Bonding Interactions

Synthesis and Reactivity of Copper(I) Complexes Based on C_3 -Symmetric Tripodal HTIM(PR₂)₃ LigandsEkaterina S. Smirnova,^[a] Ferran Acuña-Parés,^[a] Eduardo C. Escudero-Adán,^[a] Christian Jelsch,^[b] and Julio Lloret-Fillol^{*[a,c]}

Abstract: We present the first example of non-classical hydrogen bonding in Cu^I complexes. To this end, we have studied the coordination capacity of the tripodal phosphine ligands HTIM(PR₂)₃ {tris[1-(di-R-phosphanyl)-3-methyl-1*H*-indol-2-yl]methane, R = Ph, *i*Pr} towards copper, leading to a series of eight Cu^I complexes [(HTIM(PR₂)₃)CuX] [R = Ph (**1–4**), *i*Pr (**5–8**); X = Cl[–], I[–], OTf[–], BF₄[–]]. An anagostic interaction in the Cu^I complexes has been proposed based on the results of ¹H NMR, ultrahigh-resolution X-ray diffraction, and theoretical [atoms-in-molecules (AIM) and natural bonding orbital (NBO)] analyses of

the electron density. Among the different synthesized complexes, [(HTIM(PPh₂)₃)CuOTf] (**2**) shows the strongest Cu^I⋯H–C interaction with a linear geometry (179.98°) and the shortest distance described so far [*d*(Cu–H) = 1.9 Å] in its toluene solvated form. Both parameters are characteristic of 3c–4e[–] interactions. In addition, we have found that these tripodal ligands exhibit unprecedented selectivity towards Cu^I ions. The synthesized HTIM(PR₂)₃Cu^I complexes have been found to be catalytically active and selective for the hydroboration of CO₂ to formic acid.

Introduction

Chemical reactivity and supramolecular structures are often governed by multiple weak (≤40 kcal mol^{–1})^[1] interactions. Among them, hydrogen bonding is one of the most important chemical interactions as it plays a central role in many physiological and biological processes.^[2] The current accepted definition of a hydrogen bond is one that combines the interactions of three components: a hydrogen-bond donor, a hydrogen-bond acceptor and a hydrogen atom.^[3] Usually, hydrogen bonding involves the interactions of two electronegative p-block elements with a hydrogen atom. A more elusive situation is the participation of a transition metal in hydrogen bonding, which usually involves a polarized X–H bond.^[2] This 3c–4e[–] interaction can be described as the donation of a filled d orbital of the metal centre into a σ* orbital of the polarized X–H fragment and/or as the electrostatic interaction between a partially positively charged hydrogen and a filled d orbital of a metal (Figure 1).^[4]

A better understanding of this non-classical hydrogen bond may provide valuable information to identify the reaction intermediates involved in X–H bond-activation mechanisms by

Figure 1. Attractive 3c–4e[–] M⋯H–C hydrogen bonding in which the transition metal plays the role of a hydrogen-bond acceptor. σ* represents the σ anti-bonding orbital.

metal centres. However, these types of interactions are difficult to study, especially for metal⋯H–C anagostic interactions.^[5] Indeed, the characterization of anagostic interactions are rare, most probably due to the fact that they occur in intermediates reactive towards C–H bond activation, making it challenging to stabilize them.^[3,6] Moreover, only a few examples of first-row transition metals featuring three-centre four-electron bonding (3c–4e[–]) have been reported.^[6,7]

In 2006, the first example of a C_3 -symmetric phosphorus-based tripodal ligand with a carbon atom as anchor {HTIM(PPh₂)₃, tris[1-(diphenylphosphanyl)-3-methyl-1*H*-indol-2-yl]methane, Figure 2} was reported.^[8]

The HTIM(PPh₂)₃ ligand has an unusual C_3 geometry, related to the highly versatile P₃^{SiH}^[9] {tris[2-*R*-(phosphanyl)phenyl]-silane} and P₃^{CH}^[10] {tris[2-*R*-(phosphanyl)phenyl]methane} ligands reported by Peters and co-workers (Figure 1)^[9,11] and P₃B {tris[2-*R*-(phosphanyl)phenyl]borane} described by Bourissou and co-workers.^[12] The unusual geometry of the P₃CH-type ligands could potentially impose and force the formation of non-

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Figure 2. HTIM(PR₂)₃ ligands employed in this study (left). Tripodal triphosphine ligands based on carbon and silicon anchors (right).

classical (C–H)⋯M hydrogen bonds, allowing the study of exceptional (C–H)⋯M interactions. Despite its potential, there is only a single example of an X-ray diffraction structure in which (C–H)⋯M hydrogen bonding has been studied, the HTIM(PPh₂)₃ molybdenum tricarbonyl complex.^[7] To this end, we present herein the synthesis of the new HTIM(P*i*Pr₂)₃ ligand, the atypical reactivity of HTIM(PR₂)₃ (R = Ph, *i*Pr) ligands with first-row transition metals and the synthesis of the copper complexes [{HTIM(PR₂)₃}CuX] [R = Ph; X = BF₄[−] (**1**), OTf[−] (**2**), Cl[−] (**3**), I[−] (**4**); R = *i*Pr, X = BF₄[−] (**5**), OTf[−] (**6**), Cl[−] (**7**), I[−] (**8**)]. Interestingly, we observed selective complexation of Cu^I ions by these tripodal ligands in the presence of other first-row transition metals.^[13] This selectivity has been rationalized by means of DFT calculations and is of interest for the separation or processing of copper salts, because radioactive copper (⁶⁴Cu) is well known for its use in immuno-positron emission tomography (PET).^[14–16]

We have also explored the capacity of the synthesized complexes to act as catalysts in CO₂ hydroboration, to study how the basicity of the ligand affects the reactivity. Copper complexes based on N-heterocyclic carbenes^[17–20] and polyphosphine^[21] ligands provide platforms for catalysing this interesting transformation. Interestingly, copper complexes are among the few systems able to selectively reduce CO₂ to HCO₂BBN.^[17] With respect to the development of new systems with the same selectivity pattern, it is important to establish the origin of the selectivity in order to advance the development of synthetically useful transformations of CO₂.

Of the synthesized complexes, [{HTIM(PPh₂)₃}CuOTf] (**2**) has allowed the first study of a non-classical (X–H)⋯M hydrogen-bonding interaction in Cu^I complexes. We have characterized and further clarified the (C–H)⋯Cu interaction through a combination of experimental electron density map studies obtained by X-ray diffraction and atoms-in-molecules (AIM) and natural bonding orbital (NBO) analyses. This experimental and theoretical combination has allowed us to pinpoint the geometrical and electronic features of the (C–H)⋯Cu interaction in the C₃-symmetric phosphorus-based tripodal system described herein.

Results and Discussion

Synthesis of HTIM(PR₂)₃ (R = Ph, *i*Pr) Ligands and their Reactivity with First-Row Transition Metals

The modular HTIM(PPh₂)₃ ligand was synthesized by the reported procedure in 75 % yield.^[8] We also developed the syn-

thesis of the analogous, more electron-rich phosphine bearing isopropyl substituents, HTIM(P*i*Pr₂)₃, which was isolated in 87 % yield. Both ligands show exceptional thermal stability and are robust with respect to oxygen and moisture. For instance, no traces of ligand oxidation/degradation were observed after heating for 24 h at 150 °C in DMF (wet) or after being suspended in distilled water and left for 24 h in air.

The coordination ability of the HTIM(PR₂)₃ ligands towards first-row transition metals is singular. For instance, the direct reactions of M(OTf)₂ or MCl₂ (M = Fe, Ni, Co or Zn) with the HTIM(PPh₂)₃ and HTIM(P*i*Pr₂)₃ ligands did not yield any complex, even when forcing the reaction conditions to high temperature for an extended period of time (48 hours reflux in xylene). This contrasts with the expected coordinating properties of tridentate phosphines, which typically react easily with metal salt precursors to form the respective complexes. We observed different behaviour when Cu^I salts were treated with the HTIM(PPh₂)₃ and HTIM(P*i*Pr₂)₃ ligands. We accessed copper complexes **1–8** (Scheme 1) by the direct reaction of appropriate metal salts [{Cu(MeCN)₄}BF₄, [Cu(MeCN)₄]OTf, CuCl and (CuI)₄(SMe₂)₃] with the ligands in dichloromethane at room temperature in less than 20 minutes, with the exception of the CuCl precursor (18 h) due to its poor solubility in CH₂Cl₂.

- i) 3.5 equiv. NaH, THF, 23 °C; ii) 3.5 equiv. R₂PCl, THF, 23 °C;
iii) CH₂Cl₂, Cu(MeCN)₄BF₄ or Cu(MeCN)₄OTf, R = Ph;
iv) CH₂Cl₂, Cu(MeCN)₄BF₄ or Cu(MeCN)₄OTf or (CuI)₄(SMe₂)₃ or CuCl or CuCl₂, R = Ph; *i*Pr
v) CH₂Cl₂ (r.t.) or toluene (110 °C) or xylene (135 °C) or MeCN (80 °C)
vi) toluene, 110 °C or xylene, 130 °C or 10 bar O₂, MeCN, 80 °C, or H₂O, air, DMF, 150 °C all 24–36 h

Scheme 1. Modular synthesis of the HTIM(PR₂)₃ (R = Ph, *i*Pr) ligands and the new copper(I) complexes with HTIM(PR₂)₃ ligands.

Remarkably, the reaction of Cu^{II}Cl₂ with the phosphines [HTIM(PR₂)₃ (R = Ph, *i*Pr)] in MeOH under air yielded the same copper complexes (**3** and **7**, respectively), in similar yields as when starting with Cu^ICl (70 and 84 % in the case of **3** and 67 and 78 % for **7**). Nevertheless, when starting with the Cu^{II}Cl₂

salt, the reaction was faster (<20 min). A titration experiment of HTIM(PiPr)₂₃ with Cu^{II}Cl₂ in CD₃OD in an NMR tube indicated that the reaction was stoichiometric. Half an equivalent of CuCl₂ led to a 1:1 mixture of HTIM(PiPr)₂₃ and complex **7**, whereas 1 equiv. of CuCl₂ reacted cleanly to form complex **7** and no further changes were observed upon the addition of further CuCl₂ (see Figure SI-1 in the Supporting Information). The easy formation of the Cu^I complexes can be ascribed to their high stability and to the fact that Cu^{II}-to-Cu^I reduction is facilitated by methanol. In addition, this also indicates the capacity of the ligand to stabilize low oxidation states of Cu, which is known to adapt to several coordination geometries.

In total, eight new complexes were synthesized and characterized both in the solid state and in solution (Scheme 1 and Figure 3) by polynuclear NMR spectroscopy, HRMS and X-ray diffraction analysis, except for complexes **5** (the X-ray data were not of sufficient quality for CIF although we can confirm the κ^2 -coordination mode of the ligand) and **8**. The obtained complexes did not degrade with time under ambient conditions and no traces of decomposition were observed after their solutions in [D₃]MeCN were heated at reflux for 24 h. The solid-state analysis showed two different triphosphine coordination geometries. For stronger binding anions, such as Cl[−] or I[−], and the HTIM(PiPr)₂₃ ligand, κ^2 -coordination of the phosphorus atom was observed, and C₃-symmetric complexes were obtained only in the case of weakly coordinating anions or solvent molecules like CH₃CN with the HTIM(PPh)₂₃ ligand. Besides the

(C–H)⋯Cu^I hydrogen-bonding interaction, which will be discussed later in more detail, the other geometric parameters are in the expected ranges.

Ligand Coordination Selectivity

We tested the unusual selectivity for the formation of copper complexes by treating the HTIM(PiPr)₂₃ ligand with a pool of metal triflates (Fe²⁺, Ni²⁺, Co²⁺, Cu⁺ and Zn²⁺) in CD₂Cl₂/CD₃CN (3:1). The only compound detected by ³¹P{¹H} NMR spectroscopy and ESI-HRMS was [κ^2 P-HTIM(PiPr)₂₃]Cu(CD₃CN)]⁺ (see Figures SI-2 and SI-3 in the Supporting Information). Moreover, under biphasic reaction conditions, the reactions of Fe²⁺, Ni²⁺, Co²⁺, Cu²⁺ and Zn²⁺ chlorides in water with HTIM(PiPr)₂₃ in organic solvent (CD₂Cl₂/EtOD, 10:1, v/v) at room temperature and under air exclusively led to the formation of [HTIM(PiPr)₂₃–CuCl]. From the organic phase, we selectively isolated [HTIM(PiPr)₂₃]CuCl (**7**) from a metal chloride salt pool in 67 % yield (Figure 4 and Figure SI-4); the purity of the compound was proven by elemental analysis. To the best of our knowledge, this marked selectivity is unprecedented for phosphine ligands.

The selectivity observed is in agreement with the Irving–Williams series of relative complex stabilities of first-row divalent metal ions, which identifies Cu²⁺ as the most stable ion, attributed to Jahn–Teller distortion.^[13a,22,23] Nevertheless, it is difficult to explain the lack of reaction with the other M²⁺ salts.

Figure 3. ORTEP plots (ellipsoids drawn at the 50 % probability level) of **1** [$d(\text{Cu}–\text{P}) = 2.3158(8)–2.4133(9)$, $d(\text{Cu} \cdots \text{H}) = 1.994 \text{ \AA}$], **2** [$d(\text{Cu}–\text{P}) = 2.3056(4)–2.3759(4)$, $d(\text{Cu} \cdots \text{H}) = 1.934 \text{ \AA}$], **3** [$d(\text{Cu}–\text{P}) = 2.2339(5)–2.2551(5)$, $d(\text{Cu} \cdots \text{H}) = 2.328 \text{ \AA}$], **7** [$d(\text{Cu}–\text{P}) = 2.2657(5)–2.2687(5)$, $d(\text{Cu} \cdots \text{H}) = 2.232 \text{ \AA}$]. Ph and *i*Pr substituents and CH₃CN molecules are simplified to C, OTf[−] to O and non-coordinating anions have been omitted for clarity.

Figure 4. Selective formation of complex $[\kappa^2P\text{-HTIM}(\text{P}i\text{Pr}_2)_3]\text{CuCl}$ in the presence of Fe^{2+} , Ni^{2+} , Co^{2+} , Cu^{2+} and Zn^{2+} chlorides.

The origin of this unusual reactivity may involve a balance between metal–phosphorus binding energy and ligand reorganization energy due to coordination. To gain some insight into the effect of these energetic contributions, we performed DFT calculations on copper and nickel complexes of $\text{HTIM}(\text{PPh}_2)_3$ (including dispersion and solvent effects, see the Supporting Information for complete computational details).

First, we located the possible coordination isomers of the copper and nickel complexes of the $\text{HTIM}(\text{PPh}_2)_3$ ligand. For both metals, the dicoordinated isomer is the most stable, that is, $[\kappa^2P\text{-HTIM}(\text{PPh}_2)_3]\text{Cu}(\text{CH}_3\text{CN})]^+$ and $[\kappa^2P\text{-HTIM}(\text{PPh}_2)_3]\text{Ni}(\text{CH}_3\text{CN})_2]^{2+}$ (see Figure SI-5B,D in the Supporting Information). Interestingly, the formation of $[\kappa^2P\text{-HTIM}(\text{PPh}_2)_3]\text{Cu}(\text{CH}_3\text{CN})]^+$ is clearly exergonic ($-16.5 \text{ kcal mol}^{-1}$), but the formation of $[\kappa^2P\text{-HTIM}(\text{PPh}_2)_3]\text{Ni}(\text{CH}_3\text{CN})_2]^{2+}$ is virtually iso-energetic. Thus, the formation energy favours $[\kappa^2P\text{-HTIM}(\text{PPh}_2)_3]\text{Cu}(\text{CH}_3\text{CN})]^+$ by around 15 kcal mol^{-1} , in agreement with the experimentally observed high selectivity for the copper complex. The ligand reorganization energies for the copper and nickel complexes, calculated as the energy difference between the free and complexed ligand, are 5.4 and $9.8 \text{ kcal mol}^{-1}$, respectively, which suggests that coordination to the smaller metal ion is favoured by $4.4 \text{ kcal mol}^{-1}$. The smaller

reorganization energy for the copper complex can be rationalized by comparing the M–P distances [$d(\text{Cu-P})_{\text{avg}}$ and $d(\text{Ni-P})_{\text{avg}}$ of $2.24 \text{ \AA}$ and $2.36 \text{ \AA}$, respectively]. We also estimated the metal–phosphorus binding energy,^[24] which is more favourable for the copper(I) than for the nickel(II) complex by $8.9 \text{ kcal mol}^{-1}$, again in line with the experimental selectivity. Based on our computational results, we can rationalize that both the ligand distortion and binding energy play an important role in the selectivity. This selectivity may be exploited in the separation or processing of radioactive copper salts (^{64}Cu), well known as immuno-positron emission tomography (PET) agents.^[25,26]

Coordination Behaviour in Solution

Complexes **1** and **2** present a singlet in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at room temperature, as expected from the C_3 κ^3P -coordination mode observed in the solid state. The ^1H NMR signals only suffer signal broadening upon cooling to 183 K . Interestingly, complexes **3**, **6** and **7** show the same behaviour despite the fact that they present a κ^2P -coordination mode in their X-ray diffraction structures.

Complex **4** shows a broad signal in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at room temperature, which suggests dynamic behaviour (Figure 5). Indeed, NMR studies at different temperatures revealed the transformation of the broad $^{31}\text{P}\{^1\text{H}\}$ signal into a multiplet at low temperature. Unfortunatly, the multiplet was not fully resolved even at 183 K , which makes it difficult to draw conclusions. Clearer is the behaviour of complex **8**, for which the sharp singlet at room temperature transforms into two doublets and a singlet with relative integration 1:1:1 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, which strongly suggests the κ^2P -coordination mode in solution at 183 K , as in the X-ray diffraction structure. In the

Figure 5. T correlation $^{31}\text{P}\{^1\text{H}\}$ NMR studies for complexes **2–4** and **8** (CD_2Cl_2 , 298 and 183 K).

case of complex **6**, the appearance of two doublets was also observed (see Figure SI-7 in the Supporting Information).

The singlet generally observed in the $^{31}\text{P}\{^1\text{H}\}$ spectra at room temperature is consistent with κ^3P -coordination, especially for those systems that do not present two doublets and a singlet with a 1:1:1 $^{31}\text{P}\{^1\text{H}\}$ NMR integration pattern. Nevertheless, we cannot discard a fast equilibrium between the three possible C_2 -symmetric Cu^I coordinations at room temperature.

Catalytic CO_2 Reduction to HCO_2BBN

We next investigated the catalytic activity of our copper complexes in the hydroboration of CO_2 , which is challenging due to the high enthalpy ($127.3 \text{ kJ mol}^{-1}$) of the $\text{C}=\text{O}$ double bond and frequently presents kinetic difficulties. However, it has been reported that complexes based on polydentate phosphine ligands can catalyse this transformation by using strong reducing agents. In particular, tridentate Cu^I complexes have been shown very effective.^[17,27] We observed that complexes **1–4**, which contain Ph substituents on the phosphorus atoms, are active and selective catalysts for the transformation of CO_2 into HCO_2BBN (BBN = 9-borabicyclo[3.3.1]nonane) in $[\text{D}_8]\text{THF}$ (in CDCl_3 the catalytic activity decreases, see Table S1 in the Supporting Information) with TON values in the range of 20–22 (Table 1). We discarded the formation of BBN ether (**C**) and methoxy-BBN (**D**) because they were not detected by ^1H NMR spectroscopy.

Table 1. Catalytic CO_2 hydroboration tests.^[a]

Entry	Catalyst	Selectivity (A/B)	TON
1	HTIM($\text{P}i\text{Pr}_2$) ₃	100:0	≤2
2	HTIM(PPh_2) ₃	100:0	≤2
3	$[\text{Cu}(\text{MeCN})_4]\text{OTf}$	100:0	≤2
4	CuCl	100:0	≤2
5	$[\text{Cu}(\text{MeCN})_4]\text{BF}_4$	100:0	≤2
6	1	100:0	19
7	2	97:3	22
8	3	95:5	20
9	4	99:1	20
10	5	98:2	22
11	6	97:3	22
12	7	99:1	25
13	8	99:1	31

[a] Reagents: CO_2 (1 atm), $(9\text{-BBN})_2$ (0.09 mmol), catalyst (2 mol-%). The yields and selectivities were determined by ^1H NMR analysis using mesitylene as internal standard.

At the end of the reaction, only a signal corresponding to the free ligand was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, which shows that the Cu metal decoordinated during catalysis. The formation of a metallic mirror on the wall of the reaction tube suggests the formation of metallic copper. In contrast, complexes bearing the *i*Pr-substituted phosphines, which show slightly higher catalytic activity (22–31 TON), remained intact

after catalysis. The absence of clear differences between the different complexes among the series with $\text{HTIM}(\text{PPh}_2)_3$ may again be an indication of similar coordination geometries for these complexes in solution, which will be discussed later.

The selective formation of HCO_2BBN is interesting from a fundamental point of view. The number of catalysts that can selectively reduce CO_2 to HCO_2H is rather limited.^[17] Consequently, the development of new catalysts for this transformation is relevant to establish the origins of the selectivity and to advance the development of synthetically useful transformations for CO_2 functionalization.

Experimental and Theoretical Characterization of the $\text{C}_{\text{sp}^3}\text{-H}\cdots\text{Cu}$ Interaction

We have studied the $(\text{C-H})\cdots\text{Cu}^I$ interaction by X-ray diffraction analysis, ^1H NMR spectroscopy and computational modelling by DFT (see the Supporting Information for the computational details).

Comparison of the $\text{Cu}\cdots\text{H}$ distances determined by X-ray diffraction analysis and DFT calculations showed a good geometric match; the $\text{Cu}\cdots\text{H}-\text{C}_{\text{sp}^3}$ distance falls in the range 1.9–2.3 Å, and most of the structures have an angle close to 180° , consistent with a possible $3c-4e^-$ interaction.

The shortest $\text{Cu}\cdots\text{H}-\text{C}_{\text{sp}^3}$ distances were found for complexes **1** and **2**, which have a κ^3P -coordination mode (1.934 Å for **2** and 1.994 Å for **1**, Figure 6), in good agreement with the calculated distances (Table 2). The results of a natural bond orbital (NBO) analysis^[14,28] of the selected compounds indicate that charge donation occurs from Cu^I to the C-H bond [$\Delta q(\text{H}) < 0$]. The intramolecular charge transfer decreases with theoretical $\text{Cu}\cdots\text{H}$ distance (Table 2). The donor–acceptor delocalization energy from the copper orbitals to the $\sigma_{\text{C-H}}^*$ orbital in complex **2** is remarkable ($16.3 \text{ kcal mol}^{-1}$), and the energies of the charge transfer from the $\sigma_{\text{C-H}}$ orbital to copper [$\Delta E_{\text{total}}(\sigma_{\text{C-H}} \rightarrow n_{\text{Cu}})$] are significantly lower than those reported for agostic interactions,^[15] which suggests an agostic character of the $\text{Cu}\cdots\text{H}-\text{C}_{\text{sp}^3}$ interaction.

$\text{C-H}\cdots\text{Cu}$ distance, solid state (X-ray)

Figure 6. $\text{C-H}\cdots\text{Cu}$ distances [Å] derived from X-ray diffraction data (top) and ^1H NMR chemical shifts for $\text{C}_{\text{sp}^3}\text{-H}$ in CD_2Cl_2 (bottom).

Likewise, we also inspected the chemical shifts of the $\text{C}_{\text{sp}^3}\text{-H}$ proton in the ^1H NMR spectra. In CD_2Cl_2 solution, we observed a downfield shift for all the synthesized complexes compared with the corresponding free ligand (Figure 6),^[5e,29] which is consistent with previously studied non-classical

Table 2. Summary of the Cu^I–H and C_{sp3}–H bond lengths, the ¹H NMR chemical shifts of the C_{sp3}–H moiety (δ), the changes in the ¹H NMR chemical shift upon complexation ($\Delta\delta$), the NPA charge transferred from the metal to the H–C_{sp3} bond (Δq), the total donor–acceptor interaction energy [$\Delta E_{\text{total}}(\sigma_{\text{C-H}} \rightarrow n_{\text{Cu}})$], the bond critical point parameters of the Cu^I...H interaction [$\rho(r)$, $\nabla^2\rho(r)$, $G(r)$, $V(r)$, and $H(r)$] and its energy (ΔE_{HB}) for selected copper complexes.

Exp. (calcd.)	2	7
$d_{\text{H-C}}$ [Å]	1.092 (1.098)	0.980 (1.100)
$d_{\text{H...Cu}}$ [Å]	1.934 (1.904)	2.231 (1.998)
δ_{H} [ppm]	10.8 (11.3)	8.05 (8.6)
$\Delta\delta_{\text{H}}^{[a]}$ [ppm]	2.1 (2.3)	0.55 (1.0)
$\Delta q_{\text{H}}^{[b]}$ [a.u.]	–0.11	–0.09
$\Delta E_{\text{total}}(\sigma_{\text{C-H}} \rightarrow n_{\text{Cu}})$ [kcal mol ^{–1}]	6.2	6.3
$\rho(r_{\text{cp}})$ [a.u.]	0.030 (0.044)	(0.034)
$\nabla^2\rho(r_{\text{cp}})$ [a.u.]	–0.039 (–0.032) ^[c]	(–0.028)
$G(r_{\text{cp}})$ [a.u.]	0.036 (0.040) ^[c]	(0.032)
$V(r_{\text{cp}})$ [a.u.]	–0.030 (–0.088) ^[c]	(–0.071)
$H(r_{\text{cp}})$ [a.u.]	0.005 (–0.048) ^[c]	(–0.039)
$\Delta E_{\text{HB}}^{[d]}$ [kcal mol ^{–1}]	–27.6	–22.3

[a] $\Delta\delta_{\text{H}} = \delta_{\text{H,complex}} - \delta_{\text{H,free ligand}}$. [b] $\Delta q_{\text{H}} = q_{\text{H,complex}} - q_{\text{H,free ligand}}$. [c] The Cu^I...H bond critical points were derived from high-resolution X-ray diffraction data. [d] The hydrogen bond interaction energy was computed as $\Delta E_{\text{HB}} = 0.5V(r) \times 627.51$.

hydrogen bonding in d⁸ complexes.^[6,7] For the less donating and bulky substituents [the HTIM(PPh₂)₃ ligand], the deshielding effect is more than 1.5 ppm in comparison with the free phosphine ligand [$\delta = 8.7$ ppm (q, CD₂Cl₂)], whereas for the HTIM(PiPr₂)₃ tripod phosphine, a small shift of up to 0.6 ppm is observed. The DFT data are again in good agreement with the experimental results; nevertheless the predicted deshielding effect is in general larger by around 0.5 ppm (Table 2).

It is worth mentioning that in a variable-temperature ¹H NMR study of complexes **3** and **4** (see Figure SI-8 in the Supporting Information), the characteristic downfield shift observed upon lowering the temperature, which has been described in the literature^[6] for anagostic interactions, stopped at 213 K. Owing to this slowing of the exchange of Cu^I coordination to the phosphorus atoms of the ligand, we observed a decrease in the deshielding effect of the C_{sp3}–H proton (see Figure SI-8).

The experimental charge density was refined by using the Hansen and Coppens multipolar atom model with the MoPro program.^[30] The X–H distances were constrained to standard neutron diffraction values,^[31] the C1–H1 distance was set to $d = 1.099$ Å and the Cu atom was modelled up to the hexadecapole level. By using this model, the X-ray diffraction structure of **2** with toluene solvate (**2'**) gave a very low *R* factor of 1.890 % (Table 2).

The experimental Laplacian density map (Figure 7) and the Cu^I...H bond critical points for complex **2'** were obtained from high-resolution X-ray diffraction data and compared with the theoretical ones. The atoms-in-molecules (AIM) theory was applied to both models (Figure 7).^[21] The two approaches revealed the existence of a Cu^I...H bond path interaction. The deformation electron density shows a small electron accumulation on the copper atom that is directed towards the H1 atom, whereas the density is depleted in the direction of the phosphorus atoms.

The experimental and DFT approaches present similar Laplacian contour maps. DFT underestimates the $V(r)$ and $H(r)$ values, but $\rho(r)$, $\nabla^2\rho(r)$ and $V(r)$ are in good agreement with the

Figure 7. Contour diagrams in the Cu–H–C_{sp3} plane for complex **2'** for experimental model deformations of the electron density: dynamic ($F_{\text{mult}} - F_{\text{sph}}$, top right), static ($\rho_{\text{mult}} - \rho_{\text{sph}}$, top left), experimental Laplacian map (bottom right) and DFT Laplacian map ($-\nabla^2\rho(r)$, bottom-left). Red regions represent negative values and blue regions represent positive values.

parameters derived from the X-ray diffraction data (Table 2). The slight divergences may have their origin in the inaccurate modelling of the non-covalent interactions at this level of theory. Thus, both analyses show a Cu^I...H interaction described as a 3c–4e[−] anagostic bond with partial covalent character.

Conclusions

The first systematic study of the (C–H)···Cu^I intramolecular interaction in a newly synthesized family of copper complexes based on C₃-symmetric tripodal ligands has been reported herein. The experimental data indicate that the HTIM(PR₂)₃ ligands coordinate exclusively with Cu^I in the presence of other first-row transition metals in the oxidation state II. DFT calculations predict that the coordination ability has its origin in the lower phosphorus binding energy and ligand reorganization energy required to capture small metal cations such as Cu^I. This behaviour may be exploited in analytical cation separation procedures.

The crystallographic and ¹H NMR spectroscopic data reveal that these complexes present different κP-coordination modes according to the steric effects of the *i*Pr and Ph groups and the nature of the counterion. A careful analysis of the geometrical features and electronic structures of these complexes suggests that the (C–H)···Cu^I contact is best described as a 3c–4e[−] anagostic interaction with partial covalent character. Charge donation from the metal to the C–H bond is more pronounced for copper systems with a κ³P-coordination mode due to shorter Cu···H distances, leading to a pronounced downfield shift of the C_{sp³}–H···Cu^I proton signal.

The interplay between binding affinity, ligand reorganization energy and geometrical parameters that facilitate the Cu···H contact should be considered to analyse the impact of this interaction on X–H bond-activation mechanisms.

Experimental Section

General: Unless otherwise mentioned, all reactions were performed under N₂ using standard Schlenk techniques or conducted after preparation in a glove box. Anhydrous solvents for synthesis were obtained by passing them through the activated alumina column of a PureSolvTM solvent purification system (Innovative Technologies, Inc., MA). Deuteriated solvents were purchased from Sigma-Aldrich. NMR spectra were recorded with a Bruker Avance 400 or 500 Ultrashield spectrometer. The chemical shifts (δ) in the ¹H and ³¹P{¹H} spectra are referenced to residual solvent resonances and external 85 % H₃PO₄, respectively. Coupling constants (*J*) are reported in Hertz. Mass spectra were recorded with a Water LCT Premier Spectrometer (ESI and APCI), an Autoflex Bruker Daltonics (MALDI and LDI), or an AgilentMSD-5975B (GC-MS) spectrometer. Elemental analyses were performed with a LECO CHNS 932 micro-analyser at the Universidad Complutense (Madrid). Crystal structure determinations were carried out by using a MM-007HF diffractometer equipped with an Pilatus 200K hybrid pixel detector, a rotating anode for Mo-K_α radiation and an Oxford Cryostream 700 plus low-temperature device (*T* = −183 °C). Full-sphere data collection was used with ω scans. Data collection and data reduction was performed with CrysAlisPro^[32] and absorption correction with SADABS.^[33] Structure solution and refinement was achieved by us-

ing the VLD procedure implemented in SIR2014.^[34] Spherical model refinement was performed by using the ShelXle program.^[35] All non-hydrogen atoms were refined by including anisotropic displacement parameters. Copper(I) chloride, copper(II) chloride, copper(I) tetrakis(acetonitrile)triflate, copper(I) tetrakis(acetonitrile)-tetrafluoroborate, diphenylphosphine chloride (99 % purity) and diisopropylphosphine chloride (98 % purity) were purchased from Merck (Sigma-Aldrich) and used without further purification. Unless otherwise stated, all other reagents were purchased from commercial sources and used without further purification.

Synthesis of Tris(*N*-diisopropylphosphino-3-methylindol-2-yl)methane [HTIM(P*i*Pr)₃]: The ligand was synthesized by a modification of the protocol used for the synthesis of tris(*N*-diphenylphosphino-3-methylindol-2-yl)methane. Tris(3-methylindol-2-yl)methane (2.00 g, 4.95 mmol) in THF (70 mL) was added to a stirred solution of washed NaH (416 mg, 17.3 mmol, 3.5 equiv.) in THF (60 mL) at 23 °C during 15 min. After vigorous stirring at 50 °C for 1.5 h, the solution was cooled to 23 °C. A solution of ClP*i*Pr₂ (98 % purity, 2.76 mL, 17.33 mmol, 3.5 equiv.) in THF (50 mL) was added dropwise and the reaction mixture was stirred at 23 °C over a period of 16 h. The resulting reaction mixture (yellow-orange) was filtered under a flow of nitrogen and the resulting orange filtrate was concentrated in vacuo to 20 mL. Addition of dry MeCN (100 mL) resulted in the immediate formation of a crystalline white precipitate, which could be separated by filtration in air with a membrane pump. The new tripodal phosphine was found to be soluble in chlorinated alkane solvents, diethyl ether, toluene, hexane and alcohols. Yield: 3.25 g, 4.31 mmol (87 %). Once precipitated from the reaction mixture, the new ligand could be kept in the presence of moisture and air without any trace of degradation. ¹H NMR (500 Hz, CDCl₃): δ = 7.53–7.51 (m, 3 H), 7.48 (q, ⁴*J*_{H-P} = 5.1 Hz, 1 H), 7.41–7.40 (m, 3 H), 7.15–7.07 (m, 6 H), 2.79 (sept., *J* = 4.2 Hz), 1.67 (s, 9 H), 1.32–1.26 (m, 9 H), 1.17–1.13 (m, 9 H), 0.89–0.84 (m, 9 H), 0.42–0.38 (m, 9 H) ppm. ¹H NMR (500 Hz, CD₂Cl₂): δ = 7.55–7.53 (m, 3 H), 7.50 (q, *J* = 5.1 Hz, 1 H), 7.41–7.38 (m, 3 H), 7.15–7.05 (m, 6 H), 2.80 (sept., *J* = 4.2 Hz), 1.67 (s, 9 H), 1.33–1.27 (m, 9 H), 1.17–1.12 (m, 9 H), 0.90–0.84 (m, 9 H), 0.42–0.37 (m, 9 H) ppm. ¹³C NMR (125 Hz, CDCl₃): δ = 140.6 (s, C), 139.2 (s, C), 132.4 (s, C), 121.6 (s, CH), 119.6 (s, CH), 118.6 (s, CH), 115.8 (s, C), 113.3 (s, CH), 38.6 (q, ³*J*_{C-P} = 22.5 Hz, H-C_{sp³}), 28.3–27.5 (m, CH₃), 22.6–22.1 (m, CH₃), 20.2–19.3 (m, CH₃), 9.3 (s, CH₃) ppm. ¹³C DEPTQ NMR (125 Hz, CD₂Cl₂): δ = 141.2 (m, C), 140.9 (s, C), 139.7 (s, C), 132.8 (s, C), 121.1 (s, CH), 119.9 (s, CH), 118.9 (s, CH), 116.2 (s, C), 113.8 (s, CH), 39.0 (q, ³*J*_{C-P} = 28.8 Hz, H-C_{sp³}), 28.0–27.8 (m, CH₃), 23.2–22.8 (m, CH₃), 22.5 (s, CH₃), 22.2 (s, CH₃), 20.4 (s, CH₃), 20.1 (s, CH₃), 19.6–19.5 (m, CH₃), 9.4 (s, CH₃) ppm. ³¹P{¹H} NMR (202.5 Hz, CDCl₃): δ = 60.54 (s) ppm. ³¹P{¹H} NMR (202.5 Hz, CD₂Cl₂): δ = 61.13 (s) ppm. HRMS (ESI, MeOH): calcd. for [C₄₆H₆₅N₃P₃]⁺ [*M* + *H*]⁺ 752.4386; found 752.4356. X-ray-quality crystals were obtained by slowly cooling to 23 °C a concentrated solution of HTIM(P*i*Pr)₃ in acetonitrile.

General Procedure for the Synthesis of Cu^I Complexes: A solution of the corresponding copper salt (0.161 mmol) in CH₂Cl₂ (2 mL) was added to a solution (5 mL) of HTIM(PPh₂)₃ or HTIM(P*i*Pr)₃ (150 or 120 mg, 0.16 mmol) in CH₂Cl₂ (SPS grade). The reaction was usually complete within 30 min, except for the reaction with CuCl (reaction mixture was left overnight due to the insolubility of CuCl in CH₂Cl₂). For CuCl₂, MeOH (0.8 mL) was used instead of CH₂Cl₂. All the obtained complexes could be isolated by recrystallization in air from their concentrated reaction mixtures by the addition of *t*BuOMe or hexane or by the slow diffusion of diethyl ether. For a systematic study, owing to the low solubility of some compounds in CDCl₃, all the NMR spectroscopic data were obtained in CD₂Cl₂ purchased from Merck (Aldrich).

[{HTIM(PPh₂)₃}Cu(MeCN)]BF₄ (1): Yellowish crystalline solid obtained in 89 % yield by recrystallization from CH₂Cl₂/tBuOMe. ¹H NMR (400 Hz, CD₂Cl₂): δ = 10.37 (q, ⁴J_{H-P} = 12.6 Hz, 1 H), 7.53–7.50 (m, 3 H), 7.40–7.36 (m, 3 H), 7.31–7.22 (m, 15 H), 7.06 (t, J = 8.0 Hz, 3 H), 6.96 (t, J = 8.0 Hz, 6 H), 6.71 (t, J = 8.5 Hz, 3 H), 6.61–6.57 (m, 6 H), 6.34–6.32 (m, 3 H), 2.11 (s, 9 H), 1.90 (s, 3 H, CH₃CN) ppm. ¹³C NMR (101 Hz, CD₂Cl₂): δ = 139.3–139.2 (m, C), 136.8–136.6 (m, C), 133.2 (s, C), 131.2–130.9 (m, CH), 130.4 (s, CH), 129.9–129.7 (m, CH), 129.3–129.2 (m, CH), 123.2 (s, CH), 121.9 (s, CH), 119.7 (s, CH), 119.3 (s, C), 116.0 (s, C), 37.5 (q, ³J_{C-P} = 21.2 Hz, H-C_{sp3}), 8.9 (s, CH₃), 2.2 (s, CH₃) ppm. ¹⁹F{¹H} NMR (376 Hz, CD₂Cl₂): δ = –149.02 (s) ppm. ³¹P{¹H} NMR (162 Hz, CD₂Cl₂): δ = 31.40 (s) ppm. HRMS (ESI, MeOH): calcd. for [C₆₄H₅₂CuN₃P₃]⁺ [M – MeCN – BF₄]⁺ 1018.2665; found 1018.2655. X-ray-quality crystals were obtained by the slow diffusion of tBuOMe into a solution of **1** in CH₂Cl₂ at 23 °C.

[{HTIM(PPh₂)₃}Cu]OTf (2): Yellowish crystalline solid obtained in 87 % yield by recrystallization from CH₂Cl₂/tBuOMe. ¹H NMR (400 Hz, CD₂Cl₂): δ = 10.25 (q, ⁴J_{H-P} = 11.6 Hz, 1 H), 7.52–7.49 (m, 3 H), 7.41–7.37 (m, 9 H), 7.29–7.22 (m, 9 H), 7.06 (t, J = 9.0 Hz, 3 H), 6.98 (t, J = 8.1 Hz, 6 H), 6.73–6.62 (m, 9 H), 6.38–6.36 (m, 3 H), 2.07 (s, 9 H) ppm. ¹³C NMR (101 Hz, CD₂Cl₂): δ = 139.4–139.3 (s, C), 137.0–136.9 (s, C), 133.2 (s, C), 131.4–130.9 (m, CH), 130.2 (s, CH), 129.7–129.6 (m, CH), 129.1–128.8 (m, CH), 123.1 (s, CH), 121.8 (s, CH), 119.8 (s, CH), 119.2 (s, C), 115.9 (s, CH), 37.9 (q, ³J_{C-P} = 21.1 Hz, H-C_{sp3}), 8.9 (s, CH₃), 2.2 (s, CH₃) ppm. ¹⁹F{¹H} NMR (376 Hz, CD₂Cl₂): δ = –78.52 (s) ppm. ³¹P{¹H} NMR (162 Hz, CD₂Cl₂): δ = 31.78 (s) ppm. HRMS (ESI, MeOH): calcd. for [C₆₄H₅₂CuN₃P₃]⁺ [M – OTf]⁺ 1018.2665; found 1018.2664. X-ray-quality crystals were obtained by the slow diffusion of tBuOMe into a solution of **2** in CH₂Cl₂ at 23 °C.

[{HTIM(PPh₂)₃}Cu]Cl (3): Yellow crystalline solid obtained in 70 % yield when using Cu(II)Cl₂ and 84 % when using the Cu(I)Cl salt after recrystallization from CH₂Cl₂/hexane. ¹H NMR (400 Hz, CD₂Cl₂): δ = 11.20 (q, ⁴J_{H-P} = 10.3 Hz, 1 H), 7.62–7.58 (m, 6 H), 7.49–7.48 (m, 3 H), 7.32–7.29 (m, 3 H), 7.18–7.15 (m, 6 H), 7.03–6.98 (m, 6 H), 6.66 (t, J = 5.9 Hz, 6 H), 6.63 (dt, J = 4.7, 1.1 Hz, 3 H), 6.34–6.27 (m, 9 H), 2.14 (s, 9 H) ppm. ¹³C NMR (101 Hz, CD₂Cl₂): δ = 139.2 (s, C), 137.6 (s, C), 132.9 (s, C), 131.1 (s, CH), 130.2–129.8 (m, CH), 128.6 (s, CH), 128.4 (s, CH), 127.8 (s, CH), 121.9 (s, CH), 120.8 (s, CH), 118.7 (s, CH), 117.9 (s, C), 116.2 (s, CH), 36.2 (q, ³J_{C-P} = 17.7 Hz, H-C_{sp3}), 8.4 (s, CH₃) ppm. ³¹P{¹H} NMR (162 Hz, CD₂Cl₂): δ = 29.70 (s) ppm. HRMS (ESI, MeOH): calcd. for [C₆₄H₅₂CuN₃P₃]⁺ [M – Cl]⁺ 1018.2665; found 1018.2648. C₆₄H₅₂ClCuN₃P₃ (1055.06): calcd. C 72.86, H 4.97, N 3.98; found C 72.21, H 5.11, N 4.09. X-ray-quality crystals were obtained by the slow diffusion of tBuOMe into a solution of **3** in CH₂Cl₂ at 23 °C.

[{HTIM(PPh₂)₃}Cu]I (4): Yellow crystalline solid obtained in 86 % yield by recrystallization from CH₂Cl₂/hexane. ¹H NMR (400 Hz, CD₂Cl₂): δ = 11.46 (q, ⁴J_{H-P} = 9.6 Hz, 1 H), 7.67–7.66 (m, 6 H), 7.52–7.50 (m, 3 H), 7.33–7.31 (m, 3 H), 7.18–7.15 (m, 6 H), 7.02–6.97 (m, 6 H), 6.64–6.57 (m, 9 H), 6.25–6.15 (m, 9 H), 2.23 (s, 9 H) ppm. ¹³C NMR (101 Hz, CD₂Cl₂): δ = 139.8 (s, C), 138.2–138.1 (m, C), 133.4 (s, C), 132.0–131.8 (m, CH), 130.6 (s, CH), 130.4–130.3 (m, CH), 129.3 (s, CH), 128.9 (s, CH), 128.3 (s, CH), 122.5 (s, CH), 121.4 (s, CH), 119.3 (s, CH), 118.5 (s, C), 116.9 (s, CH), 36.5 (q, ³J_{C-P} = 16.8 Hz, H-C_{sp3}), 8.9 (s, CH₃) ppm. ³¹P{¹H} NMR (162 Hz, CD₂Cl₂): δ = 25.89 (s) ppm. HRMS (ESI, MeOH): calcd. for [C₆₄H₅₂CuN₃P₃Na]⁺ [M + Na]⁺ 1168.1607; found 1168.1616. C₆₄H₅₂CuN₃P₃ (1146.51): calcd. C 67.05, H 4.57, N 3.67; found C 67.00, H 4.61, N 3.89. X-ray-quality crystals were obtained by the slow diffusion of tBuOMe into a solution of **4** in CH₂Cl₂ at 23 °C.

[{HTIM(PiPr₂)₃}Cu(MeCN)]BF₄ (5): Yellow crystalline solid obtained in 85 % yield by recrystallization from CH₂Cl₂/hexane. ¹H NMR

(400 Hz, CD₂Cl₂): δ = 7.60–7.55 (m, 4 H), 7.48–7.46 (m, 3 H), 7.29–7.19 (m, 6 H), 3.25 (dsept., J = 5.6, 1.9 Hz, 3 H), 2.65 (sept., J = 5.6 Hz, 3 H), 2.41 (s, 3 H), 1.47 (s, 9 H), 1.41–1.36 (m, 9 H), 1.18–1.14 (m, 9 H), 0.95–0.84 (m, 18 H) ppm. ¹³C NMR (101 Hz, CD₂Cl₂): δ = 140.2–140.0 (m, C), 137.8–137.7 (m, C), 132.8 (s, C), 123.9 (s, CH), 121.8 (s, CH), 119.9 (s, CH), 114.1 (s, CH), 41.5 (q, ³J_{C-P} = 16.8 Hz), 30.1 (s, CH₃), 26.8 (s, CH₃), 22.2–22.0 (m, CH₃), 20.7–20.2 (m, CH₃), 19.6 (s, CH₃), 8.4 (s, CH₃), 3.1 (s, CH₃) ppm. ¹⁹F{¹H} NMR (376 Hz, CD₂Cl₂): δ = –149.02 (s) ppm. ³¹P{¹H} NMR (162 Hz, CD₂Cl₂): δ = 63.72 (s) ppm. HRMS (ESI, MeOH): calcd. for [C₆₄H₅₂CuN₃P₃]⁺ [M – MeCN – BF₄]⁺ 814.3604; found 814.3606.

[{HTIM(PiPr₂)₃}Cu]OTf (6): Yellow crystalline solid obtained in 86 % yield by recrystallization from CH₂Cl₂/hexane. ¹H NMR (400 Hz, CD₂Cl₂): δ = 7.82 (q, ⁴J_{H-P} = 4.1 Hz, 1 H), 7.61–7.59 (m, 3 H), 7.47–7.45 (m, 3 H), 7.27–7.17 (m, 6 H), 3.22 (dsept., J = 5.2, 2.1 Hz, 3 H), 2.65 (sept., J = 5.2 Hz, 3 H), 1.44 (s, 9 H), 1.43–1.37 (m, 9 H), 1.21–1.16 (m, 9 H), 1.00–0.95 (m, 9 H), 0.86–0.85 (m, 9 H) ppm. ¹³C NMR (101 Hz, CD₂Cl₂): δ = 140.3–140.2 (m, C), 138.4–138.3 (m, C), 132.9 (s, C), 123.7 (s, CH), 121.6 (s, CH), 119.9 (s, CH), 119.7 (s, C), 114.4 (s, CH), 41.6 (q, ³J_{C-P} = 17.3 Hz), 29.8 (s, CH₃), 26.7 (s, CH₃), 22.1–21.8 (m, CH₃), 20.8–20.6 (m, CH₃), 20.1–19.8 (m, CH₃), 19.6 (s, CH₃), 8.9 (s, CH₃) ppm. ¹⁹F{¹H} NMR (376 Hz, CD₂Cl₂): δ = –78.52 (s) ppm. ³¹P{¹H} NMR (162 Hz, CD₂Cl₂): δ = 64.08 (s) ppm. HRMS (ESI, MeOH): calcd. for [C₆₄H₅₂CuN₃P₃]⁺ [M – OTf]⁺ 814.3604; found 814.3578. X-ray-quality crystals were obtained by the slow diffusion of tBuOMe into a solution of **6** in CH₂Cl₂ at 23 °C.

[{HTIM(PiPr₂)₃}Cu]Cl (7): Isolated as a yellow crystalline solid in 67 % yield when using Cu(II)Cl₂ and 78 % when using the Cu(I)Cl salt by recrystallization from CH₂Cl₂/hexane. ¹H NMR (400 Hz, CD₂Cl₂): δ = 8.05 (q, ⁴J_{H-P} = 5.5 Hz, 1 H), 7.64–7.62 (m, 3 H), 7.47–7.44 (m, 3 H), 7.26–7.15 (m, 6 H), 3.26 (sept., J = 7.2 Hz, 3 H), 2.61 (sept., J = 7.2 Hz, 3 H), 1.53–1.47 (m, 9 H), 1.46 (s, 9 H), 1.23–1.17 (m, 9 H), 1.05–1.00 (m, 9 H), 0.93–0.87 (m, 9 H) ppm. ¹³C NMR (101 Hz, CD₂Cl₂): δ = 140.4–140.3 (m, C), 139.2–139.0 (m, C), 132.9 (s, C), 123.7 (s, CH), 121.2 (s, CH), 119.7 (s, CH), 118.9 (s, C), 114.4 (s, CH), 41.1 (q, ³J_{C-P} = 17.5 Hz), 30.0 (s, CH₃), 26.9 (s, CH₃), 22.0–21.7 (m, CH₃), 20.7–20.6 (m, CH₃), 19.9–19.7 (m, CH₃), 8.9 (s, CH₃) ppm. ³¹P{¹H} NMR (162 Hz, CD₂Cl₂): δ = 62.80 (s) ppm. HRMS (ESI, MeOH): calcd. for [C₄₆H₆₄ClCuN₃NaP₃]⁺ [M + Na]⁺ 872.3190; found 872.3186. C₄₆H₆₄ClCuN₃P₃ (850.95): calcd. C 64.93, H 7.58, N 4.94; found C 64.74, H 7.37, N 5.04. X-ray-quality crystals were obtained by the slow addition of hexane into a solution of **7** in CH₂Cl₂ at 23 °C.

[{HTIM(PiPr₂)₃}Cu]I (8): Yellow crystalline solid obtained in 82 % yield by recrystallization from CH₂Cl₂/hexane. ¹H NMR (400 Hz, CD₂Cl₂): δ = 7.89 (q, ⁴J_{H-P} = 5.4 Hz, 1 H), 7.61–7.59 (m, 3 H), 7.44–7.41 (m, 3 H), 7.23–7.13 (m, 6 H), 3.26 (sept., J = 7.9 Hz, 3 H), 2.65 (sept., J = 7.9 Hz, 3 H), 1.55–1.49 (m, 9 H), 1.37 (s, 9 H), 1.24–1.18 (m, 9 H), 1.06–1.00 (m, 9 H), 0.94–0.89 (m, 9 H) ppm. ¹³C NMR (101 Hz, CD₂Cl₂): δ = 140.5–140.3 (m, C), 139.6–139.3 (m, C), 133.0 (s, C), 123.1 (s, CH), 121.2 (s, CH), 119.7 (s, CH), 118.9 (s, C), 114.6 (s, CH), 40.7 (q, ³J_{C-P} = 19.6 Hz), 29.9 (s, CH₃), 26.9 (s, CH₃), 21.7–21.5 (m, CH₃), 20.9–20.7 (m, CH₃), 20.3–19.9 (m, CH₃), 8.8 (s, CH₃) ppm. ³¹P{¹H} NMR (162 Hz, CD₂Cl₂): δ = 61.96 (s) ppm. HRMS (ESI, MeOH): calcd. for [C₄₆H₆₄CuN₃P₃]⁺ [M – I]⁺ 814.3604; found 814.3588. X-ray-quality crystals were obtained by the slow addition of hexane into a solution of **8** in CH₂Cl₂ at 23 °C.

CCDC 1829080 [for HTIM(PiPr₂)₃], 1829088 (for **1**), 1829083 (for **2**), 1829078 (for **2'**), 1829087 (for **3**), 1829077 (for **4**), 1829081 (for **7**), and 1829084 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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