

Bis(*tert*-butyl isocyanide- κ C)[4-fluoro-*N*-(2-[*N*-(4-fluorophenyl)carboximidoyl]cyclopenta-2,4-dien-1-ylidene)methyl)anilinido- κ^2 N,N']-copper(I)

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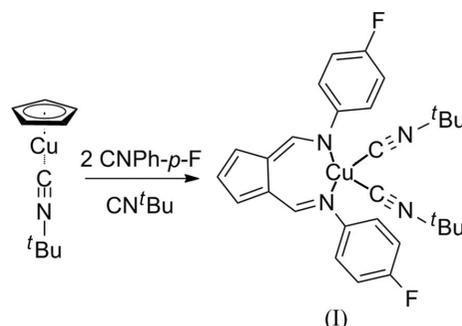
The solid-state structure of the title compound, [Cu(C₁₉H₁₃F₂N₂)(C₅H₉N)₂], shows that the Cu^I centre adopts a distorted tetrahedral coordination geometry, being coordinated by two N atoms of the 6-aminofulvene-2-aldimine (AFA) chelating ligand and by the bridgehead C atoms of the two isocyanide ligands. The cyclopentadienyl and imine components of the AFA ligand are approximately coplanar, with an angle between the planes of 5.00 (3)°. The Cu atom lies 0.6460 (3) Å above the imine plane defined by the N and C atoms of the seven-membered metallocycle. There is also an uncommon C—H···Cu anagostic interaction, with an intramolecular Cu···H distance of 2.67 Å, which is less than the sum of the van der Waals radii.

Comment

The diimine-substituted cyclopentadienyl 6-aminofulvene-2-aldimines (AFAs) have recently attracted attention as ligands for a variety of metals because of both their similarity to well established ligand systems, such as β -diketiminato, amino-troponimate or anilidoiminate ligands (Willcocks *et al.*, 2011; Bailey *et al.*, 2003, 2007, 2010), and their ability to bind to metal centres *via* the diimine donor groups or *via* the cyclopentadienyl unit (Bailey *et al.*, 2003, 2007).

As part of a wider study into the coordination chemistry of Cu^I complexes, we have recently reported the double migratory insertion of phenyl isocyanide (Ph—NC) into two vicinal *sp*² C—H bonds of the η^5 -coordinated cyclopentadienyl group in the complex [(η^5 -C₅H₅)Cu(CNPh)], resulting in the formation and isolation of the AFA complexes [(Ph₂-AFA)Cu(CNPh)] and [(Ph₂-AFA)Cu(CNPh)₂] (Johnson *et al.*, 2009).

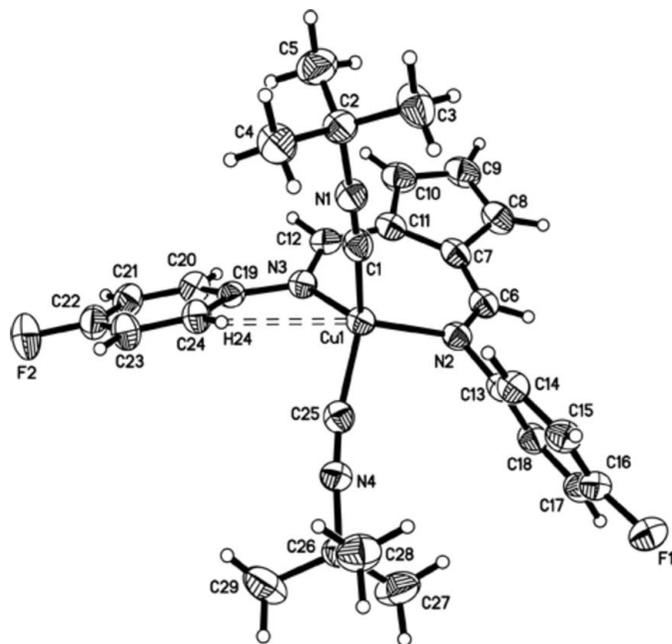
In an attempt to elucidate the mechanism by which the AFA complexes are formed and, more specifically, to understand better the effect that the isocyanide substituent has on the insertion reaction, we investigated a series of reactions between the complex [(η^5 -C₅H₅)Cu(CN^{*t*}Bu)] and varying amounts of alkyl and aryl isocyanides. The reaction of both [(η^5 -C₅H₅)Cu(CN^{*t*}Bu)] and [(η^5 -C₅H₅)Cu(CNPh)] with an excess of the alkyl isocyanide, CN^{*t*}Bu (*ca* 4 equivalents) was studied, but ¹H NMR spectroscopic studies failed to establish any evidence of reaction. However, the analogous reaction of [(η^5 -C₅H₅)Cu(CN^{*t*}Bu)] (Kruck *et al.*, 1993) with an excess (4 equivalents) of CNPh has been shown to produce the AFA complex, [(Ph₂-AFA)Cu(CNPh)₂], as evidenced by the appearance of indicative resonances for the ligand system in the ¹H NMR spectra, and provides an alternative route for the synthesis of the complex (Johnson *et al.*, 2009). We previously noted that the reaction of [(η^5 -C₅H₅)Cu(CN^{*t*}Bu)] with the electron-withdrawing isocyanides CN(*p*-C₆H₄F) and CN(*p*-C₆H₄NO₂) shows a much more rapid production of AFA complexes (<< 12 h), indicating that the electronic nature of the isocyanide is a significant factor in the migratory insertion of isocyanides into C—H bonds of the Cu—C₅H₅ systems (Johnson *et al.*, 2009).



The title complex, (I), was formed by the reaction of 4-fluorophenyl isocyanide with [(η^5 -C₅H₅)Cu(CN^{*t*}Bu)] in tetrahydrofuran in a copper-mediated insertion of two equivalents of CN(4-C₆H₄F) into two vicinal C—H bonds of the cyclopentadienyl moiety of the complex [(η^5 -C₅H₅)Cu(CN^{*t*}Bu)].

Complex (I) crystallizes in the monoclinic space group *P*2₁/*n* (Fig. 1) and an examination of the crystal packing shows no abnormally short intermolecular contacts. The shortest intermolecular interaction is 2.29 Å between atoms F1 and H20(*x* + $\frac{1}{2}$, *−y* + $\frac{1}{2}$, *z* + $\frac{1}{2}$).

The molecular structure of (I) (Fig. 1) shows the Cu^I centre to be coordinated by the two N atoms of the AFA ligand and the two divalent C atoms of the isocyanide ligands (Table 1), which are comparable with the Cu^I–AFA and Cu^I–isocyanide interactions in related complexes (Willcocks *et al.*, 2011), resulting in a coordination environment about the Cu^I centre that is best described as approximately tetrahedral. The cyclopentadienyl and imine portions of the AFA ligand are approximately coplanar. The dihedral angle between the C7–C11 and N2/C6/C7/C11/C12/N3 planes is 5.00 (3)°. The Cu^I


Figure 1

The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. The double-dashed line indicates the intramolecular C—H \cdots Cu anagostic interaction.

atom is located 0.6460 (3) Å above the imine portion of the AFA ligand (N2/C6/C7/C11/C12/N3). As with related (AFA)-Cu(CNR)₂ complexes (Willcocks *et al.*, 2011), the bite angle of the AFA ligand in (I) [N2—Cu1—N3 = 106.60 (9)°] is compressed, as a result of pyramidalization at the metal centre.

An interesting feature of this structure is the presence of an intramolecular C—H \cdots Cu anagostic interaction in the solid state. The distance between the H atom and the Cu^I cation (Cu1 \cdots H24 = 2.67 Å and Cu1 \cdots H24—C24 = 114°) is shorter than the sum of their van der Waals radii (Nag *et al.*, 2007). Similar interactions not only represent a structural curiosity, but these largely electrostatic interactions are believed to have considerable relevance to many catalytic processes (Brookhart *et al.*, 2007). The weak interaction between the *ortho*-CH group of one of the AFA imine substituents and the metal centre is facilitated by a concomitant re-orientation of the fluorophenylimine substituent, such that the angle subtended between the phenyl ring and the plane defined by the backbone atoms of the AFA ligand, [C₅(CN)₂], is considerably closer to coplanarity [37.69 (4)°] than the aryl substituent, which does not engage in an additional interaction with the Cu^I centre [67.36 (4)°].

Both isocyanide ligands are distorted away from linearity, such that isocyanide ligand C1 is oriented, or bent, towards the imine substituent on N2, and similarly isocyanide ligand C25 is oriented towards the imine substituent on N3. Density functional theory calculations (DFT) on related systems have suggested there is considerable flexibility in the coordination geometry about the copper centres in these systems, with only small energy differences between potential geometric isomers (Willcocks *et al.*, 2011).

Experimental

To a solution of CpCuCN^{*t*}Bu (0.21 g, 1.0 mmol) in tetrahydrofuran (10 ml), *p*-FPhNC (0.27 g, 2.20 mmol) was added. The reaction mixture was stirred for 16 h and the volatiles were then removed under reduced pressure. The resultant solid was extracted with warm hexane (3 × 20 ml) and filtered. Further concentration and storage at 245 K resulted in the formation of (I) as dark-yellow crystals suitable for crystallographic investigation (yield 0.25 g, 47%). Analysis calculated for C₂₉H₃₁CuF₂N₄: C 64.85, H 5.82, N 10.43%; found: C 65.01, H 5.84, N 10.35%. ¹H NMR (300 MHz, 296 K, CDCl₃): δ 1.26 (singlet, 18H, ^{*t*}Bu), 6.19 (triplet, *J* = 3.60 Hz, 1H, CHCHCH), 6.78 (doublet, *J* = 3.54 Hz, 2H, CHCHCH), 6.86–7.20 (complex multiplet, 8H, Ph—F), 8.08 (singlet, 2H, ArNCH).

Crystal data

[Cu(C₁₉H₁₃F₂N₂)(C₅H₉N)₂]
M_r = 537.12
 Monoclinic, *P*₂₁/*n*
a = 13.943 (4) Å
b = 9.240 (2) Å
c = 21.642 (5) Å
 β = 97.462 (5)°

V = 2764.6 (12) Å³
Z = 4
 Synchrotron radiation
 λ = 0.6939 Å
 μ = 0.79 mm⁻¹
T = 150 K
 0.08 × 0.03 × 0.02 mm

Data collection

Bruker APEXII area-detector diffractometer
 Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.937, *T_{max}* = 0.985

27368 measured reflections
 7148 independent reflections
 5331 reflections with *I* > 2σ(*I*)
R_{int} = 0.083

Refinement

R[*F*² > 2σ(*F*²)] = 0.058
wR(*F*²) = 0.165
S = 1.13
 7148 reflections

331 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max}$ = 0.47 e Å⁻³
 $\Delta\rho_{\min}$ = -0.70 e Å⁻³

Methyl H atoms were located in circular difference Fourier syntheses and thereafter refined as part of a rigid rotating group, with C—H = 0.98 Å and *U*_{iso}(H) = 1.5*U*_{eq}(C). The aromatic H atoms were

Table 1

Selected geometric parameters (Å, °).

Cu1—C1	1.927 (3)	N2—C6	1.303 (3)
Cu1—C25	1.928 (3)	N2—C13	1.422 (4)
Cu1—N2	2.039 (2)	N3—C12	1.311 (4)
Cu1—N3	2.056 (2)	N3—C19	1.431 (3)
Cu1—H24	2.6692	N4—C25	1.153 (4)
N1—C1	1.150 (4)	N4—C26	1.458 (4)
N1—C2	1.463 (4)		
C1—Cu1—C25	117.70 (12)	C1—Cu1—N3	104.18 (11)
C1—Cu1—N2	112.67 (10)	C25—Cu1—N3	115.54 (11)
C25—Cu1—N2	99.89 (11)	N2—Cu1—N3	106.60 (9)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C20—H20 \cdots F1 ⁱ	0.95	2.29	3.209 (4)	162

Symmetry code: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

placed geometrically and refined with $C-H = 0.95 \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3409). Services for accessing these data are described at the back of the journal.

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