)$ , N1–Cu1–N7  $165.50(11)$ , N5–Cu2–N3  $167.11(11)$ .

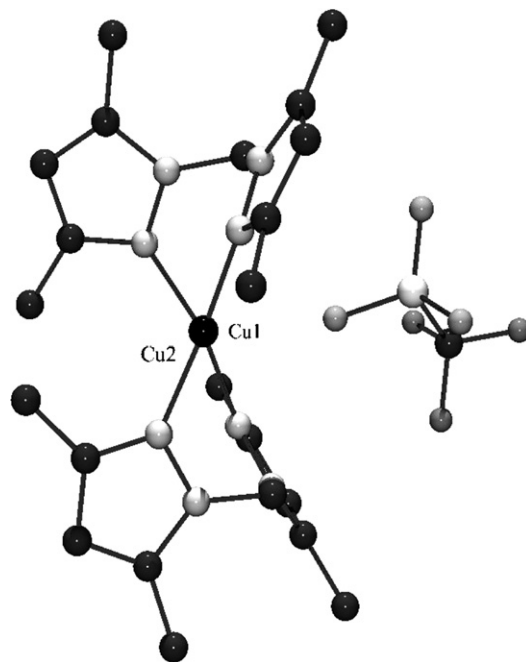


Fig. 2. View of the  $\{\text{Cu}_2[\mu\text{-CH}_2(3,5\text{-Me}_2\text{Pz})_2]_2\}^{2+}$  cation along the copper–copper axis. The closer triflate anion is also shown.

It is worth observing that Gimeno and co-workers have recently reported [8] that the reaction between  $[\text{Cu}(\text{CH}_3\text{CN})](\text{PF}_6)$  and  $\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2$  in ethanol gives to the monomeric species  $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{CH}_3\text{CN})\}(\text{PF}_6)$  and  $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2]_2\}(\text{PF}_6)$ . On the other hand, by using  $\text{Ag}(\text{OTf})$  in dichloromethane, the dimeric or the monomeric compounds  $\{\text{Ag}_2[\mu\text{-CH}_2(3,5\text{-Me}_2\text{Pz})_2]_2(\text{OH}_2)_2\}(\text{OTf})_2$  and  $\{\text{Ag}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2]_2\}(\text{OTf})$ , respectively, have been isolated and characterized according to the  $\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2/\text{Ag}(\text{OTf})$  molar ratio (1:1 in the former case and 2:1 in the latter one).

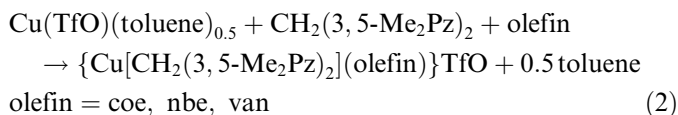
The experimental results reported by Gimeno and coworkers [8], together with the isolation of  $\{\text{Cu}_2[\mu\text{-CH}_2(3,5\text{-Me}_2\text{Pz})_2]_2\}(\text{TfO})_2 \cdot \text{CH}_2\text{Cl}_2$  from  $\text{Cu}(\text{OTf})(\text{toluene})_{0.5}$  in dichloromethane described in this paper, represent a glaring example of the effect of counteranions (triflate or hexafluorophosphate), labile ligands (acetonitrile or toluene) and solvents (ethanol or dichloromethane) in determining the overall structure of a metal complex.

Compound  $\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2]\text{TfO}$  undergoes incomplete carbonylation ( $\text{CO}_{\text{absorbed}}/\text{Cu}$  molar ratio = 0.2 in *sym*-tetrachloroethane solution at 298.3 K) and does not react with olefin (coe and nbe) to give the expected olefin compound (unreacted starting materials were recovered from the reaction mixture after prolonged contact of the reagents in  $\text{CH}_2\text{Cl}_2$  solution). This behaviour is rather unexpected because the stability of both CO- and olefin derivatives containing the bis(3,5-dimethylpyrazolyl)methane ligand is demonstrated by the complexes described in this paper and by the carbonyl derivative  $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2]\text{CO}\}\text{ClO}_4$  which has been reported in the literature [6e]. The reason for the absence of reaction between  $\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2]\text{TfO}$  and olefin might be ascribed to

the presence of dimeric species even in solution, thus preventing the formation of monomeric species by reaction with alkenes.

During one attempt to crystallize the above mentioned dinuclear species from *sym*-tetrachloroethane, crystals not containing copper were obtained. The X-ray structure showed that *N,N'*-diprotonated bis(3,5-dimethylpyrazolyl)methane cations and triflate anions are present, so that the compound can be formulated as  $[\text{CH}_2(3,5\text{-Me}_2\text{PzH})_2](\text{TfO})_2$ . This compound can be prepared in high yields from the reaction of  $\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2$  with  $\text{TfOH}$  in dichloromethane. An ORTEP view of the diprotonated species and of the triflate anions is shown in Fig. 3, the most important bond distances and angles being collected in the caption. The  $[\text{CH}_2(3,5\text{-Me}_2\text{PzH})_2]^{2+}$  cation is involved in two strong hydrogen bonds  $[\text{N}2 \cdots \text{O}3\text{t}$  2.682(3),  $\text{N}4 \cdots \text{O}5\text{t}$  2.689(3),  $\text{N}2\text{-H}2 \cdots \text{O}3\text{t}$  172.31(3),  $\text{N}4\text{-H}4 \cdots \text{O}5\text{t}$  171.35(3)] with the triflate anions.

Copper(I) bis(3,5-dimethylpyrazolyl)methane olefin derivatives have been prepared by reaction of  $\text{Cu}(\text{TfO})(\text{toluene})_{0.5}$  with  $\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2$  in the presence of the olefin, see Eq. (2)



The thermally stable olefinic compounds, which are moderately air sensitive in the solid state, have been characterized by IR, NMR and by X-ray diffraction methods (in the case of olefin = coe). The IR spectra of the three olefin compounds are rather similar, the main differences being due to the absorption of the olefinic ligands. For example, the IR spectrum of  $[\text{Cu}\{\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2\}(\text{coe})](\text{OTf})$  shows a medium absorption at  $1558 \text{ cm}^{-1}$  typical of the ancillary ligand  $\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2$ , whereas the strong sharp bands between  $1280$  and  $1146 \text{ cm}^{-1}$  and at  $1031 \text{ cm}^{-1}$  are due to the  $\text{CF}_3$  group and to the S–O stretching of the triflate anion, respectively.

The room temperature NMR spectra are typical of complexes containing the  $\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2$  ligand showing singlets at 6.1–6.4 ppm (pyr-4CH), 5.9–6.0 ppm ( $\text{CH}_2$ ), 2.4–2.5 ppm and 2.0–2.1 ppm ( $\text{CH}_3$ ). As regards the  $^{13}\text{C}$  NMR spectra, the resonances of the six non-equivalent carbon atoms are observed at 140–150 ppm (two singlets, C– $\text{CH}_3$ ), 106–107 (two singlets, pyr-4CH), 57–59 (singlet,  $\text{CH}_2$ ), and 10–13 (two singlets,  $\text{CH}_3$ ). The NMR spectra of the olefinic derivatives, show a high field shift of the resonances of the vinyl hydrogen- and carbon atoms on coordination, as it can be seen from Table 1.

A view of the structure of  $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{coe})\}\text{TfO}$  is shown in Fig. 4, together with the atomic numbering scheme. The most important bond distances and angles are collected in the caption of Fig. 4.

The coordination geometry around the copper atom is trigonal planar if the N2 and N4 atoms and the midpoint of the C12–C13 double bond (MP) of the olefin are consid-

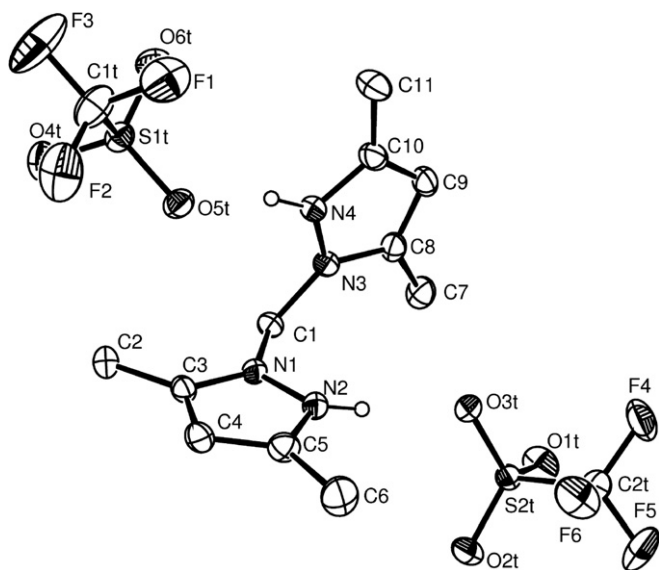


Fig. 3. ORTEP [9] view of  $[\text{CH}_2(3,5\text{-Me}_2\text{PzH})_2](\text{OTf})_2$ . Non hydrogen atoms are represented by their 30% probability ellipsoids. Selected bond lengths (Å) and angles (°): C1–N3 1.447(3), C1–N1 1.452(3), N1–N2, 1.356(3), N3–N4 1.363(3).

Table 1

{Cu[CH<sub>2</sub>(3,5-Me<sub>2</sub>Pz)<sub>2</sub>](olefin)}TfO: olefinic proton- and carbon resonances (ppm, 293 K)

Olefin	<sup>1</sup> H resonances <sup>a</sup>	<sup>13</sup> C resonances <sup>a</sup>
coe	5.28 (5.61) <sup>b</sup>	103.5 (130) <sup>b</sup>
nbe	5.33 (5.98) <sup>b</sup>	104.5 (135) <sup>b</sup>
van	6.44 (6.60), 5.08 (5.54), 4.78 (5.04) <sup>c</sup>	– <sup>d,e</sup>

<sup>a</sup> Chemical shifts of the olefinic protons and carbon atoms of the uncoordinated alkenes are reported in brackets.

<sup>b</sup> Solvent, CDCl<sub>3</sub>.

<sup>c</sup> Solvent C<sub>6</sub>D<sub>6</sub>.

<sup>d</sup> Solvent, thf-d<sub>8</sub>.

<sup>e</sup> Partial overlap with the solvent.

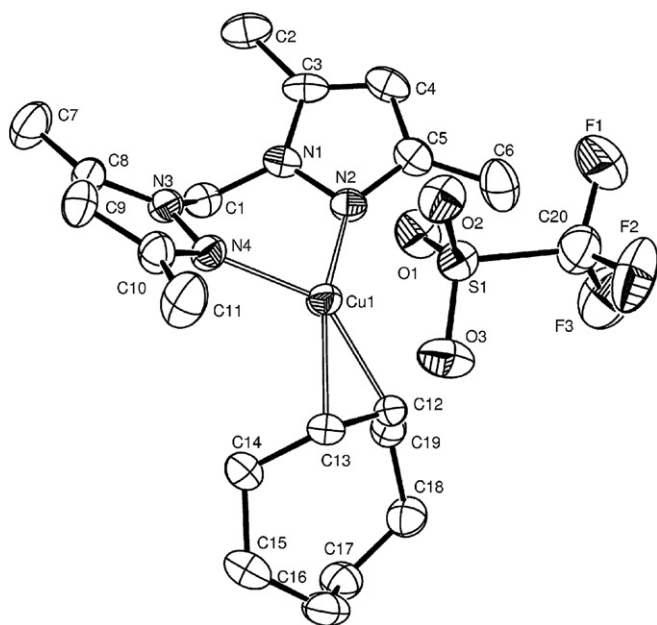


Fig. 4. ORTEP [9] view of Cu[CH<sub>2</sub>(3,5-Me<sub>2</sub>Pz)<sub>2</sub>](coe)TfO. Non hydrogen atoms are represented by their 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1–N2 2.007(2), Cu1–N4 2.009(2), Cu1–MP 1.945(2), C12–C13 1.362(3), Cu1···O1 2.437(2), N2–Cu1···O1 91.00(9), N4–Cu1···O1 98.61(9), MP–Cu1···O1 102.43(10), N2–Cu1–N4 94.57(9), N2–Cu1–MP 133.90(10), N4–Cu1–MP 125.77(10). MP is the midpoint of the C12–C13 double bond.

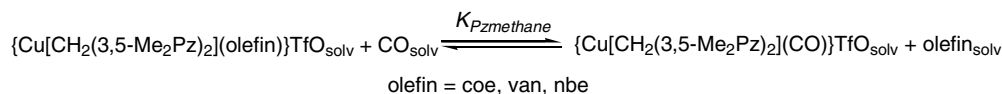
ered as coordination sites. The Cu1–N2 and Cu1–N4 bond distances are slightly longer than those found in the Cu[BH<sub>2</sub>(3,5-(CF<sub>3</sub>)<sub>2</sub>Pz)<sub>2</sub>](coe) derivative [3]. The Cu1–C12 and Cu1–C13 bond lengths, 2.072(2) and 2.050(2) Å, respectively, involving the double bond of coe are comparable with those found in the neutral (3,5-trifluoromethylpyrazolyl)borato complex [3]. The C12–C13 double bond distance (1.362(3) Å) is in the range of copper-coordinated olefins [1–3]. As in the dimeric compound Cu<sub>2</sub>[μ-CH<sub>2</sub>(3,5-Me<sub>2</sub>Pz)<sub>2</sub>]<sub>2</sub>(TfO)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>, the triflate anion is involved in a weak interaction with the copper atom through the O1 atom [Cu1···O1 = 2.437(2) Å]. The bis(pyrazolyl)methane ligand adopts the common boat conformation with bond distances and angles comparable to those reported in the literature.

Due to solubility reasons the carbonylation reactions of copper(I) olefin derivatives have been performed in *sym*-tetrachloroethane solution. Based on the fact that (pyrazolyl)methane adducts of copper(I) are generally mononuclear in the solid state [4], a mononuclear formulation has been used in our calculations (Scheme 1).

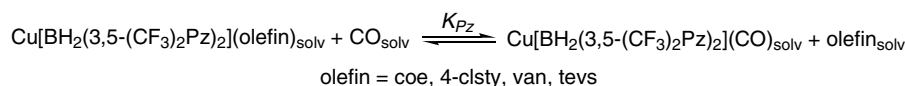
Data were collected by gas volumetric methods, the values of the equilibrium constants, the enthalpy and the entropy of the reactions obtained from van't Hoff plots, are reported in Table 2. For sake of comparison, the data for the carbonylation of the bis(3,5-trifluoromethyl)pyrazolylborato copper(I) olefin derivatives [3], see Scheme 1, are reported in the same table.

Although the carbonylation reactions have been performed in two different solvents (toluene in the case of the pyrazolylborato derivatives and *sym*-tetrachloroethane for the pyrazolylmethane compounds due to the low solubility of the latter in hydrocarbons), the values of the dielectric constants of the two media are not much different ( $\epsilon = 2.39$  and 8.01 for toluene and *sym*-tetrachloroethane, respectively [10]), so a comparison of the results can be done.

We can observe that the carbonylation enthalpies of the olefin complexes containing 4-vinylanisole are more negative than those obtained in the case of the reactions involving hydrocarbons (cyclooctene and norbornene) and that,



$$K_{Pz\text{methane}} = \frac{[\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{CO})\}\text{TfO}_{\text{solv}}][\text{olefin}_{\text{solv}}]}{[\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{olefin})\}\text{TfO}_{\text{solv}}][\text{CO}_{\text{solv}}]}$$



$$K_{Pz} = \frac{[\text{Cu}[\text{BH}_2(3,5\text{-(CF}_3)_2\text{Pz})_2](\text{CO})_{\text{solv}}][\text{olefin}_{\text{solv}}]}{[\text{Cu}[\text{BH}_2(3,5\text{-(CF}_3)_2\text{Pz})_2](\text{olefin})_{\text{solv}}][\text{CO}_{\text{solv}}]}$$

Scheme 1.



Table 2  
Equilibrium constants and thermodynamic parameters at 298.3 K for the CO/olefin exchange reported in Scheme 1

Olefin	$K_{\text{Pz methane}}$	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )
coe	3.4 ± 0.4	-26 ± 2	-77 ± 8
nbe	2.0 ± 0.2	-13 ± 1	-38 ± 5
van	5.4 ± 2.6	-40 ± 10	-120 ± 36
	$K_{\text{Pz borate}}$	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )
coe	1.4 ± 0.2	-27 ± 2	-88 ± 8
clsty	59 ± 15	-45 ± 6	-116 ± 20
van	6.3 ± 3.0	-57 ± 11	-172 ± 36
tevs	2.2 ± 0.3	-29 ± 3	-89 ± 9

within the bis(pyrazolylmethane) complexes, the nbe derivative shows lower  $\Delta H$  than coe, i.e., the stronger tendency of nbe to act as ligand. This trend, observed in analogous trifluoroacetato- and hexafluoroacetylacetonato copper(I) derivatives as well [1,2], may be explained in terms of the well-know strain relief effect of this bicyclic alkene on coordination [11].

Moreover, it can be noticed that the thermodynamic parameters do not seem to be considerably affected by the change of the ancillary ligand. As far as the relative stability of olefin- and carbonyl compounds is concerned, the electron withdrawing effect of the two CF<sub>3</sub> substituents on the pyrazolyl ligand (with respect to methyl groups) seems to be balanced by the introduction of a positive charge on the whole olefin derivative.

### 3. Conclusions

This paper deals with bis(3,5-dimethylpyrazolyl)methane derivatives of copper(I) and describes the preparation and the full characterization of some olefin derivatives. A compound of formula {Cu<sub>2</sub>[μ-CH<sub>2</sub>(3,5-Me<sub>2</sub>Pz)<sub>2</sub>]<sub>2</sub>}(TfO)<sub>2</sub> · CH<sub>2</sub>Cl<sub>2</sub> containing two bis(3,5-dimethylpyrazolyl) methane groups bridging two copper atoms has been isolated and structurally characterized. To the best of our knowledge, this represents one of the few examples of bis(pyrazolyl)methane ligand bridging two transition metal atoms, the other being the recently reported silver derivative {Ag<sub>2</sub>[μ-CH<sub>2</sub>(3,5-Me<sub>2</sub>Pz)<sub>2</sub>]<sub>2</sub>(OH)<sub>2</sub>}(OTf)<sub>2</sub>.

The X-ray characterization of the cyclooctene derivative {Cu[CH<sub>2</sub>(3,5-Me<sub>2</sub>Pz)<sub>2</sub>](coe)}TfO has shown that the coordination geometry around the copper atom is trigonal planar if the nitrogen donor atoms and the midpoint of the C12–C13 double bond of the olefin are considered as coordination sites. Moreover, a weak interaction exists between the triflate anion and copper [Cu1 ··· O1 = 2.437(2) Å]. This interaction does probably not persist in solution as shown by the observation that the conductivity of {Cu[CH<sub>2</sub>(3,5-Me<sub>2</sub>Pz)<sub>2</sub>](coe)}TfO in *sym*-tetrachloroethane is close to that of a solution of Bu<sub>4</sub><sup>n</sup>NBr of comparable concentration under the same experimental conditions, thus indicating a similar dissociation extent of the species in that solvent.

The CO/olefin exchange reaction has been studied on three olefin derivatives at different temperatures and the data reported in Table 2 confirm the general trend, i.e.,

the carbonyl complex is more stable than the olefin derivative. On the other hand, although previous studies on this subject [1–3] indicate that the thermodynamical parameters of the CO/olefin competition equilibria depend on the nature of the ancillary ligands, we observe (Table 2) that they do not vary greatly on going from the fluorinated, neutral bis(pyrazolyl)borato derivative to the cationic bis(3,5-dimethylpyrazolyl)methane compounds.

Work is in progress aiming to extend this study to other substituted bis(pyrazolyl)methane derivatives.

### 4. Experimental

#### 4.1. General procedures

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use. *cis*-Cyclooctene (coe) (Aldrich), norbornene (nbe) (Aldrich), 4-vinylansole (van) (Aldrich) were distilled under reduced pressure and stored at ca. -30 °C. Trifluoromethanesulphonic acid, trifluoromethanesulphonic anhydride (Aldrich) and 3,5-dimethylpyrazole (Aldrich) were used as received. Bis(3,5-dimethyl-1-pyrazolyl)methane, CH<sub>2</sub>(3,5-Me<sub>2</sub>Pz)<sub>2</sub>, was prepared using a modification of the published procedure [12]. Dichloromethane (30 mL) was added to a mixture of 3,5-dimethylpyrazole (3.0 g, 31.2 mmol), tetrabutylammonium bromide (0.77 g, 2.40 mmol), powdered KOH (2.7 g, 48.1 mmol), and K<sub>2</sub>CO<sub>3</sub> (6.6 g, 48.0 mmol). The reaction mixture was stirred and heated under reflux for 36 h. After filtration, the solid was washed with hot CH<sub>2</sub>Cl<sub>2</sub> (50 mL), and the organic portions were combined. The solvent was removed by evaporation under reduced pressure. The resulting solid (which contained also tetrabutylammonium bromide) was recrystallized from hot heptane to give CH<sub>2</sub>(3,5-Me<sub>2</sub>Pz)<sub>2</sub> as a colourless crystalline compound (2.9 g, 91% yield). Cu(TfO)(toluene)<sub>0.5</sub> was prepared according to the literature [13]; we noticed that the colourless compound turns dark brown on standing at room temperature but it can be stored indefinitely at ca. -30 °C. IR spectra were recorded on a FT-1725X instrument on nujol or polychlorotrifluoroethylene (PCTFE) mulls or on a FTIR-Spectrometer equipped with a Perkin–Elmer UATR sampling accessory. NMR spectra (<sup>1</sup>H, 200 MHz; <sup>13</sup>C, 50.31 MHz,

with TMS as reference) were recorded at 293 K with a Varian Gemini 200BB spectrometer. Gas volumetric measurements were performed with the apparatus described by Calderazzo and Cotton [14].

#### 4.2. Synthesis of $\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2]\text{TfO}$

$\text{Cu}(\text{TfO})(\text{toluene})_{0.5}$  (1.24 g, 4.80 mmol) was added to a dichloromethane solution (70 mL) of  $\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2$  (0.98 g, 4.80 mmol). The resulting solution was allowed to stir at room temperature for 24 h. The volume of the solution was reduced to 15 mL by evaporation of the solvent and toluene was added (30 mL). The colourless microcrystalline solid which separated out was recovered by filtration, dried in vacuo and identified as  $\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2]\text{TfO}$  (1.66 g, 83%). Anal. Calc. for  $\text{C}_{12}\text{H}_{16}\text{CuF}_3\text{N}_4\text{O}_3\text{S}$ : C, 34.6, H, 3.9, N, 13.4. Found: C, 34.2, H, 4.1, N, 13.6%. IR (solid state):  $\tilde{\nu}/\text{cm}^{-1}$  2923mw, 1599mw, 1556ms, 1463m, 1420ms, 1389m, 1255vs, 1223vs, 1146vs, 1030vs, 990m, 818s, 755m, 734mw, 706m, 681s, 661m.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.28 (s, 2H,  $\text{CH}_{\text{pyr}}$ ), 5.89 (s, 2H,  $\text{CH}_2$ ), 2.47 (s, 6H,  $\text{CH}_3$ ), 1.90 (s, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  149.6 (s,  $\text{C}-\text{CH}_3$ ), 140.5 (s,  $\text{C}-\text{CH}_3$ ), 106.5 (s,  $\text{CH}_{\text{pyr}}$ ), 57.5 (s,  $\text{CH}_2$ ), 13.2 (s,  $\text{CH}_3$ ), 11.1 (s,  $\text{CH}_3$ ).

#### 4.3. Synthesis of $[\text{CH}_2(3,5\text{-Me}_2\text{PzH})_2](\text{TfO})_2$

Trifluoromethanesulphonic acid (0.22 ml, 2.5 mmol) was added to a dichloromethane solution (5 mL) of  $\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2$  (243 mg, 1.2 mmol). The colourless solution was stirred at room temperature overnight. The solvent was evaporated under reduced pressure affording a colourless waxy solid, which was recrystallized from THF/diethyl ether (435 mg, 73% yield). Anal. Calc. for  $\text{C}_{13}\text{H}_{18}\text{F}_6\text{N}_4\text{O}_6\text{S}_2$ : C, 30.9; H, 3.6; N, 11.1. Found: C, 30.6; H, 3.6; N, 10.9%. IR  $\tilde{\nu}/\text{cm}^{-1}$  (Neat): 3147w, 3021w, 2611br, 1599m, 1527w, 1435mw, 1383w, 1296s, 1222vs, 1150s, 1024vs, 990m, 847m, 831m, 806m, 758mw, 666mw.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  11.6 (br, 2H,  $\text{NH}$ , disappears on addition of  $\text{D}_2\text{O}$ ), 6.79 (s, 2H,  $\text{pyr}-\text{CH}$ ), 6.49 (s, 2H,  $\text{CH}_2$ ), 2.61 (s, 3H,  $\text{CH}_3$ ), 2.44 (s, 3H,  $\text{CH}_3$ ).

#### 4.4. Synthesis of $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{olefin})\}\text{TfO}$ ; $\text{olefin} = \text{coe}, \text{nbe}, \text{van}$

Only the preparation of  $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{coe})\}\text{TfO}$  is described in detail, the other being performed in a similar way.  $\text{Cu}(\text{TfO})(\text{toluene})_{0.5}$  (1.26 g, 4.86 mmol) was added to a mixture of  $\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2$  (1.0 g, 4.86 mmol) and *coe* (0.68 g, 6.18 mmol) in dichloromethane (20 mL). The resulting solution was allowed to stir at room temperature for 24 h. The solution was concentrated to 5 mL and pentane was added (30 mL).  $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{coe})\}\text{TfO}$  was obtained as an almost colourless precipitate, which was recovered by filtration and dried in vacuo (2.1 g, 82%). Crystallization from  $\text{CH}_2\text{Cl}_2$ /heptane at room temperature afforded  $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2]$

(*coe*) $\}\text{TfO}$  as crystalline compound. Anal. Calc. for  $\text{C}_{20}\text{H}_{30}\text{CuF}_3\text{N}_4\text{O}_3\text{S}$ : C, 45.6; H, 5.7; N, 10.6. Found: C, 45.1; H, 5.7; N, 10.8%. IR (solid state):  $\tilde{\nu}/\text{cm}^{-1}$  3136w, 3036w, 2927m, 2868w, 2846w, 1558m, 1469m, 1446m, 1393m, 1280vs, 1265vs, 1221s, 1146s, 1031vs, 975m, 832m, 791m, 752mw, 706w, 680ms, 659w.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.34 (s, 2H,  $\text{CH}_{\text{pyr}}$ ), 5.96 (s, 2H,  $\text{CH}_2$ ), 5.28 (m, 2H,  $\text{CH}=\text{CH}$ ), 2.46 (s, 6H,  $\text{CH}_3$ ), 2.3–2.1 (m, 10H,  $\text{CH}_3$  and  $\text{CH}_2\text{CH}=\text{}$ ), 1.7–1.4 (m, 8H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  150.9 (s,  $\text{C}-\text{CH}_3$ ), 142.5 (s,  $\text{C}-\text{CH}_3$ ), 107.3 (s,  $\text{pyr}-\text{CH}$ ), 103.5 (s,  $\text{CH}=\text{CH}$ ), 57.6 (s,  $\text{CH}_2$ ), 29.8 (s,  $\text{CH}_2\text{CH}=\text{}$ ), 26.7 (s,  $\text{CH}_2$ ), 25.9 (s,  $\text{CH}_2$ ), 13.2 (s,  $\text{CH}_3$ ), 11.0 (s,  $\text{CH}_3$ ).

##### 4.4.1. $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{nbe})\}\text{TfO}$

Colourless solid (85% yield). Anal. Calc. for  $\text{C}_{17}\text{H}_{26}\text{CuF}_3\text{N}_4\text{O}_3\text{S}$ : C, 44.6; H, 5.1; N, 11.0. Found: C, 44.2; H, 5.1; N, 12.8%. IR (solid state):  $\tilde{\nu}/\text{cm}^{-1}$  2966w, 2926w, 1599w, 1556m, 1466m, 1420m, 1390m, 1274vs, 1252vs, 1222s, 1152vs, 1076w, 1028vs, 966mw, 945w, 898mw, 832m, 813m, 755mw, 730w, 707mw, 677m, 660mw.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.29 (s, 2H,  $\text{pyr}-\text{CH}$ ), 5.91 (s, 2H,  $\text{CH}_2$ ), 5.33 (s, 2H,  $\text{CH}=\text{CH}$ ), 3.17 (s, 2H,  $\text{CH}-\text{CH}=\text{CH}$ ), 2.45 (s, 6H,  $\text{CH}_3$ ), 2.10 (s, 6H,  $\text{CH}_3$ ), 1.8–1.6 (m, 3H), 1.3–1.0 (m, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  150.9 ( $\text{C}-\text{CH}_3$ ), 142.0 ( $\text{C}-\text{CH}_3$ ), 107.2 ( $\text{pyr}-\text{CH}$ ), 104.5 ( $\text{CH}=\text{CH}$ ), 57.7 (s,  $\text{CH}_2$ ), 45.3 ( $\text{CH}-\text{CH}=\text{}$ ), 43.9 ( $\text{CH}-\text{CH}_2-\text{CH}$ ), 25.1 ( $\text{CH}_2-\text{CH}_2$ ), 13.8 (s,  $\text{CH}_3$ ), 11.3 (s,  $\text{CH}_3$ ).

##### 4.4.2. $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{van})\}\text{TfO}$

Pale green solid (95% yield). Anal. Calc. for  $\text{C}_{21}\text{H}_{26}\text{CuF}_3\text{N}_4\text{O}_4\text{S}$ : C, 45.8; H, 4.8; N, 10.2. Found: C, 45.4; H, 4.8; N, 10.1%. IR  $\tilde{\nu}/\text{cm}^{-1}$  (solid state) 3134w, 2925m, 2835w, 1608m, 1582w, 1557m, 1509ms, 1465m, 1422m, 1392m, 1243vs, 1223s, 1151s, 1030vs, 828ms, 755mw, 734m, 696mw, 681m, 660w.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.34 (d, 2H,  $^3J = 8.4$  Hz, *m-CH*), 6.83 (d, 2H,  $^3J = 8.4$  Hz, *o-CH*), 6.44 (dd, 1H,  $J_{\text{trans}} = 16.4$  Hz,  $J_{\text{cis}} = 9.6$  Hz,  $\text{CH}=\text{CH}_2$ ), 6.15 (s, 2H,  $\text{pyr}-\text{CH}$ ), 5.89 (s, 2H,  $\text{CH}_2$ ), 5.08 (d, 1H,  $J_{\text{trans}} = 16.3$  Hz, *cis H*), 4.78 (d, 1H,  $J_{\text{cis}} = 9.6$  Hz, *trans H*), 3.78 (s, 3H,  $\text{OCH}_3$ ), 2.39 (s, 6H,  $\text{CH}_3$ ), 2.12 (s, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{thf}-d_8$ ):  $\delta$  158.7 (s,  $\text{C}-\text{OCH}_3$ ), 150.9 (s,  $\text{C}-\text{CH}_3$ ), 142.1 (s,  $\text{C}-\text{CH}_3$ ), 129.3 (s, ring-CH), 128.0 (s, ring-CH), 114.6 (s, ring-CH), 106.9 (s,  $\text{pyr}-\text{CH}$ ), 58.6 (s,  $\text{CH}=\text{CH}_2$ ), 55.4 (s,  $\text{OCH}_3$ ), 13.5 (s,  $\text{CH}_3$ ), 10.9 (s,  $\text{CH}_3$ ).

#### 4.5. Carbonylation reactions of $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{olefin})\}\text{TfO}$ , $\text{olefin} = \text{coe}, \text{nbe}, \text{van}$

*Sym*-tetrachloroethane (50 mL) and a thin-walled sealed glass container containing the copper(I) derivative were introduced into an Erlenmeyer flask equipped with a lateral stopcock. The system was connected to a gas volumetric burette and saturated with CO at atmospheric pressure at the temperature of the experiment. The glass container was then broken by magnetic stirring and the absorption of gas was measured. The concentration of CO in *sym*-tet-

Table 3  
Carbonylation reactions of  $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{olefin})\}\text{TfO}$

<i>T</i> (K)	$[\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{coe})\}\text{TfO}]_j \times 10^3$	CO/Cu molar ratio	$K_{\text{coe}}$
278.7	8.6	0.85	8.4
288.5	11.4	0.76	5.6
298.1	13.8	0.65	3.4
308.3	13.6	0.63	3.0
318.3	13.0	0.53	1.6
331.7	9.2	0.57	1.4
<hr/>			
	$[\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{nbe})\}\text{TfO}]_j \times 10^3$	CO/Cu molar ratio	$K_{\text{nbe}}$
278.6	13.4	0.63	2.9
288.2	11.0	0.64	2.6
298.2	11.2	0.62	2.3
307.7	11.0	0.58	1.8
318.3	9.0	0.58	1.5
<hr/>			
	$[\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{van})\}\text{TfO}]_j \times 10^3$	CO/Cu molar ratio	$K_{\text{van}}$
278.6	6.4	0.94	19.2
288.2	9.4	0.86	9.9
298.2	10.6	0.85	9.2
307.7	7.8	0.73	3.1

chloroethane at the different temperature was obtained from [15]. The gas volumetric experiments were repeated twice, thus obtaining consistent  $\text{CO}_{\text{absorbed}}/\text{Cu}$  molar ratios. The details of the experiments together with the measured  $\text{CO}_{\text{absorbed}}/\text{Cu}$  molar ratios (CO/Cu) at equilibrium, respectively, are reported in Table 3.

#### 4.6. X-ray structure determination of $\{\text{Cu}_2[\mu\text{-CH}_2(3,5\text{-Me}_2\text{Pz})_2]\}(\text{TfO})_2$ , $[\text{CH}_2(3,5\text{-Me}_2\text{PzH})_2](\text{TfO})_2$ and $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{coe})\}\text{TfO}$

Crystals of  $\{\text{Cu}_2[\mu\text{-CH}_2(3,5\text{-Me}_2\text{Pz})_2]\}(\text{TfO})_2$  and  $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{coe})\}\text{TfO}$  were grown from dichloromethane/heptane mixture and the data were collected

at 298 K on a Bruker SMART 1000 single-crystal diffractometer equipped with area detector. Crystals of  $[\text{CH}_2(3,5\text{-Me}_2\text{PzH})_2](\text{TfO})_2$  were grown from *sym*-tetrachloroethane solution and the data were collected at 203 K on a Enraf Nonius CAD 4 single-crystal diffractometer (Cu  $K\alpha$  radiation,  $\lambda = 1.54183 \text{ \AA}$ ). Details for the X-ray data collections are listed in Table 4. The structures were solved by Patterson and by direct methods with SHELXS-97 and refined against  $F^2$  with SHELXL-97 [16], with anisotropic thermal parameters for all non-hydrogen atoms. Idealized geometries were assigned to the hydrogen atoms, excepted H2n and H4n hydrogen atoms in  $[\text{CH}_2(3,5\text{-Me}_2\text{PzH})_2](\text{TfO})_2$ , which were found in the  $\Delta F$  map and refined isotropically.

Table 4  
Crystallographic data for compounds  $\{\text{Cu}_2[\mu\text{-CH}_2(3,5\text{-Me}_2\text{Pz})_2]\}(\text{TfO})_2 \cdot \text{CH}_2\text{Cl}_2$ ,  $[\text{CH}_2(3,5\text{-Me}_2\text{PzH})_2](\text{TfO})_2$  and  $\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{coe})\}\text{TfO}$

	$\{\text{Cu}_2[\mu\text{-CH}_2(3,5\text{-Me}_2\text{Pz})_2]\}(\text{TfO})_2 \cdot \text{CH}_2\text{Cl}_2$	$[\text{CH}_2(3,5\text{-Me}_2\text{PzH})_2](\text{TfO})_2$	$\{\text{Cu}[\text{CH}_2(3,5\text{-Me}_2\text{Pz})_2](\text{coe})\}\text{TfO}$
Formula	$\text{C}_{25}\text{H}_{34}\text{Cl}_2\text{Cu}_2\text{F}_6\text{N}_8\text{O}_6\text{S}_2$	$\text{C}_{13}\text{H}_{18}\text{F}_6\text{N}_4\text{O}_6\text{S}_2$	$\text{C}_{20}\text{H}_{30}\text{CuF}_3\text{N}_4\text{O}_3\text{S}$
Formula weight	918.70	504.43	527.08
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	<i>Pbca</i>	$P2_1/n$
<i>a</i> (Å)	11.254(3)	16.960(5)	10.539(4)
<i>b</i> (Å)	11.415(3)	15.918(4)	15.720(6)
<i>c</i> (Å)	16.716(4)	15.636(4)	14.831(5)
$\alpha$ (°)	90.198(4)	90	90
$\beta$ (°)	105.083(4)	90	90.077(6)
$\gamma$ (°)	111.915(3)	90	90
<i>V</i> (Å <sup>3</sup> )	1911(1)	4221(2)	2457(2)
<i>Z</i> , $D_{\text{calcd}}$ (g cm <sup>-3</sup> )	2, 1.596	8, 1.587	4, 1.425
<i>F</i> (000)	932	2064	1096
$\mu$ (cm <sup>-1</sup> )	14.39	31.51	10.24
Reflections collected	20098	3928	25836
Reflections unique [ $R_{\text{int}}$ ]	8130 [0.0322]	3928 [0.0]	5521 [0.0422]
Observed reflections [ $I > 2\sigma I$ ]	5424	3124	3051
Parameters	468	353	293
Final <i>R</i> indices [ $I > 2\sigma I$ ]	$R_1 = 0.0464$ , $wR_2 = 0.1317$	$R_1 = 0.0498$ , $wR_2 = 0.1356$	$R_1 = 0.0399$ , $wR_2 = 0.0862$
Final <i>R</i> indices [all data]	$R_1 = 0.0713$ , $wR_2 = 0.1447$	$R_1 = 0.0618$ , $wR_2 = 0.1489$	$R_1 = 0.0877$ , $wR_2 = 0.0966$

$$R_1 = \sum \|F_o\| - |F_c| / \sum (F_o); wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$$

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## Appendix A. Supplementary data

CCDC 612169, 612167, and 612168 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.09.006](https://doi.org/10.1016/j.jorganchem.2006.09.006).

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