Dalton Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 1189

www.rsc.org/dalton

PAPER

Demonstration of remote steric differentiation of *cis*/*trans* alkene coordination in copper(I) complexes of aryl-substituted bis(2-pyridyl)amine†

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Received 28th September 2010, Accepted 26th November 2010
DOI: 10.1039/c0dt01301c

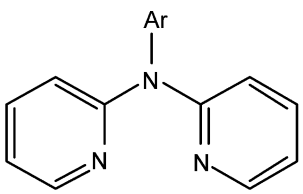
Complexes of the type [Cu(R-dpa)(η²-olefin)]BF_4 (R = Mes and 2-^{i}PrC_6H_4) for *cis*- and *trans*- isomers of 3-octene, as well as those for *cis*- and *trans*-4-octene (R = 2-^{i}PrC_6H_4) have been prepared and characterized by ^{1}H and ^{13}C NMR, FTIR, and TGA. The crystal structure of [Cu(Mes-dpa)(η²-*trans*-3-octene)]BF_4 (**2**) has been determined *via* X-ray crystallography. The asymmetric unit in the crystal lattice of **2** contains two unique conformations of the complex cation related by a pseudo center of symmetry, which differ primarily in the orientation of the olefin with respect to the rest of the molecule. The ^{1}H and ^{13}C NMR spectra of [Cu(Ar-dpa)(η²-olefin)]BF_4 exhibit olefin resonances shifted upfield with respect to free olefin. The difference in $\Delta\delta(^{13}C)$ relative magnitudes between *cis*- and *trans*- complexes, *i.e.*, the binding, correlates with the degree of substitution at the amine nitrogen. The identity of the remote ligand substituent (Ar) controls the differentiation of binding between *cis* and *trans* isomers as a consequence of increased folding of the Ar-dpa ligand along the Cu···N axis.

Introduction

As the largest volume feedstock in the chemical and petrochemical industry, olefins are used in the production of polymers, acids, alcohols, esters, and ethers. Unfortunately, olefin production is extremely energy intensive, generally requiring separation from their alkane counterparts (olefin/paraffin separation).[1] More problematic is the separation of particular olefins from a mixture, considering the range of phase-transition temperatures for a given set of isomers is usually small. For instance, the seven *n*-octene isomers have a boiling range of 121.3–125.6 °C.[2] The large volumes of olefins produced and the required purity for most applications provides strong incentives for novel purification approaches. The use of chemically specific separation reagents is a potentially inexpensive and efficient approach for separation.[3] The development of metal complexes incorporating sterically directive ancillary ligands tailored to the selective removal of olefins from their isomeric counterparts is currently of great interest in the petroleum/petrochemical industries.

The control over the selective binding of olefins to a metal center has the potential as a simple route to overcoming the inherent difficulty in the separation of different olefins with near identical boiling points. To this end, various complexing reagents have been described,[4] where the function of the complexing agent is to coordinate one particular isomer of an olefin in preference to another.[5] The control over the selective binding of olefins to a metal center in processes such as reactive extractive distillation and reactive absorption to a supported medium offer potential alternatives in overcoming the issues inherent with their separation.[5]

In designing a suitable coordination system for olefins, several groups have based the system on a biological model for ethylene complexation.[6,7] These studies have also demonstrated that stable Cu···olefin interactions can be achieved using multidentate, electron rich N-donor ligands.[8–10] The class of ligand most commonly used for robust, yet reversibly bound olefin complexes, is the neutral N-donor heterocyclic compounds.[11–15] Of these, it was the report by Thompson and Whitney that has formed the basis for our studies.[16,17] They showed that stable copper complexes with ethylene are formed with the chelate ligand bis(2-pyridyl)amine (H-dpa, **I** where R = H).



Ar = H; 2,4,6-$Me_3C_6H_2$ (Mes); 2-^{i}PrC_6H_4

(**I**)

Our previous studies[16,18] have shown that steric hindrance between the olefin and H-dpa manifests as both a twisting of the olefin out of the plane of the H-dpa ligand and a concomitant folding of the H-dpa ligand. During a study of the consequences of increased steric effects in quinolyl analogs we have observed that

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† CCDC reference numbers 733204 (**2**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01301c

the presence of a sterically hindered aryl group on the amine nitrogen results in a further distortion about the amine nitrogen.[19,20] Subsequently we have prepared a range of N-substituted bis(2-pyridyl)amines, and studied the effects of aryl steric bulk with regard to olefin binding. For a range of olefin complexes, [Cu(Ar-dpa)(olefin)]$^+$, it was found that the distortion of pyridyl ring geometries about the copper centers, and concomitant bending of the aryl groups away from the Cu$\cdots$N$_{(amine)}$ vectors, resulted in a folding of the R-dpa ligand. Furthermore, as may be seen from Fig. 1, there is a clear steric consequence of the butterfly conformation of the Ar-dpa ligand on the olefin ligand. Based upon this observation we proposed that the complexation of a mono-substituted or *cis*-substituted olefin should be favored over complexation of a *trans*-substituted olefin in complexes where the Ar-dpa ligand has the most distortion due to a sterically large aryl substituent (Ar). Thus, for the *trans*-olefin (**II**) there will be inter-ligand interactions irrespective of the olefin conformation, while for a *cis*-olefin (**III**) the substituents could adopt a conformation that limits steric interactions.

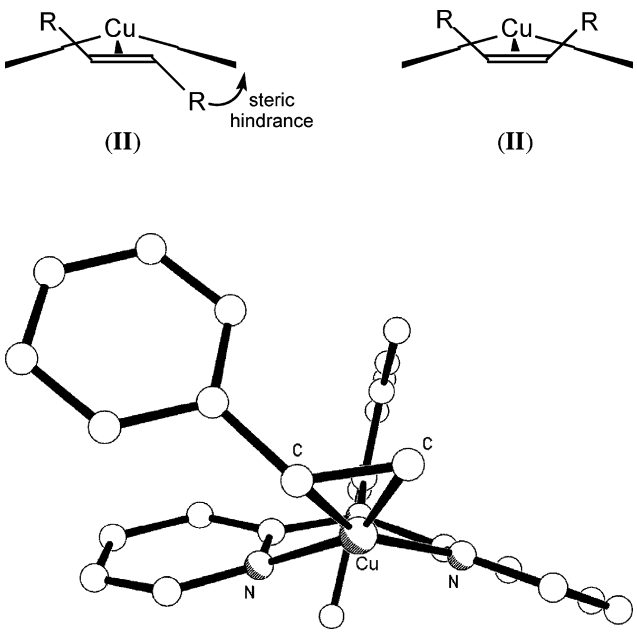

Fig. 1 An example of the folding of the Ar-dpa ligand in the [Cu(Mes-dpa)(η^2-styrene)]$^+$ cation as viewed along the Cu$\cdots$N vector. Adapted from J. J. Allen, C. E. Hamilton, and A. R. Barron, *Dalton Trans.*, 2010, DOI: 10.1039/c0dt00608d.

In our previous work we have shown that the ^{1}H and ^{13}C NMR spectra of [Cu(H-dpa)(olefin)]BF$_4$ exhibit an upfield shift in the olefin signal as compared to free olefin. A comparison of the $\Delta\delta$ values for olefins with olefin dissociation temperatures (as determined by TG/DTA) confirms that the shift of the olefin NMR resonances upon coordination is associated with the binding strength of the complex, making this a simple method for comparing the binding of isomers.

The results reported herein are aimed at determining the differentiation in binding between *cis* and *trans* olefins by N-substituted bis(2-pyridyl)amine copper complexes. In particular the effect of the aryl substituent on the binding of *cis versus trans* isomers of 3- and 4-octene.

Results and discussion

The reaction of [Cu(MeCN)$_4$]BF$_4$ with either *cis* or *trans* 3-octene in the presence of the appropriate Ar-dpa results in the formation of the olefin complex, [Cu(Ar-dpa)(η^2-olefin)]BF$_4$ (eqn (1)) where Ar = H for *cis*-3-octene and *trans*-3-octene;[16] Ar = Mes for *cis*-3-octene (**1**) and *trans*-3-octene (**2**); Ar = 2-^{i}PrC$_6$H$_4$ for *cis*-3-octene (**3**) and *trans*-3-octene (**4**). In addition the 4-octene derivatives were prepared, where Ar = 2-^{i}PrC$_6$H$_4$ for *cis*-4-octene (**5**) and *trans*-4-octene (**6**). New compounds **1–6** are soluble in alcohols and show instability in air and have been characterized by ^{1}H and ^{13}C NMR, FT-IR, and TG/DTA. The crystal structure of compound **2** has been determined.†

$$[Cu(MeCN)_4]BF_4 + \text{Ar-dpa} + \text{olefin} \rightarrow [Cu(\text{Ar-dpa})(\eta^2\text{-olefin})]BF_4 + 4\ \text{MeCN} \quad (1)$$

The structures of the two unique conformations of the complex cation, [Cu(Mes-dpa)(η^2-*trans*-3-octene)]$^+$, in compound **2** are shown in Fig. 2. The two conformations are related by a pseudo center of symmetry, *i.e.*, a non-crystallographic inversion center, but are shown to be unique in other structural aspects. Selected bond lengths and angles are compared in Table 1. Both conformers exhibit a pseudo-trigonal planar geometry about copper centers, with coordination sites occupied by the two pyridine nitrogen atoms and the midpoint of the olefin C=C bond. The copper atoms are each coordinated to two pyridine nitrogen atoms and the olefin; consistent with three-coordinate Cu(I) cation. The Cu–N distances are within experimental error of the analogous ethylene and cyclohexene complexes [1.949(3)–1.973(3) Å].[17] In a similar manner the Cu–C distances overlap the range for the previously reported derivatives [1.972(5)–2.064(2) Å].[17] The structure of compound **2** fits in with the other olefin complexes we have structurally characterized. As may be seen from Fig. 3, there is a correlation between the C$_{py}$–N–C$_{py'}$ bond angle and both the fold of the Ar-dpa ligand (*i.e.*, the mean-plane angle difference between pyridyl rings), as well as the out of plane bend of the aryl substituent (*i.e.*, the angle resulting from Cu$\cdots$N$_{amine}$–C$_{Ar}$).

Munakata *et al.* have previously demonstrated that ^{1}H NMR can be used to assess the binding efficacy of various ligand/olefin combinations in Cu(I) olefin complexes,[15] while we have previously used similar methods for Lewis acid–base complexes.[21] We have

Table 1 Selected bond lengths (Å) and angles (°) in the unique conformers of compound **2**

	Molecule 1	Molecule 2
Cu–C	2.038(7)	2.016(8)
Cu–C′	2.014(7)	2.059(6)
Cu–N	1.967(5)	1.980(5)
Cu–N′	1.936(5)	1.991(6)
C–C′	1.36(1)	1.39(1)
N–C$_{Ar}$	1.435(9)	1.416(9)
N–C$_{py}$	1.429(8)	1.439(9)
N–C$_{py'}$	1.423(8)	1.487(8)
N–Cu–N′	92.9(2)	92.5(2)
C–Cu–C′	39.3(3)	40.0(3)
C$_{py}$–N–C$_{py'}$	125.2(6)	122.5(6)
C$_{py}$–N–C	119.3(5)	121.8(5)
C$_{py'}$–N–C	115.5(5)	115.1(6)
Cu$\cdots$N–C$_{Ar}$	156.0(5)	159.0(5)
Twist	11.2(6)	2.5(7)
ΔMPLN$_{(py\text{-}py')}$	32.2(4)	34.5(4)

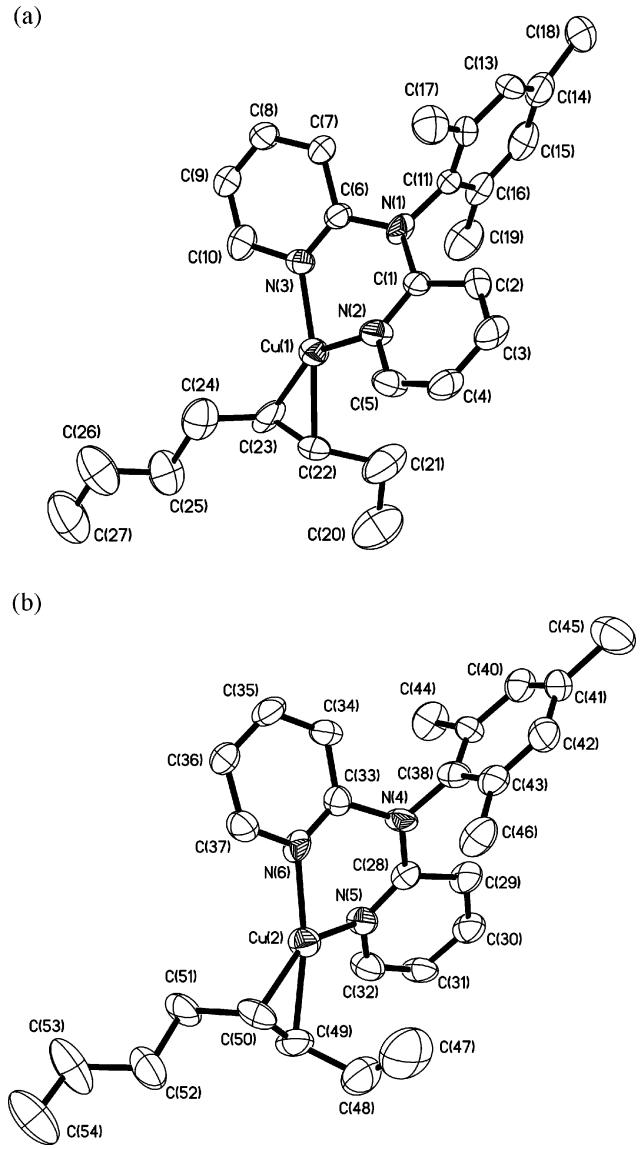

Fig. 2 Molecular structures of the two unique cation conformers in **2**. Thermal ellipsoids are shown at the 30% level, and hydrogen atoms are omitted for clarity.

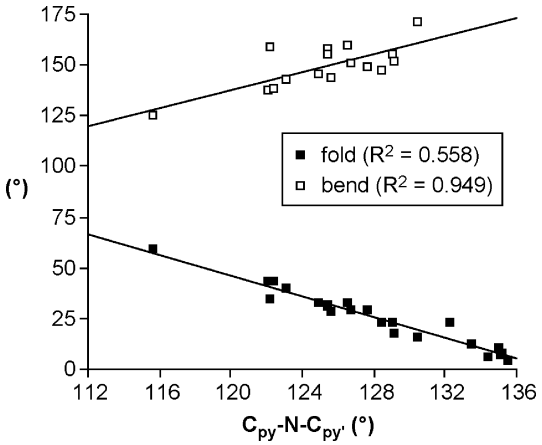

Fig. 3 Correlation between aspects of structural geometries in copper complexes of aryl-functionalized dipyridylamines.

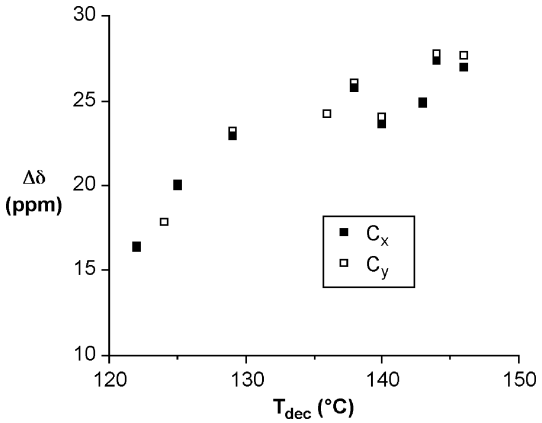

Fig. 4 Change in ^{13}C NMR olefin chemical shifts ($\Delta\delta$) upon coordination in complexes [Cu(Ar-dpa)(η^2-olefin)]BF_4 as a function of decomposition temperature.

Table 2 Olefin dissociation temperatures and change in ^{13}C NMR chemical shift for olefin signals upon coordination in complexes [Cu(Ar-dpa)(η^2-olefin)]BF_4

Ar	Olefin	$\Delta\delta$ C_Y (ppm)	$\Delta\delta$ C_Z (ppm)	T_d (°C)
H	*cis*-3-octene	27.80	27.40	143–146
H	*trans*-3-octene	24.80	25.00	144–146
Mes	*cis*-3-octene	24.01	23.68	135–137
Mes	*trans*-3-octene	20.06	19.95	123–125
2-^{i}PrC$_6$H$_4$	*cis*-3-octene	26.07	25.78	134–136
2-^{i}PrC$_6$H$_4$	*trans*-3-octene	16.46	16.35	122–124
2-^{i}PrC$_6$H$_4$	*cis*-4-octene	24.20	—	136–138
2-^{i}PrC$_6$H$_4$	*trans*-4-octene	17.85	—	121–123

previously shown that the change in NMR shift correlates with the decomposition temperature (T_{dec}) of the complex that is associated with the dissociation of the olefin. Thus, the change in chemical shift is a direct measure of the relative bonding energy of an olefin to the copper complex. However, for the present class of compounds (*i.e.*, internal olefins) the shift in the ^{13}C NMR provides a better comparison (Fig. 4).

The ^{13}C NMR spectra of [Cu(Ar-dpa)(olefin)]BF4 exhibits an upfield shift in the olefin signal as compared to free olefin (consistent with the difference between complexed and free olefin). In simple terms, the further upfield (lower δ) peaks are, the more complexed the olefin. Consideration of the data in Table 2 shows that the change in the ^{13}C NMR shifts upon coordination is greater for the *cis* isomers than the *trans* isomers. Thus, the binding of the *cis* isomer of both 3-octene and 4-octene is stronger to the copper than the *trans* isomers. As such this is consistent with the concept that the folded Ar-dpa ligand provides steric differentiation between *trans* and *cis* olefins (*i.e.*, **II** *versus* **III**).

Using the alteration in the ^{13}C NMR shift of the C=C unit upon coordination ($\Delta\delta$), it is possible to compare the differentiation in binding efficiency as a function of the Ar group. Fig. 5 shows that while there is a small difference between *cis*-3-octene *versus trans*-3-octene for the parent H-dpa complex, this difference increases with increased steric bulk, *i.e.*, H < Mes ≪ 2-^{i}PrC$_6$H$_4$. Again this result is consistent with our view of steric differentiation as a consequence of the folding of the Ar-dpa ligand, since we have previously shown that the folding is increased with increasing

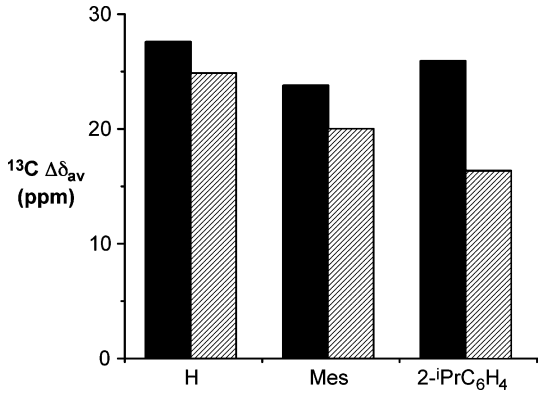

Fig. 5 Comparison of averaged $\Delta\delta$ C values for olefin resonances in *cis*- (■) and *trans*- (▨) 3-octene complexes with [Cu(Ar-dpa)(3-octene)]BF_4 as the substituent, Ar is varied.

steric bulk and more importantly steric asymmetry (2-^{i}PrC$_6$H$_4$ *versus* 2,6-^{i}Pr$_2$C$_6$H$_3$). This result suggests that differentiation of complexation of *cis* and *trans* isomers is possible for the 2-^{i}PrC$_6$H$_4$-dpa ligand complex. It is finally interesting to note that the difference in binding between *cis* and *trans* is greater for the asymmetrical 3-octene than the symmetrical 4-octene.

Conclusions

We have shown that the complexation of *cis* and *trans* olefins to a copper coordination center can be differentiated by changes of a remote substituent rather than the coordination pocket *per se*. Thus, remote alteration of steric bulk (*i.e.*, the Ar substituent) results in the folding of the Ar-dpa ligand with a consequential change in the orientation of the pyridine groups with regard to the substituents on the olefin. The resulting asymmetry results in preferential binding of *cis* olefins (**III**) over a *trans* olefin (**II**).

Experimental

All reagents in this study were used as received from commercial suppliers and were stored under an argon atmosphere in a drybox. Precursor complex [Cu(MeCN)$_4$]BF_4 was prepared according to Hathaway *et al.*[22] Aryl-functionalized di-(2-pyridyl)amines (Mes-dpa and 2-^{i}PrC$_6$H$_4$-dpa) were prepared according to established methods.[17] All solvents were distilled and degassed *via* freeze–pump–thaw immediately prior to use. Glassware was thoroughly cleaned and dried prior to use. All manipulations were performed under an argon atmosphere using standard Schlenk line techniques. ^{1}H and ^{13}C NMR spectra were obtained at room temperature using Bruker Avance 400 and 500 MHz spectrometers. Chemical shifts are reported relative to internal solvent resonances. IR spectra were obtained using a Nicolet FTIR spectrometer equipped with ATR accessory. Thermogravimetric analyses were performed on a Seiko I TG/DTA 200 under an argon gas flow of 15–20 mL min^{-1}.

[Cu(Mes-dpa)(η²-cis-3-octene)]BF_4 (1)

In a drybox, [Cu(MeCN)$_4$]BF_4 (0.314 g, 1.0 mmol) and Mes-dpa (0.291 g, 1.0 mmol) were charged to separate Schlenk flasks. After removal from the drybox, EtOH (20 mL) was added *via* cannula to the flask containing the ligand, which was stirred to dissolve the solid. *cis*-3-octene (*ca.* 4 mL) in ^{i}PrOH (25 mL) was added *via* cannula to the flask containing the copper precursor. After stirring for one hour, the ligand solution was added to the copper–olefin mixture, and the combined solutions were stirred under an argon atmosphere overnight. The solution volume was then reduced by approximately half under vacuum, warmed gently with a water bath to redissolve the product, and then filtered through a medium porosity glass frit to remove insoluble impurities. Argon was vigorously bubbled through the resulting pale green solution to further reduce its volume to *ca.* 15 mL. The solution was gently warmed to dissolve any precipitate, and upon cooling to –12 °C for several days, afforded 0.292 g colorless semi-crystalline powder. Yield: 53%. MP (TGA; decomp.) 137–139 °C. FTIR (neat, ATR, cm^{-1}): 3100 (w, aromatic ν_{C-H}), 3039 (w, alkene ν_{C-H}), 2964 (m, alkyl ν_{C-H}), 2929 (m, alkyl ν_{C-H}), 2872 (w, alkyl ν_{C-H}), 2859 (w, alkyl ν_{C-H}), 1600 (s), 1581–1429 (s, aromatic $\delta_{C=C}$), 1327 (s, aromatic ν_{C-N}), 1233 (m), 1168 (m), 1025 (br vs, ν_{B-F}), 930 (w), 909 (w), 856 (w), 777 (s). ^{1}H NMR (298 K; CD_3OD): δ 8.32 (2H, br s, *6*-py), 7.78 (2H, br t, *4*-py), 7.20 (2H, s, C*H*, *m*-mes), 7.19 (2H, br s, 5-py), 6.57 (2H, br d, 3-py), 5.04 (2H, m, *H*C=C*H*), 2.38 (3H, s, *p*-CH_3), 2.02 (6H, s, *o*-CH_3), 1.96 (4H, m, CHCH_2), 1.36 (4H, m, CH_2CH_2CH$_3$), 1.01 [3H, t, J(H–H) = 7.5 Hz, CHCH$_2$CH_3], 0.89 [3H, t, J(H–H) = 7.1 Hz, CH$_2$CH$_2$CH_3]. ^{13}C NMR (298 K; CD_3OD): δ 156.19, 149.93, 141.98, 141.66, 138.12, 137.59, 132.40, 119.88, 116.48, 108.54 (*C*HEt), 106.57 (*C*HCH$_2$), 33.80, 28.84, 23.59, 22.46, 21.32, 17.99, 15.18, 14.36.

[Cu(Mes-dpa)(η²-*trans*-3-octene)]BF_4 (2)

This compound was prepared in an analogous manner to that of (**1**), using the olefin *trans*-3-octene. Yield: 45%. MP (TGA; decomp.) 123–125 °C. FTIR (neat, ATR, cm^{-1}): 3123 (w, aromatic ν_{C-H}), 3097 (w, aromatic ν_{C-H}), 3043 (w, alkene ν_{C-H}), 2960 (w, alkyl ν_{C-H}), 2930 (w, alkyl ν_{C-H}), 2871 (w, alkyl ν_{C-H}), 1599 (s), 1581–1426 (s, aromatic $\delta_{C=C}$), 1383 (w), 1327 (s, aromatic ν_{C-N}), 1234 (m), 1171 (m), 1034 (br vs, ν_{B-F}), 931 (w), 908 (w), 881 (w), 777 (s). ^{1}H NMR (298 K; CD_3OD): δ 8.30 (2H, br s, py, 6-C*H*), 7.77 (2H, br t, py, 4-C*H*), 7.18 (2H, br s, C$_6H_2$), 7.16 (2H, br t, py, 5-C*H*), 6.55 (2H, br d, py, 3-C*H*), 5.05 (2H, m, *H*C=C*H*), 2.37 (3H, s, *p*-CH_3), 2.00 (4H, m, CHCH_2), 1.96 (6H, s, *o*-CH_3), 1.37 (4H, m, CH_2CH_2CH$_3$), 1.02 [3H, t, J(H–H) = 7.4 Hz, CHCH$_2$CH_3], 0.90 [3H, t, J(H–H) = 7.1 Hz, CH$_2$CH$_2$CH_3]. ^{13}C NMR (298 K; CD_3OD): δ 156.29, 149.84, 141.98, 141.69, 141.06, 138.04, 132.47, 119.84, 116.49, 113.19, 110.51, 34.05, 33.87, 27.38, 23.24, 21.33, 17.95, 15.48, 14.36.

[Cu(2-^{i}PrC$_6$H$_4$-dpa)(η²-*cis*-3-octene)]BF_4 (3)

This compound was prepared in an analogous manner to that of (**1**), using the ligand 2-^{i}PrC$_6$H$_4$-dpa. Yield: 49%. MP (TGA; decomp.) 133–135 °C. FTIR (neat, ATR, cm^{-1}): 3120 (w, aromatic ν_{C-H}), 3073 (w, aromatic ν_{C-H}), 3027 (w, alkene ν_{C-H}), 2963 (w, alkene ν_{C-H}), 2931 (w, alkyl ν_{C-H}), 2870 (w, alkyl ν_{C-H}), 1598 (m), 1582–1430 (s, aromatic $\delta_{C=C}$), 1328 (s, aromatic ν_{C-N}), 1282 (w), 1243 (m), 1168 (m), 1050 (br vs, ν_{B-F}), 931 (w), 764 (s). ^{1}H NMR (298 K; CD_3OD): δ 8.21 (2H, br s, py, 6-C*H*), 7.82 (2H, br t, py, 4-C*H*), 7.62 (1H, m, C$_6H_4$), 7.59 (1H, m, C$_6H_4$), 7.45 (1H, br s, C$_6H_4$), 7.43 (1H, br s, C$_6H_4$), 7.21 (2H, br t, py, 5-C*H*), 6.87

(2H, br d, py, 3-C*H*), 5.02 (2H, m, *H*C═C*H*), 2.92 [1H, br sept, C*H*(CH_3)$_2$], 1.95 (4H, m, CHCH_2), 1.36 (4H, m, CH_2C$H_2$$CH_3$), 1.01 [3H, t, *J*(H–H) = 7.5 Hz, CHCH$_2$CH_3], 0.96 [6H, br d, CH(CH_3)$_2$], 0.89 [3H, t, *J*(H–H) = 7.1 Hz, $CH_2CH_2CH_3$]. ^{13}C NMR (298 K; CD_3OD): δ 157.66, 149.88, 148.38, 141.66, 140.05, 132.25, 131.76, 130.52, 129.57, 120.68, 118.94, 106.49, 104.47, 33.79, 29.53, 29.05, 23.89, 23.66, 22.61, 15.19, 14.35.

[Cu(2-^{i}PrC$_6$H$_4$-dpa)(η^2-*trans*-3-octene)]BF$_4$ (4)

This compound was prepared in an analogous manner to that of (**1**), using the ligand 2-^{i}PrC$_6$H$_4$-dpa and olefin *trans*-3-octene. Yield: 39%. MP (TGA; decomp.) 123–125 °C. FTIR (neat, ATR, cm^{-1}): 3123 (w, aromatic ν_{C-H}), 3094 (w, aromatic ν_{C-H}), 3071 (w, aromatic ν_{C-H}), 3037 (w, alkene ν_{C-H}), 2961 (w, alkene ν_{C-H}), 2927 (w, alkyl ν_{C-H}), 2870 (w, alkyl ν_{C-H}), 1598 (m), 1582–1431 (s, aromatic $\delta_{C=C}$), 1324 (s, aromatic ν_{C-N}), 1281 (w), 1242 (m), 1170 (m), 1052 (br vs, ν_{B-F}), 930 (w), 783 (m), 772 (m), 764 (m). ^{1}H NMR (298 K; CD_3OD): δ 8.22 (2H, br s, py, 6-C*H*), 7.80 (2H, br t, py, 4-C*H*), 7.63 (1H, m, C$_6H_4$), 7.60 (1H, m, C$_6H_4$), 7.42 (2H, br m, C$_6H_4$), 7.18 (2H, br t, py, 5-C*H*), 6.78 (2H, br d, py, 3-C*H*), 5.09 (2H, m, *H*C═C*H*), 2.91 [1H, br sept, C*H*(CH_3)$_2$], 1.99 (4H, m, CHCH_2), 1.36 (4H, m, CH_2C$H^2$$CH_3$), 1.02 [3H, t, *J*(H–H) = 7.3 Hz, CHCH$_2$CH_3], 0.97 [6H, br d, C*H*(CH_3)$_2$], 0.91 [3H, t, *J*(H–H) = 7.2 Hz, $CH_2CH_2CH_3$]. ^{13}C NMR (298 K; CD_3OD): δ 157.73, 149.64, 148.44, 141.54, 140.18, 132.04, 131.80, 130.55, 129.80, 120.37, 118.55, 116.59, 114.03, 33.93, 33.85, 29.45, 27.32, 23.88, 23.28, 15.31, 14.38.

[Cu(2-^{i}PrC$_6$H$_4$-dpa)(η^2-*cis*-4-octene)]BF$_4$ (5)

This compound was prepared in an analogous manner to that of (**1**), using the ligand 2-^{i}PrC$_6$H$_4$-dpa and olefin *cis*-4-octene. Yield: 65%. MP (TGA; decomp.) 132–134 °C. FTIR (neat, ATR, cm^{-1}): 3127 (w, aromatic ν_{C-H}), 3068 (w, aromatic ν_{C-H}), 2959 (m, alkyl ν_{C-H}), 2930 (w, alkyl ν_{C-H}), 2869 (w, alkyl ν_{C-H}), 1599 (m), 1582–1431 (s, aromatic $\delta_{C=C}$), 1327 (s, amine ν_{C-N}), 1242 (m), 1167 (w), 1057 (br vs, ν_{B-F}), 1025 (br vs), 783 (s). ^{1}H NMR (298 K; CD_3OD): δ 8.28 (2H, br s, py, 6-C*H*), 7.82 (2H, br t, py, 4-C*H*), 7.64 (1H, m, C$_6H_4$), 7.60 (1H, m, C$_6H_4$), 7.53 (1H, br s, C$_6H_4$), 7.49 (1H, br s, C$_6H_4$), 7.23 (2H, br t, py, 5-C*H*), 6.88 (2H, br d, py, 3-C*H*), 5.08 (2H, m, *H*C═C*H*), 2.97 [1H, br s, C*H*(CH_3)$_2$], 1.93 (4H, m, CHCH_2), 1.42 [4H, sext, *J*(H–H) = 7.4 Hz, C$H_2$$CH_3$], 0.97 [6H, br s, CH(C$H_3$)$_2$], 0.92 [6H, t, *J*(H–H) = 7.4 Hz, CH_2CH_3]. ^{13}C NMR (298 K; CD_3OD): δ 157.40, 149.75, 148.42, 141.62, 139.92, 132.66, 131.83, 130.53, 129.53, 120.57, 118.60, 107.40, 31.46, 29.52, 24.69, 23.94, 14.35.

[Cu(2-^{i}PrC$_6$H$_4$-dpa)(η^2-*trans*-4-octene)]BF$_4$ (6)

This compound was prepared in an analogous manner to that of (**1**), using the ligand 2-^{i}PrC$_6$H$_4$-dpa and olefin *trans*-4-octene. Yield: 59%. MP (TGA; decomp.) 124–125 °C. FTIR (neat, ATR, cm^{-1}): 3121 (w, aromatic ν_{C-H}), 3069 (w, aromatic ν_{C-H}), 2960 (m, alkyl ν_{C-H}), 2928 (w, alkyl ν_{C-H}), 2868 (w, alkyl ν_{C-H}), 1596 (m), 1580–1429 (s, aromatic $\delta_{C=C}$), 1325 (s, amine ν_{C-N}), 1243 (m), 1168 (w), 1052 (br vs), 1025 (br vs, ν_{B-F}), 783 (s). ^{1}H NMR (298 K; CD_3OD): δ 8.18 (2H, br s, py, 6-C*H*), 7.81 (2H, br t, py, 4-C*H*), 7.64 (1H, m, C$_6H_4$), 7.59 (1H, m, C$_6H_4$), 7.42 (2H, br m, C$_6H_4$), 7.19 (2H, br t, py, 5-C*H*), 6.81 (2H, br s, py, 3-C*H*), 5.06 (2H, m, *H*C═C*H*), 2.92 [1H, br s, C*H*(CH_3)$_2$], 1.96 (4H, m, CHCH_2), 1.44 [4H, sext, *J*(H–H) = 7.4 Hz, C$H_2$$CH_3$], 0.98 [6H, br s, CH(C$H_3$)$_2$], 0.93 [6H, t, *J*(H–H) = 7.4 Hz, CH_2CH_3]. ^{13}C NMR (298 K; CD_3OD): δ 157.80, 149.67, 148.42, 141.54, 140.26, 132.01, 131.75, 130.54, 129.73, 120.55, 118.73, 113.75, 36.38, 29.47, 24.96, 23.88, 14.04.

Crystallographic studies

X-ray data for compound **2** was collected at room temperature on a Bruker SMART 1000 CCD diffractometer equipped with graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) and a fixed-χ 3-circle GGCS configuration, and corrected for Lorentz and polarization effects. The sample was prepared by suspension in mineral oil under an inert atmosphere (facilitating separation and selection of a single crystal), followed by sealing in a thin layer of epoxy resin and securing to the end of a glass fiber. The fiber was fastened to a brass pin and mounted onto the goniometer head. Data collection and unit cell refinement were carried out according to established methods[23] using the program SMART.[24] The program SAINT[25] was used for data reduction, and absorption correction was applied using SADABS.[26] Pertinent details are given in Table 3. The structure was solved by direct methods, and the model was refined using full-matrix least squares techniques.[27] All non-hydrogen atoms were first refined as having isotropic thermal parameters, followed by having anisotropic thermal parameters: shift/error less than 0.01. Refinement of the noncentrosymmetric structure (space group $P2_1$) was performed according to established methods, using TWIN/BASF instructions.[28,29] This treatment (refinement of the structure as having an inversion twin) refined the absolute structure with a fractional presence, *i.e.* Flack × parameter, of 0.45(2), with 6210 (79.9%) measured Friedel pairs. All hydrogen atoms were placed in calculated positions [C–H (alkene) = 0.98 Å, C–H (methylene) = 0.97 Å, C–H (methyl) = 0.96 Å, and C–H (aromatic) = 0.93 Å] and refined using a riding model with fixed isotropic displacement parameters. Neutral-atom scattering factors were taken from the usual source.[30] Refinement of positional and anisotropic displacement parameters led to convergence for all data. The program

Table 3 Summary of X-ray diffraction data for compound **2**

Empirical formula	$CuC_{27}H_{35}N_3BF_4$
M_w	551.93
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	9.943(2)
b/Å	21.275(4)
c/Å	13.874(3)
β/°	107.19(3)
V/Å^3	2804(1)
Z	4
D_{calc}/g cm^{-3}	1.308
μ/mm^{-1}	0.825
2θ range/°	3.08–58.34
No. collected	68486
No. ind. (R_{int})	13982 (0.0885)
No. obsd. ($\|F_0\| > 4.0\sigma \|F_0\|$)	6381
R	0.0937
R_w	0.2139
Largest difference peak and hole/eÅ^{-3}	2.449, –0.624
Weights	0.0926, 0
CCDC no.	733204

used for structure solution and refinement was SHELXTL Version 6.14.[31] Selected bond lengths and angles are given in Table 1.

The program PLATON was employed for structure validation,[32,33] which revealed solvent accessible voids in the crystal lattice (see .cif file in ESI† for platon squeeze details). The CALC SQUEEZE instruction was used to correct data of residual electron density in these voids, and all subsequent refinement was performed using the corrected data set. Some disorder is apparent in C(23) of conformer 1, which required treatment of the atom as having approximately isotropic behavior (ISOR), with rigid bond restraints (DELU) for carbon atoms C(21)–C(24), as well as a fixed distance restraint for the Cu(1)–C(23) bond distance (DFIX = 2.010). BUMP and DAMP restraints were used in preliminary refinement, but lifted for the final cycles.

Acknowledgements

Financial support for this work is provided by Trans Ionics Corporation and the Robert A. Welch Foundation (C-0002).

References

1 J. L. Humphrey, A. F. Seibert and R. A. Koort, *Separation Technologies: Advances and Priorities*, DOE/ID/12920-1, Washington, DC, 1001.
2 K. N. Campbell and L. T. Eby, *J. Am. Chem. Soc.*, 1941, **63**, 216.
3 National Research Council, *Separation and Purification: Critical Needs and Opportunities*, National Academy Press, Washington, DC, 1987.
4 E. R. Brown and R. L. Hair, *Monoolefin/paraffin separation by selective adsorption*, Phillips Petroleum Company, 1993.
5 K. Wang and E. I. Stiefel, *Science*, 2001, **291**, 106; A. E. Wentink, D. Kockman, N. J. M. Kuipers, A. B. de Hassn, J. Scholtz and H. Mulder, *Sep. Purif. Technol.*, 2005, **43**, 149; A. E. Wentink, N. J. M. Kuipers, A. B. de Hassn, J. Scholtz and H. Mulder, *Chem. Eng. Process.*, 2007, **46**, 800; L. Cavallo, M. E. Cucciolito, A. de Martino, F. Giordano, I. Orabona and A. Vitagliano, *Chem.–Eur. J.*, 2000, **6**, 1127; D. J. Safarik and R. B. Eldridge, *Ind. Eng. Chem. Res.*, 1998, **37**, 2571.
6 J. S. Thompson, R. L. Harlow and J. F. Whitney, *J. Am. Chem. Soc.*, 1983, **105**, 3522.
7 F. I. Rodriguez, J. J. Esch, A. E. Hall, B. M. Binder, G. E. Schaller and A. B. Bleeker, *Science*, 1999, **283**, 996; G. E. Schaller and A. B. Bleeker, *Science*, 1995, **270**, 1809; J. R. Ecker, *Science*, 1995, **268**, 667.
8 W. A. Braunecker, T. Pintauer, N. V. Tsarevsky, G. Kickelbick and K. Matyjaszewski, *J. Organomet. Chem.*, 2005, **690**, 916.
9 X. Dai and T. H. Warren, *Chem. Commun.*, 2001, 1998.
10 B. F. Straub, F. Eisentrager and P. Hofmann, *Chem. Commun.*, 1999, 2507.
11 A. Boni, G. Pampaloni, R. Peloso, D. Belleti, C. Graiff and A. Tiripicchio, *J. Organomet. Chem.*, 2006, **691**, 5602.
12 J. S. Thompson and J. F. Whitney, *Inorg. Chem.*, 1984, **23**, 2813.
13 J. S. Thompson, J. C. Calabrese and J. F. Whitney, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1985, **41**, 890.
14 J. Zhang, R.-G. Xiong, J.-L. Zuo and X.-Z. You, *Chem. Commun.*, 2000, 1495; J. Zhang, R.-G. Xiong, J.-L. Zuo, C.-M. Che and X.-Z. You, *J. Chem. Soc., Dalton Trans.*, 2000, 2898.
15 M. Munakata, S. Kitagawa, S. Kosome and A. Asahara, *Inorg. Chem.*, 1986, **25**, 2622.
16 J. J. Allen and A. R. Barron, *Dalton Trans.*, 2009, 878.
17 J. J. Allen, C. E. Hamilton and A. R. Barron, *Dalton Trans.*, 2010, **39**, 11451, DOI: 10.1039/c0dt00608d.
18 J. J. Allen, C. E. Hamilton and A. R. Barron, *J. Chem. Crystallogr.*, 2009, **39**, 573.
19 J. J. Allen, C. E. Hamilton and A. R. Barron, *J. Chem. Crystallogr.*, 2010, **2**, 130.
20 J. J. Allen, C. E. Hamilton and A. R. Barron, *J. Chem. Crystallogr.*, 2010, **2**, 137.
21 M. B. Power, J. R. Nash, M. D. Healy and A. R. Barron, *Organometallics*, 1992, **11**, 1830.
22 B. J. Hathaway, D. G. Holah and J. D. Postlethwaite, *J. Chem. Soc.*, 1961, 3215.
23 S. Ruhl and M. Bolte, *Z. Kristallogr.*, 2000, **215**, 499.
24 Bruker, *SMART v5.63*, 2003, Bruker AXS Inc., Madison, WI.
25 Bruker, *SAINT v6.45*, 2003, Bruker AXS Inc., Madison, WI.
26 G. M. Sheldrick, *SADABS*, 2008, H, Germany.
27 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2007, **64**, 112.
28 H. D. Flack and G. Bernardinelli, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1999, **55**, 908.
29 H. D. Flack and G. Bernardinelli, *J. Appl. Crystallogr.*, 2000, **33**, 1143.
30 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *International Tables for Crystallography*, 1995, Volume C, ed. A. J. C. Wilson, pp. 685-706, Dordrecht, Kluwer.
31 G. M. Sheldrick, *SHELXTL v6.14*, 2000, Bruker AXS Inc., Madison, WI.
32 A. L. Spek, *PLATON, Molecular Geometry Program*, 2008, Utrecht, The Netherlands.
33 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 380.

