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PREPARATION OF NEW MONO AND POLYNUCLEAR BIS(TRIPHENYLPHOSPHINE) COPPER(I) DERIVATIVES CONTAINING MONO AND BIDENTATE N-HETEROCYCLES, 8-HYDROXYQUINOLINE AND OXALATE LIGANDS

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Abstract—Novel mono and binuclear complexes of the type $Cu\{H(N—N)_2\}(PPh_3)_2$ [$H(N—N)_2^-$ = Hbibzim$^-$ (bibenzimidazolate), Htmbiim$^-$(tetramethylbiimidazolate)], $Cu(oxine)(PPh_3)_2$ and $Cu_2(\mu\text{-}C_2O_4)(PPh_3)_4$ [oxine = $C_9NH_6O^-$, $C_2O_4^{2-}$ = oxalate] have been obtained by reaction of $Cu(acac)(PPh_3)_2$ with the corresponding ligands. The reaction of $[Cu(CH_3CN)_2(PPh_3)_2]BF_4$ with imidazole or pyrazole derivatives renders tetrahedral mononuclear cationic complexes $[Cu(N—N)_x(PPh_3)_2]BF_4$ [$x = 1$, (N—N) = 2,2′-biimidazol (H_2biim), (H_2bibzim), (H_2tmbiim); $x = 2$, (N—N) = imidazole (Him), pyrazole (Hpz)]; the neutral tetranuclear complexes $[Cu_2\{\mu\text{-}(N—N)_2\}(PPh_3)_2]_2$ are formed when the corresponding bibenzimidazolate or tetramethylbiimidazolate are used as ligands. The structures of the resulting complexes have been elucidated by IR spectroscopy, ^1H, $^{31}P\{^1H\}$ NMR, molecular weight and conductance studies.

Copper(I) coordination chemistry is currently receiving much attention due mainly to the role of the metal in biological systems.[1] Copper(I) complexes, relevant to the understanding of copper-containing enzymes, are potentially air-sensitive, labile in solution and in some instances disproportionate to copper(0) and copper(II), but a large number of them have been described recently.[2] Recent structural studies in mononuclear Cu(I) complexes, namely $[CuL_n]^+$ (n = 2, 3, 4) or $CuXL_n$ (X = chloride, bromide, iodide) show their ability to adopt a range of different geometries. Thus, copper(I) complexes are known exhibiting di,[2] tri,[3] tetra[4] and penta[5] coordination which basically depends upon the bulk as well as the electronic properties of the N and/or P ligands.

Following our interest on coordination properties of N-donor heterocycles of the type of 2,2′-biimidazole and its derivatives[6] we describe in this paper the synthesis and characterization of novel copper(I) complexes containing Cu—N and/or Cu—O bonds, which are obtained by reactions of the type:

$$Cu(acac)(PPh_3)_2 + Y—H \rightarrow CuY(PPh_3)_2 + Hacac$$

[acac = acetylacetonate, Y—H = acidic N—H and O—H bidentate chelating ligands].

A method widely used by us, previously, for other M(acac) derivatives M = Rh,[7] Pd,[8] Au.[9] Thus, by reactions in appropriate conditions of $Cu(acac)(PPh_3)_2$ (**B**) with $H_2(N—N)_2$ (bibenzimidazole = H_2bibzim; 2,2′,4,4′-tetramethylbiimidazole = H_2tmbiim), mononuclear $Cu\{H(N—N)_2\}(PPh_3)_2$ and tetranuclear $[Cu_2\{\mu\text{-}(N—N)_2\}(PPh_3)_2]_2$ complexes are prepared. Similarly, $Cu(C_9NH_6O)(PPh_3)_2$ and $Cu_2(\mu\text{-}C_2O_4)(PPh_3)_4$ are obtained by reactions of (**B**) with 8-hydroxyquinoline and oxalic acid, respectively. This method of synthesis has only revealed to be of general utility with mild acidic ligands.

New tetrahedral mononuclear cationic copper(I) complexes of general formula $[Cu\{(N—N)_x\}(PPh_3)_2]BF_4$, $x = 1$, (N—N) = 2,2′-biimidazole (H_2biim), H_2bibzim, H_2tmbiim; $x = 2$, (N—N) = imidazole(Him), pyrazole (Hpz) are also described. These complexes can be of potential interest since photocatalytic reduction of dicationic methylviologen by similar copper(I) derivatives, namely $[Cu(N—N)(PPh_3)_2]^+$ (N—N = 1,10-phenanthroline, 2,2′-bipyridine and their derivatives) has been recently reported.[10] Table 1 lists the copper(I)

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complexes synthesized along with analytical, conductance and molecular weight data.

RESULTS AND DISCUSSION

(a) *Neutral complexes* (I–VI)

Reaction between dichloromethane solutions of $Cu(acac)(PPh_3)_2$ (acac = acetylacetonate) and $H_2(N—N)_2$, in 1/1 molar ratio leads according to eq. 1

$$Cu(acac)(PPh_3)_2 + H_2(N—N)_2 \xrightarrow{H_2CCl_2} Cu\{H(N—N)_2\}(PPh_3)_2 + Hacac \quad (1)$$

$[H(N—N)_2 = Hbibzim^-$ **(I)**, $Htmbiim^-$ **(II)**$]$

to a colourless solution from which complexes **(I)** and **(II)** can be obtained.

However, the reaction with H_2biim (2,2′-biimidazole) leads to a solid characterized as a mixture of the corresponding mononuclear and tetranuclear $[Cu_2(\mu\text{-biim})(PPh_3)_2]_2$ complexes, in a similar way as is described below (eq. 2). IR spectra of **(I)** and **(II)** (KBr mulls) show a ν(N—H) broad absorption band at *ca* 3000 cm^{-1} suggesting[8a] some intermolecular association via hydrogen protons of the ligands. (Fig. 1.)

^1H NMR spectra in $CDCl_3$ show resonances which are characteristic for aromatic protons along with two single peaks, in the case of the complex **(II)**, at δ 1.6 and 2.1 ppm assigned to the two chemically non-equivalent *exo* and *endo* methyl groups of the imidazole rings. The spectrum of **(II)** also shows a resonance at δ 5.2 ppm due to the presence of dichloromethane of crystallization.

Attempts to obtain binuclear derivatives of the type "$Cu[\mu\text{-}(N—N)_2]Cu$" by using the appropriate stoichiometric amounts (1/0.5) were unsuccessful, the reaction leading instead to a complex mixture. Thus, when $H_2tmbiim$ is used, a white solid is isolated which is characterized by ^1H NMR ($CDCl_3$ solution) as a mixture of $Cu(Htmbiim)(PPh_3)_2$ **(II)** and $[Cu_2(\mu\text{-tmbiim})(PPh_3)_2]_2$ **(VI)**. The spectrum

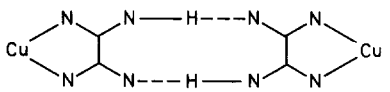


Fig. 1.

Table 1. Analytical data, colours, conductivity and molecular weight measurements of the novel complexes

	Compound	Found (Calc.) C	N	H	Colour	Λ_M or M.W[a]
(I)	$[Cu(Hbibzim)(PPh_3)_2]$	72.5 (73.2)	6.3 (6.8)	4.9 (4.7)	yellow	890 (821)[a]
(II)	$[Cu(Htmbiim)(PPh_3)_2]$	67.8 (67.7)[b]	6.9 (6.9)[b]	5.5 (5.5)[b]	white	890 (776)[a]
(III)	$[Cu(oxine)(PPh_3)_2]$	72.9 (73.8)	2.3 (1.9)	5.1 (4.9)	yellow	710 (732.2)[a]
(IV)	$[Cu_2(\mu\text{-}C_2O_4)(PPh_3)_4]$	69.7 (69.2)		5.2 (4.7)	white	1056 (1264)[a]
(V)	$[Cu_2(\mu\text{-bibzim})(PPh_3)_2]_2$	66.8 (64.4)	6.3 (6.3)	4.5 (4.3)	cream	1941 (1766)[a]
(VI)	$[Cu_2(\mu\text{-tmbiim})(PPh_3)_2]_2$	65.6 (65.8)	6.5 (6.7)	5.6 (5.0)	green	1570 (1678)[a]
(VII)	$[Cu(H_2biim)(PPh_3)_2]BF_4$	62.6 (62.4)	7.1 (6.9)	4.4 (4.5)	white	121[c]
(VIII)	$[Cu(H_2bibzim)(PPh_3)_2]BF_4$	65.0 (66.1)	5.9 (6.8)	4.8 (4.4)	yellow	111[c]
(IX)	$[Cu(H_2tmbiim)(PPh_3)_2]BF_4$	63.6 (63.9)	6.8 (6.5)	5.1 (5.1)	white	113[c]
(X)	$[Cu(Him)_2(PPh_3)_2]BF_4$	61.1 (62.3)	6.6 (6.9)	4.8 (4.7)	white	113.5[c]
(XI)	$[Cu(Hpz)_2(PPh_3)_2]BF_4$	60.9 (62.2)	6.9 (6.9)	4.6 (4.7)	white	126[c]
(XII)	$[Cu(3,5\text{-}Me_2Hpz)(CH_3CN)(PPh_3)_2]BF_4$	63.9 (63.7)	4.9 (5.2)	5.0 (5.0)	white	132.7[c]

[a] Molecular weight, ($CHCl_3$): Found (Calc.). [b] Calculated with $\frac{1}{2}H_2CCl_2$ of crystallization. [c] Acetone solutions ($\Omega^{-1}\,cm^2\,mol^{-1}$).

shows in the methyl protons range, four single peaks located at identical frequencies to those exhibited by pure samples of complexes (**II**) and (**VI**) (see below). No differences have been observed by increasing the time of reaction (30 min, 3 h), thus pointing to a process such as:

$$4Cu(acac)(PPh_3)_2 + 3H_2(N{-}N)_2 \xrightarrow{H_2CCl_2} 2Cu[H(N{-}N)_2](PPh_3)_2 + \tfrac{1}{2}[Cu_2\{\mu\text{-}(N{-}N)_2\}(PPh_3)_2]_2 + 2PPh_3 + 4Hacac \quad (2)$$

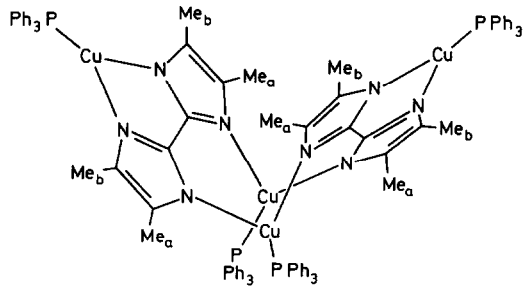
$[(N{-}N)_2^{2-}$ = biim^{2-}, tmbiim^{2-}].

A variety of other acid ligands Y—H react similarly through elimination of acetylacetone and lead to the formation of copper(I) complexes. Thus, previously known trigonal complexes, Cu(imide)$(PPh_3)_2$[11] [imide = $C_2H_4(CO)_2N^-$, $(C_6H_4)(CO)_2N^-$] and the tetrahedral $Cu(O_2CH)(PPh_3)_2$[12] (HCO_2^- = formiate) or novel ones, Cu(oxine)$(PPh_3)_2$ (**III**) (oxine = $C_9NH_6O^-$) and $Cu_2(\mu\text{-}C_2O_4)(PPh_3)_4$ (**IV**) ($C_2O_4^{2-}$ = oxalate) can be prepared in high yields by reaction with succinimide, phtalimide, formic acid, 8-hydroxiquinoline and oxalic acid, respectively.

IR spectra of (**III**) and (**IV**) show absorptions due to the presence of the ligands:[13] (**III**), 1560 (m), 1490 (w), 1455 (s) and 1110 cm^{-1}; (**IV**), 1600 (s) $\nu(CO_2)$ asym., 1300 (m) $\nu(CO_2)$ sym. cm^{-1}. Molecular weight determinations (see Table 1) reveals the chelate character of both anions and so forming, respectively, mono and binuclear derivatives. In contrast, the reaction with weaker acidic ligands such as pyrazole, imidazole and *o*-aminophenol do not take place, recovering the starting copper–acac complex unchanged. The chelate effect, which is supposedly acting in the reactions with H_2biim and their derivatives (eq. 1, see also below), can explain the reactivity of these very weak acid ligands.

Solutions of $[Cu(CH_3CN)_2(PPh_3)_2]BF_4$ in THF or CH_2Cl_2 react in 1/0.5 mol ratio with K_2bibzim and K_2tmbiim[$K_2(N{-}N)_2$] (prepared from $H_2(N{-}N)_2$ and an excess of potassium hydroxide in *ca* 3 : 1 THF/MeOH or CH_2Cl_2/MeOH) to give, respectively, cream and light green complexes (**V–VI**). The absence of ν(N—H) absorptions in the IR spectra and the values of molecular weights (determined osmometrically in chloroform, see Table 1) indicate a tetranuclear molecular structure of the type shown in Fig. 2.

The ^{1}H NMR ($CDCl_3$) spectrum of (**VI**) confirms the proposed structure, since it shows two single resonances at δ 2.3 and 1.7 ppm as expected for the two chemically non-equivalent methyl protons.



(*VI*)

Fig. 2.

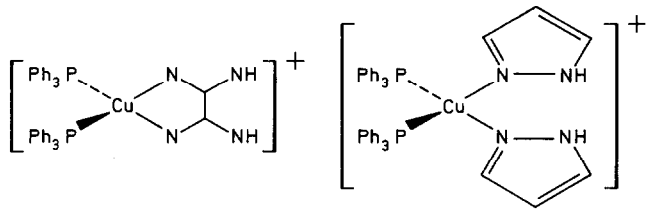
Similar tetranuclear structures have been found in related Pd(II),[8a] Rh(I),[14] and Ir(I)[14] complexes. $^{31}P\{^1H\}$ NMR spectrum of (**VI**) shows one broad singlet at δ −4.28 ppm indicating possibly a fast intramolecular exchange process of phosphines (on the NMR time scale) which makes them chemically equivalent. These structures are further examples of the ability of copper(I) to adopt trigonal geometries in the presence of either a bulky S-donor[15a] or N-donor, with mild bulky substituents[15b] ligands.

Cationic complexes. (**VII–XII**)

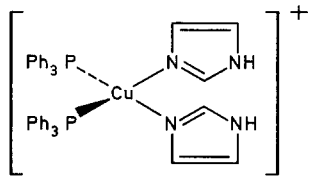
Addition of stoichiometric amounts of the N-donor ligands $H_2(N{-}N)_2$ (H_2biim, H_2bibzim, H_2tmbiim) or H(N—N) (Hpz, Him) to dichloromethane solutions of $[Cu(CH_3CN)_2(PPh_3)_2]BF_4$ leads to the displacement of acetonitrile ligands to give tetrahedral cationic complexes (**VII–XII**), which can be precipitated as white or light yellow (**VIII**) solids by addition of diethyl ether to the partially evaporated solutions. (Fig. 3.)

Conductance data of all the complexes (Table 1) are typical of uni–univalent electrolytes and IR spectra (KBr pellets) show a broad ν(N—H) absorption band at *ca* 3360 cm^{-1} and strong broad absorption at 1150 cm^{-1} assigned to ν(B—F) vibrations. ^{1}H NMR spectra reveal resonaces of aromatic protons along with those expected for the corresponding in heterocyclic rings (see experimental).

Unexpectedly, the reaction with an excess of 3,5-dimethylpyrazole proceeds in a different way, to give a white solid formulated as $[Cu(3,5\text{-}Me_2Hpz)(CH_3CN)(PPh_3)_2]BF_4$ (**XII**), in which only one of the two originally coordinated acetonitrile ligands, has been substituted. The IR spectrum shows typical absorptions of the dimethyl pyrazol ligand (see experimental) and a weak $\nu(C{\equiv}N)$ band at 2260 cm^{-1} due to the still coordinated acetonitrile ligand, which is confirmed by the presence of a methyl single resonance at δ 1.95 ppm in the ^{1}H NMR spectrum ($CDCl_3$). In



(VII - VIII - IX) *(X)*



(XI)

Fig. 3.

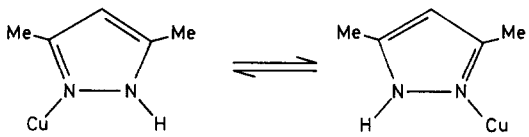


Fig. 4.

addition, instead of the two expected signals for the two methyl pyrazole groups only one slightly broad signal at δ 2.05 ppm is observed. This behaviour may be due to a rapid interexchange of pyrazole, in a dissociative process or "shuttling" of the H and the metal atom between the pair of N atoms.[16] (Fig. 4).

All the complexes described herein are air-stable in the solid state but their solutions are rapidly oxidized in air and decompose before melting. Table 1 lists their analytical data, molecular weights of the neutral complexes along with the conductivity data of the cationic complexes. Other relevant information on IR and ^1H or $^{31}P\{^1H\}$ NMR ($CDCl_3$) spectra are given in the experimental section.

EXPERIMENTAL

Measurements

C, H, N analyses were carried out with a Perkin–Elmer 240 microanalyzer. The IR spectra were recorded over the 4000–200 cm^{-1} range on a Perkin–Elmer 577 spectrophotometer using KBr discs or Nujol mulls between NaCl plates. Conductivities were measured at room temperature, in *ca* 10^{-3} mol dm^3 acetone solutions, with a Jenway PCM3 conductimeter. NMR spectra were recorded on a Varian FT-80A spectrometer at 79.54 MHz (^1H) or 32.20 MHz (^{31}P) using $SiMe_4$ and 85% H_3PO_4 respectively, as internal or external standard references. The molecular weights were determined in chloroform solutions with a Knauer vapour pressure osmometer (2×10^{-3} M solutions).

Synthesis

All reactions were performed under argon and the solvents were dried and deoxygenated before use. The ligands were used as purchased, except H_2biim, H_2bibzim and H_2tmbiim which are prepared as described elsewhere.[17,18] The reactions were carried out using 1 mmol of $Cu(acac)(PPh_3)_2$[19] or $[Cu(CH_3CN)_2(PPh_3)_2]BF_4$ as starting materials. The preparation of the acetonitrile complex is described below, since as far as we know it has not been isolated previously.

Neutral complexes

$Cu\{H(N—N)_2\}(PPh_3)_2$; $H(N—N)_2^-$ = Hbibzim$^-$ (**I**), Htmbiim$^-$ (**II**). A mixture of $Cu(acac)(PPh_3)_2$ and $H_2(N—N)_2$ (1 : 1 mol ratio) was stirred in dichloromethane at room temperature for 12 h. After filtration the resulting solution was concentrated and hexane was added yielding by precipitation a yellow (**I**) or white (**II**) solid. (**I**) yield: 60%. M.W.($CHCl_3$) Found(Calc.): 890(821). ^1H NMR ($CDCl_3$): δ 7.3 (m, 38H, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −1.3(s) ppm. (**II**) yield: 65%. M.W.($CHCl_3$) Found(Calc.): 890(776). ^1H NMR ($CDCl_3$): δ 7.2 (s, 30H, C_6H_5), 5.2 (s, 1H, $\frac{1}{2}CH_2Cl_2$

crystallization), 2.1 (s, 6H, *exo* CH_3), 1.6 (s, 6H, *endo* CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −1.5 (s) ppm. IR ν(N—H) (KBr) (**I**, **II**): 3000–2800 cm^{-1}.

Cu(oxine)$(PPh_3)_2$ (**III**) *and* $Cu_2(\mu\text{-}C_2O_4)(PPh_3)_4$ (**IV**). A mixture of Cu(acac)$(PPh_3)_2$ and 8-hydroxyquinoline (1:1 mol ratio) or $H_2C_2O_4 \cdot 2H_2O$ (1:0.5 mol ratio) were respectively stirred in dichloromethane or H_2CCl_2/MeOH (10:1) at room temperature for 24 h. The corresponding complexes were obtained from the filtered solutions as follows: (**III**) by precipitation after partial evaporation and addition of hexane. Yield: 90% M.W. ($CHCl_3$) Found (Calc.): 710(732.2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −2.5(s) ppm. (**IV**) dryness evaporation, extraction of solid residue with dichloromethane and addition of diethylether to the partially evaporated resulting solution. Yield: 90% M.W.($CHCl_3$) Found (Calc.): 1056 (1264). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −3.9(s) ppm.

$[Cu_2\{\mu\text{-}(N—N)_2\}(PPh_3)_2]_2$; $(N—N)_2$ = bibzim^{2-}(**V**), tmbiim^{2-}(**VI**). A mixture of $H_2(N—N)$ (0.5 mmol) and KOH (2 mmol) in 30 ml of THF/MeOH (*ca* 3:1) was stirred for 0.5 h at room temperature and then $[Cu(CH_3CN)_2(PPh_3)_2]BF_4$ (1 mmol) was added. After stirring for 24 h the suspension was dryness evaporated and the solid residue extracted with 2×20 ml of H_2CCl_2. Partial evaporation under reduced pressure and addition of hexane led to the precipitation of cream (**V**) and light green (**VI**) microcrystalline solids. (**V**) Yield: 60%. M.W. ($CHCl_3$) Found (Calc.): 1941 (1766). ^1H NMR ($CDCl_3$) δ 7.1 (m, Ph) ppm. (**VI**) Yield: 75%. M.W. ($CHCl_3$) Found (Calc.): 1570 (1678). ^1H NMR ($CDCl_3$): δ 7.1 (m, 30H, Ph) δ 2.3 (s, 6H, CH_3), δ 1.7 (s, 6H, CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −4.3 (s) ppm.

Reactions of $[Cu(CH_3CN)_2(PPh_3)_2]BF_4$ *with* H_2biim/KOH *and of* Cu(acac)$(PPh_3)_2$ *with* H_2biim (1:1 *mol ratio*). Reactions were carried out as described above for the preparation of (**I**) and (**II**) or (**V**) and (**VI**). Working up analogously, a white solid was obtained for both reactions. Both solids show identical IR (KBr pellet) spectra (ν(N—H) = 3000–2800 (m,br) cm^{-1}, biim, ring st, 1400(s), 1130(s) cm^{-1}) and elemental C, H, N analyses identified them as a mixture of Cu(Hbiim)$(PPh_3)_2$ and $[Cu_2(\mu\text{-biim})(PPh_3)_2]_2$.

Reaction of Cu(acac)$(PPh_3)_2$ *with* H_2tmbiim (1:0.5 *mol ratio*). A mixture of Cu(acac)$(PPh_3)_2$ and H_2tmbiim (1:0.5 mol ratio) was stirred in dichloromethane at room temperature for 24 h. Working up as described above for (**I**) and (**II**), a white microcrystalline solid was obtained. This was characterized as a mixture of (**II**) and (**VI**) by comparison of the ^1H NMR spectrum with those of the original samples.

Cationic complexes

$[Cu(CH_3CN)_2(PPh_3)_2]BF_4$. A mixture of $[Cu(CH_3CN)_4]BF_4$[20] and PPh_3 in dichloromethane (1:2 molar ratio) was stirred at room temperature for 6 h. After filtration a white microscrystalline solid is obtained by addition of hexane to the partially evaporated solution. Yield: 90%. C, N, H, Analyses: Found (Calc.): C 64.0 (63.5); N 3.8 (3.7); H 4.9 (4.8). Conductivity $\Lambda_M(\Omega^{-1}\,cm^2\,mol^{-1})$ (acetone): 132. ^1H NMR ($CDCl_3$): δ 7.18 (m, 30H, Ph), δ 2.07 (s, 6H, Me) ppm. IR (Nujol) μ(C≡N): 2285(vw), 2250(w) cm^{-1}.

$[Cu\{H_2(N—N)_2\}(PPh_3)_2]BF_4$; $H_2(N—N)_2$ = H_2biim (**VII**), H_2bibzim (**VIII**), H_2tmbiim (**IX**). To a dichloromethane solution of $[Cu(CH_3CN)_2(PPh_3)_2]BF_4$ (1 mmol), $H_2(N—N)_2$ (1 mmol) was added and then stirred at room temperature for 24 h. Complexes (**VII–IX**) were obtained from the filtered solutions after partial evaporation of the solvent and addition of diethylether. (**VII**) Yield: 75%. ^1H NMR ($CDCl_3$): δ 6.5–7.5 (m, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 1.05(s) ppm. (**VIII**) Yield: 60%. ^1H NMR ($CDCl_3$): δ 7.2 (m, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 0.0 (s) ppm. (**IX**) Yield: 90%. ^1H NMR ($CDCl_3$): δ 7.1 (m, Ph), δ 2.2 (s, 6H, *exo* CH_3), δ 1.75 (s, 6H, *endo* CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −1.5 (s) ppm.

$[Cu\{H(N—N)\}_2(PPh_3)_2]BF_4$; H(N—N) = Him (**X**), Hpz (**XI**) *and* $[Cu(3,5\text{-}Me_2Hpz)(CH_3CN)(PPh_3)_2]BF_4$ (**XII**). To a dichloromethane solution of $[Cu(CH_3CN)_2(PPh_3)_2]BF_4$ (1 mmol), H(N—N) (2 mmol) was added and then stirred at room temperature for 24 h. Working up as above, complexes (**X**) and (**XI**) were obtained as white microcrystalline solids. (**X**) Yield: 80%. ^1H NMR ($CDCl_3$): δ 7.2, 7.1 (m, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −2.5 (s) ppm. (**XI**) Yield: 70%. ^1H NMR ($CDCl_3$): δ 7.1 (m, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −0.65 (s) ppm. (**XII**) Yield: 75%. IR (Nujol mull): ν(N—H) 3360 (m, br) cm^{-1}, ν(C≡N) 2260 (w) cm^{-1}, ν(C—N) ring 1580 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.30, 7.15 (m, 30H, Ph), δ 2.05 (s, 6H, Me_2-pz), δ 1.95 (s, 3H, MeCN) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −0.65 (s) ppm.

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