

# Burning Rate Performance Study of Ammonium Perchlorate Catalyzed by Heteroleptic Copper(I) Complexes with Pyrazino[2,3-f][1,10]phenanthroline-Based Ligands

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This contribution describes the catalytic effect of heteroleptic Cu(I) complexes with pyrazino[2,3-f][1,10]phenanthroline-based ligands (C1-7) on the thermal decomposition of ammonium perchlorate (AP). The complexes C2 and C4-7 were synthesized and characterized by NMR, HRMS and, in the case of C7, by X-ray diffraction. The burning rate performance of C1-7 on thermal decomposition of AP was studied by differential scanning calorimetry technique. The effect of the counter ion

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type, the number of metal centers and ligand substitution was evaluated. These AP + complex mixtures exerted a shift to lower ignition temperatures and an increase in the released heats during thermal decomposition compared with pure AP. The compound **C4** showed the higher catalytic effect among the complexes series, and **C5** exerted the highest energy release, in contrast to the other evaluated complexes and to the reported compounds CuO,  $[Cu_2(en)_2(HBTI)_2]_2$  and Catocene.

# 1. Introduction

Currently, research on energetic materials is directed towards the synthesis of simple molecules with high density, high heat resistance and low sensitivity.<sup>[1]</sup> Ammonium perchlorate (AP) is a common oxidizer in composite solid propellants. The thermal decomposition of AP has a close relationship with the combustion process of the propellants.<sup>[2]</sup> Nowadays, in the field of the solid-propellant rocket motor, the lower combustion temperature and higher specific volume of combustion of AP could improve the specific impulse of the rocket motor and decrease its internal erosion.<sup>[2a]</sup> Therefore, the combustion effect of a burning rate (BR) catalysts on the composite propellants' combustion behavior is usually assessed by its impact on AP's thermal degradation.<sup>[3]</sup> Many effective combustion catalysts, such as ferrocene derivatives,<sup>[4]</sup> metal oxides,<sup>[5]</sup> nanoparticles<sup>[6]</sup> and transition-metal coordination complexes<sup>[1b,7]</sup> have been reported as BR catalysts.

CuO powder has been used as combustion catalyst, were its particles, with smaller sizes and better dispersion, exhibit a better catalytic effect compared with bulky grains or coarsely dispersed catalysts.<sup>[6f]</sup> On the other hand, when copper coordination complexes are used they produce CuO nanoparticles after the burnt up. These nanoparticles with high surface areas are much more effective in comparison with common metal oxide powder.<sup>[6f]</sup> Gao and co-workers gave a more visual description of the burning process.<sup>[1b]</sup> Under heating, the monometallic copper compound begins to decompose under the attack of the oxygen atom formed from the AP's decomposition. Then the organic ligands are oxidized to generate carbon dioxide, molecular nitrogen, and other gaseous products of the decomposition of the ligand, according to its structure. Meanwhile, the copper atoms and the oxygen atoms react quickly to form nanoscale CuO fine particles. These



particles possess a larger specific surface area than the standard CuO powder. These nanosized CuO particles, coming from thermal decomposition of copper complexes, are excellent BR catalyst and can accelerate AP's thermal decomposition, as mentioned above.<sup>[1b,6f,7]</sup>

Considerable attention has been paid in the study of complexes with ligands that contain high-energy N–N and C–N bonds, because the promising applications as burning catalyst of solid-propellants.<sup>[8]</sup> In contrast to conventional energetic materials, this class of substances does not gain its energy from the oxidation of a carbon backbone or a fuel but rather from their high heats of formation. For pyrotechnics, these high-energy density materials serve as potential propellants, coloring agents, and fuels – eventually in combination with less-toxic metal ions such as Cu(II) instead of Ba(II). In addition, nitrogenrich materials combine several advantages: (i) only or mostly gaseous products (smokeless combustion), (ii) high heats of formation, (iii) high propulsive power, (iv) high specific impulse, and (v) high flame temperatures.<sup>[8b]</sup>

Among the most studied polypyridine ligands are the phenanthrolines (phen) and their derivatives.<sup>[9]</sup> These have a rigid conjugated structure caused by its fused rings core, with at least two N atoms being juxtaposed. This spatial position of N atoms generates that *phen* can rapidly coordinate to metal ions, producing highly stable compounds. This chelate effect is a critical feature for obtaining stable complexes and, for that reasons, our research focus on the structure of pyrazino[2,3f][1,10] phenanthroline (ppl) ligands. This contains a phen scaffold fused to pyrazine moiety. These structures have more nitrogen content than phen, and in some cases, can offer twice as many pairs of nitrogen atoms for bimetallic coordination. Also, ppl ligands provides new substitution sites for further structure improvement, hydrogen bridge sites and  $\pi$ - $\pi$  intermolecular interactions.<sup>[10]</sup> Despite the wide variety of applications founded for phen- and ppl-based ligands, e.g., bioinorganic chemistry,<sup>[11]</sup> optoelectronics,<sup>[12]</sup> catalysis,<sup>[13]</sup> etc., there is no literature about its energetic property so far. On the other hand, several metal centers have been tested as efficient catalysts for the decomposition of solid propellants.<sup>[14]</sup> However, well-defined molecular Cu(I) complexes, composed of phenand ppl-based ligands, have never been studied for this purpose, regardless of its well know applications in several subjects.  $\ensuremath{^{[15]}}$ 

Previous studies of Cu(*N*,*N*) complexes for thermal decomposition of AP has been reported. In 2011 Yang *et al.* reported a bistetrazole dinitrate Cu(II) complex  $[Cu(Mtta)_2(NO_3)_2]$  as additive for the AP burning.<sup>[1b]</sup> The nitrogen content (%N) is round 66%. The high-temperature decomposition round to 318.0°C and the heat released is 3950 J×g<sup>-1</sup>. By other hand, Liu *et al.* synthesized a bimetallic complex employing diethylamine and 5,5'-(1*H*-imidazole-4,5-diyl)*bis*(1*H*-tetrazole) as ligands. The authors found that the high-temperature decomposition was 336.1°C, with an energy released round to 2526.0 J×g<sup>-1</sup> (see Figure 1).<sup>[7]</sup>

In order to provide more in-depth knowledge in the development of copper complexes as additives for burning of ammonium perchlorate-based propellants, we report the synthesis and characterization of heteroleptic Cu(I) complexes (C1-7), with different *ppl*-based ligands and a diphosphine ligand (bis[2-(diphenylphosphino)-phenyl]ether, POP). This strongly hindered phosphine ligand improves the mixed-ligands complexes' stability by reducing the flattening effect over the Cu(I) metal, preventing another molecule's bonding in the fifthcoordination site.<sup>[16]</sup> These heteroleptic Cu(I) complexes are easily synthesized and characterized by spectroscopic and spectrometric media, in contrast to Cu(II) complexes and copper oxide nanoparticles. In a more technical advantage, these compounds' ionic nature and their high molecular weights gather the ideal characteristics to contribute to zero migration and losses by sublimation during curing and processing the composite solid propellant. The catalytic performance toward the AP's thermal decomposition was explored by differential scanning calorimetry for all compounds here reported.

### 2. Results and Discussion

#### 2.1. Synthesis of heteroleptic Cu(I) complexes

Heteroleptic Cu(I) complexes (C1-7) of the type  $[Cu(N,N)(POP)]^+$ were synthesized according to the literature methods, through strict stoichiometric control of the reaction. C1 and C3 complexes have been previously reported.<sup>[17]</sup> In this work, six



Figure 1. (a) Previous works reported in Cu(II) complexes for AP burning. (b) Our work displayed in this article.



*N,N* ligands derived from *ppl* (L1-6), and commercially available POP phosphine were used. The *N,N* ligands corresponds to: L1: *ppl*;<sup>[18]</sup> L2: *dppz*;<sup>[19]</sup> L3: *deppl*;<sup>[20]</sup> L4: *n2ppl*;<sup>[21]</sup> L5: *sppl*;<sup>[22]</sup> L6: *ppz*.<sup>[23]</sup> The complexes C1-7 were obtained in a two-step reaction: (1) the addition of one molar equivalent of the *N,N* ligand to a solution of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]X (X: BF<sub>4</sub> or PF<sub>6</sub>) in acetonitrile / CH<sub>2</sub>Cl<sub>2</sub> (1:1), followed by (2) the addition of one molar equivalent of the POP ligand (see Scheme 1). The five new heteroleptic Cu(I) complexes (C2 and C4-7) were obtained with yields between 80–90%. All synthesized complexes showed high air and thermal stability in the solid state. Furthermore, these were stable in CH<sub>2</sub>Cl<sub>2</sub> solution for several days. Once Cu(I) complexes were successfully synthesized and isolated, characterization through NMR, HRMS, and X-ray diffraction (XRD) for **C7** was achieved.

The spectroscopic and spectrometric characterization of C2 and C4-7 is consistent with the molecular structures shown in Scheme 1. In the case of C2 and C4-6, the NMR and HRMS data are consistent with mononuclear heteroleptic Cu(I) complexes. The <sup>1</sup>H NMR of these complexes exhibited a 1:1 integral ratio between the N,N, and the POP ligands protons. The most significant signals to appreciate this are the protons in para positions to the N-phenanthroline and to the P-oxyphenyl mojeties. These signals are in approximately 9.55 ppm and 6.77 ppm, respectively. On the other hand, in the <sup>1</sup>H NMR and <sup>13</sup>C NMR of C5, a pseudo-diasterotopic behavior in the phenanthroline part of L4 is observed, exerted by the asymmetric pyrazole segment in the ligand. The <sup>31</sup>P{<sup>1</sup>H} NMR for complexes C2 and C4-6 showed typical chemical shift related with a bidentate POP–Cu bond formation, in -10.4 ppm for the four complexes.<sup>[24]</sup> Regarding the molecular structure of C7, it was confirmed the binuclear nature of the heteroleptic complex by NMR, HRMS, and XRD. In this case, the <sup>1</sup>H NMR exhibited a 2:1 integral ratio between the POP and the N,N ligand, as was observed in the same signals as for C2 and C4-6, which appears in 9.69 ppm and 6.66 ppm. For a detailed 1D and 2D NMR characterization, as well as HRMS, see the ESI.

For C7, crystals suitable for XRD analysis were obtained by controlled evaporation of a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex into toluene. Its molecular structure is shown in Figure 2 and selected distances, angles, and torsions are summarized in Table S1, Table S2, and Table S3, respectively. Both metal centers exhibited equal bond distances and angles between each other, which agrees with the symmetry and planarity of the N,N ligand. This equivalent environment surrounding the copper centers can be seen in all angles and torsions involved, e.g., the angles P1-Cu1-P2 and P1<sup>i</sup>-Cu1<sup>i</sup>-P2<sup>i</sup> have the same value (115.95(8)°), or the torsions N1<sup>i</sup>-C5<sup>i</sup>-C6<sup>i</sup>-N2<sup>i</sup> and N2-C6-C5-N1 have the value of  $-2.3(9)^{\circ}$ . Besides, C7 exhibit distorted tetrahedral geometry in both metal centers, with angles ranging from 80.7(2)° (N1-Cu1-N2) to 114.9(2)° (P2-Cu1-N2). In addition, L4 shown elevated planarity expected for this type of N,N ligand, despite the coordination of two metal centers, with torsions of 176.7(6)° (C4-C5-C6-N2) and 177.4(6)° (N1-C5-C4-C4<sup>i</sup>). For a more detailed XRD characterization, see the ESI.

#### 2.2. Redox properties

The redox properties of all compounds were studied by cyclic voltammetry in dichloromethane solution. This, to evaluate their oxidation and reduction abilities, according to the nature of the *N*,*N* ligand, number of metallic centers and type of counter anion. The assignment of the redox processes was carried out by comparison with electrochemical data reported for similar Cu(I) complexes.<sup>[16c,25]</sup> The measured redox potentials of copper compounds are collected in Table 1, and voltammetric profiles are shown in Figure 3. It should be pointed out that cyclic voltammetry measurements exhibited quasi-reversible processes and low defined redox waves (especially in oxidations). Possibly due to adsorption phenomena and/or exchange reactions, obtaining a dynamic equilibrium between the heteroleptic and the homoleptic complexes.<sup>[16c]</sup> In fact,



Scheme 1. Synthetic route of heteroleptic Cu(I) complexes studied (C1-7).





Figure 2. ORTEP plot of compound C7, with partial numeration scheme. Hydrogen atoms were removed for clarity. Thermal ellipsoids were drawn with 30% of probability (Symmetry code i: +*x*, 3/2-*y*, +*z*).

Table 1. Values of the redox processes for complexes C1-7.					
Compound	$E_{ox}(Cu^{2+/+})$ [V]	$E_{red}(L/L^{-})$ [V]			
C1	1.32	-1.41			
C2	1.32	-1.17			
C3	1.32	-1.19			
C4	1.32	-1.17			
C5	1.32	-1.12			
C6	1.31	-0.91			
C7	1.47	-0.81			
[a] L is referred to <i>N</i> , <i>N</i> ligand. [b] Dichloromethane/TBAPF <sub>6</sub> 0.1 M, vs. Ag/AgCl.					

after continuous scans, some peaks associated with adsorbed species increased their currents, changing the original voltammetric profiles. Therefore, the redox potentials for all complexes were determined from the first scan.

The oxidation potentials of the Cu(I) mono- and bimetallic compounds are less positive compared to the oxidation potential of metal in CuO, since the redox process from Cu(II) to Cu(III) involve very high energy (~2.5 V).<sup>[26]</sup> This evidence is important to ensure the *in situ* formation of CuO nanoparticles, from the Cu(I) complexes, during the burning process. The voltammetric profiles exhibit quasi-reversible behavior at positive potentials, attributed to Cu(I)/Cu(II) oxidation in the copper complexes, with contributions of POP ligand.<sup>[16c,25c]</sup> For the oxidation processes of **C1-6**, the oxidation potentials are around 1.32 V, due the similar structure between them. The only differentiation factor corresponds to the *N*,*N* ligand, and no strong contribution on the value is observed. Only **C7** is more positive, were the ligand (*ppz*) is a bridge that links two Cu(I) metal centers, resulting in the oxidation process at 1.47 V.

The reduction processes, attributable to *N*,*N* ligands, can be observed towards the cathodic sweep. These follow a trend from lower to higher negative potential as C7 < C6 < C5 < C4-C2 < C3 < C1, where the less negative value is assigned to C7



Figure 3. Cyclic voltammetry profiles recorded in dry dichloromethane solution at 0.1  $\text{Vs}^{-1}$  for C1-7.

(-0.81 V), the closest to 0 potential of the series. Similar behavior has been reported on bimetallic Re(I) complexes with *ppz*-based ligands.<sup>[12d]</sup> Regarding the counterion effect on **C1-2** complexes, a less negative reduction potential is observed



using  $PF_6^-$  (**C2**: -1.17 V) instead of  $BF_4^-$  (**C1**: -1.41 V). This difference can be explained by the diffusion of each counterion species towards the electrodes. As  $PF_6^-$  is bigger than  $BF_4^-$ , this should diffuse slowly and therefore, reduces at a more negative potential.

# 2.3. Catalytic Effects on thermal decomposition of ammonium perchlorate and possible burning rate catalytic mechanism

The copper compounds were explored as promoters to the thermal decomposition of ammonium perchlorate (AP), the key component of solid composite propellants. The catalytic effects of the copper complexes on the thermal decomposition of AP were investigated by DSC measurements with a heating rate of  $5^{\circ}$ C/min in N<sub>2</sub> atmosphere in the range of 140–450 °C. Figure 4 shows the DSC curves of both AP and the mixture of AP with the title compound. In this work, 5 mass % of catalyst was used. It was observed that the phase transition endothermic process of AP, peaked at 243 °C, has almost no shift and exhibit a similar shape with 5 wt% for all the catalysts here reported. This indicates that the catalysts exert little effect on the AP's crystallographic transition temperature, as usually observed. Both the low-temperature decomposition (LTD) stage (peak



Figure 4. DSC curves of AP and mixture of AP with 5 mass % of C1-7.

temperature at 293.7 °C) and the high-temperature decomposition (HTD) stage (peak temperature at 429.3 °C) of the AP are significantly affected by the addition of all compounds, except for compound **C2**. The latter exerted a small increase in the thermal decomposition temperature (413.6 °C), suggesting that the counterion  $[PF_6]^-$  deactivates the catalytic effect, producing a retarding effect, compared with its analogue **C1**. After adding **C1**, **C3-7** the highest thermal decomposition temperatures are 367.0, 370.4, 359.4, 370.8, 386.9, and 368.0 °C, respectively, decreased by 47.4, 44.0, 55.0, 43.4, 17.5, and 46.4 °C compared with pure AP. These results indicate that copper complexes have a positive catalytic effect on AP's thermal decomposition temperature.

Furthermore, the exothermic peaks become sharper, indicating the decomposition process of AP becomes more quickly. It is noted that the DSC curves for compounds **C3-5** and **C7** only one exothermic peak became sharper, suggesting that the decomposition process of AP occurred more quickly. Regarding complexes **C1** and **C6** displayed a similar shape with two peaks in each DSC curve, implying that an identical decomposition mechanism of the mixture systems should be expected, except that of pure AP and **C2**.

In their DSC curves, it was noticed that the exothermic heats were in the range of 2053–2820 J/g. In general, the contribution of the Cu(I) complexes to the catalytic burning of AP corresponds to a growth of the heat released in order of more than 2 times. The mixtures AP + C1 and AP + C2 contribute with 2.74 and 2.18 times over than AP alone, respectively (entries 2 and 3, Table 2). The difference on the results from AP+C1 and AP + C2 is attributed to the counterion in each complex, where PF<sub>6</sub><sup>-</sup> could affect to the process by inhibiting or retarding the burning process. Between AP + C3, AP + C4 and AP + C6(entries 4, 5 and 7, respectively), having the same nitrogen content, the heat released with AP + C6 is 4.9% higher than that of AP + C3, and AP + C6 is 4.2% higher than AP + C4. When AP + C1 and AP + C7 are compared in their role as catalysts of the burning process, a difference of 5.1% of heat released is determined in favor of AP + C1, confirming that a monometallic copper complex is more efficient than a binuclear complex for

Table 2. Comparison of the catalytic effects of copper complexes with classical catalysts on the thermal decomposition of AP. <sup>[a]</sup>						
Entry	Compound	Wt [%]	HTD of AP [°C]	Heat released [J g <sup>-1</sup> ]	[%] N	Heat released ratio <sup>[b]</sup>
1	NH <sub>4</sub> ClO <sub>4</sub> (AP)		414.4	943.4	3.4	1
2	AP+C1	5	367.0	2581.5	6.7	2.74
3	AP + C2	5	413.6	2053.0	6.7	2.18
4	AP + <b>C3</b>	5	370.4	2441.8	6.3	2.59
5	AP + <b>C4</b>	5	359.4	2459.3	6.3	2.61
6	AP + <b>C5</b>	5	370.8	2820.9	8.7	2.99
7	AP + <b>C6</b>	5	386.9	2568.1	6.3	2.72
8	AP + <b>C7</b>	5	368.0	2448.8	4.2	2.60
9	AP+CuO <sup>[6f]</sup>	3	345.6	1321.4	-	1.40
10	$AP + [Cu(Mtta)_2(NO_3)_2]^{[1b]}$	33	318.0	3950.0	66.0	4.19
11	$AP + [Cu_2(en)_2(HBTI)_2]_2^{[7]}$	10	336.1	2526.0	7.8	2.68
12	AP+Catocene <sup>[4d]</sup>	5	346.0	2476.0	-	2.63
13	$AP + Cu_2O^{[27]}$	6	384.0	NR	-	-

[a] NR: Not reported. [b] Ratio between the heat released by the mixture and the heat released by the neat AP.



the burning process. The AP+C5 (entry 6, Table 2) showed the higher heat released in comparison with the other copper complexes, exhibiting 8.4% more heat release in comparison with AP+C1. This is due to the higher nitrogen content in C5, where the 1-methyl-1*H*-pyrazole scaffold plays a key role. This is consistent with the literature findings. Yang *et al.* described the employment of 4,5-bis(1*H*-tetrazol-5-yl)-1*H*-imidazole, a nitrogen rich compound, as ligand for metal-organic catalysts for thermal decomposition of AP.<sup>[7]</sup> The authors sustain the selection of this compound as high energy species, because its capacity to increase the energy of composite propellants as consequence of the nitrogen content of the ligand.<sup>[7-8]</sup>

The analysis of AP + **C5** against the reported catalyst, AP +  $[Cu(Mtta)_2(NO_3)_2]$ , is 28.6% in favor of AP +  $[Cu(Mtta)_2(NO_3)_2]$ . However, the nitrogen content in the latter is 7.6 times higher than AP + **C5**. A second comparison can be established between AP +  $[Cu_2(en)_2(HTBTI)_2]_2$  against AP + **C5**, where heat released is in the order of 10.5% in favor of AP + **C5**. Finally, by a quick inspection, AP + **C5** has higher heat released against AP + CuO and AP + Catocene. Concerning AP + Cu<sub>2</sub>O (entry 13, Table 2), Ramdani *et al.* reported a study of Cu<sub>2</sub>O microparticles with and without additives. The proportions of the additives and AP in the mixture were respectively chosen as 6% and 94%, obtaining a catalytic effect on AP's thermal decomposition, shifting the HTD at 384°C, comparable with some of our catalysts.<sup>[27]</sup>

Finally, the mixtures AP + Ligands are an inefficient catalyst for the burning of AP, compared to their respective mixtures of AP + Complexes, mainly because the ligands do not produce an active enough catalytic species to ensure a well-performed burning process. Summarizing, **C5** is close to the described catalytic efficiencies. Even more, in some cases, this complex displayed higher energy at lower concentrations of the catalyst, and a lower percentage of nitrogen per molecule, improving the thermal decomposition of AP significantly.

## 3. Conclusion

Five new heteroleptic Cu(I) complexes (C2 and C4-7) were synthesized and isolated in good yields (80-90%). These complexes were highly air- and thermally stable in the solid state and in  $CH_2CI_2$  solution for several days. Besides, C2 and C4-7 were characterized through NMR, HRMS, and X-ray diffraction (for C7). For C2 and C4-6, this is consistent with mononuclear heteroleptic Cu(I) complexes. For C7, the binuclear nature of the heteroleptic complex was confirmed by NMR, HRMS, and XRD.

All compounds showed a quasi-reversible redox process to the positive potential associated with Cu(I)/Cu(II) oxidation. The oxidation potentials of all evaluated complexes were less positive than the oxidation potential of metal in CuO, showing higher oxidation ability for AP's catalytic process. For **C7**, the oxidation potential was more positive due to the bridge nature of the ligand *ppz*.

The catalytic evaluation results, by mean DSC technique, confirmed that the copper complexes derived from pyrazino

[2,3-f][4,7]phenanthroline ligands showed high catalytic activity for the thermal decomposition of ammonium perchlorate. The compound C4 exhibited a higher catalytic effect than the other complexes, observed as the lowest thermal decomposition temperature in the study. In terms of the energy released, the best mixture was AP+C5 in contrast to the other mixtures of AP+Complex (almost 3 times higher than neat AP), attributable to the nitrogen-content of C5, the highest in the Cx series. Besides, C5 showed highest energy release than the reported compounds CuO, [Cu<sub>2</sub>(en)<sub>2</sub>(HBTI)<sub>2</sub>]<sub>2</sub> and Catocene. On the other hand, the efficiency of compound C2 was diminished presumably for the retardant effect due to counterion PF<sub>6</sub><sup>-</sup>. Regarding the effect of the bimetallic complex C7, we confirmed that a monometallic nature of the complex its more efficient than a bimetallic one. Though the effect of BR catalysts cannot only be focused on the influence on the thermal decomposition of AP, the results confirm that these copper derivatives could have potential applications as burning rate catalysts in solid composite propellants, obtaining long periods of storage time, increase lifespan without presenting changes on the initial burning parameters, due to their ionic character.

# **Experimental Section**

### **General Information**

All reagents were purchased from commercial sources, unless otherwise specified and used as received. Ligands and complexes C1 and C3 were prepared as described in literature.<sup>[17-23]</sup> NMR spectra were recorded on NMR Bruker AV 400. Chemical shifts are given in parts per million relative to TMS [<sup>1</sup>H and <sup>13</sup>C,  $\delta$ (SiMe<sub>4</sub>)=0] or an external standard [ $\delta$ (CFCI<sub>3</sub>)=0 for <sup>19</sup>F NMR]. Most NMR assignments were supported by additional 2D experiments. HRMS-ESI-MS experiments were carried out using a Thermo Scientific Exactive Plus Orbitrap Spectrometer. Cyclic voltammograms were recorded using a PalmSens 3 Potentiostat, in a three-electrode cell configuration with a platinum disc working electrode of 0.02 cm<sup>2</sup> geometric area, a saturated Ag/AgCl reference electrode and a platinum wire counter electrode. All electrochemical measurements were carried out in anhydrous dichloromethane solutions of Cu(I) complexes (1 mM) with tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) (0.1 M) as the supporting electrolyte at a scan rate of  $0.1 \text{ V s}^{-1}$ . Before each measure all solutions were degassed with N<sub>2</sub>. For X-ray crystal structure analysis, data sets were collected with a STOE IPDS II two-circle-diffractometer using Mo K $\alpha$  radiation ( $\lambda =$ 0.71073 Å). The intensities were corrected for absorption by an empirical correction with X-Area.<sup>[28]</sup> The structures were solved by direct methods (SHELXS)<sup>[29]</sup> and refined by full-matrix least-squares calculations on F2 (SHELXL-97). Anisotropic displacement parameters were refined for all non-hydrogen atoms.

#### Thermal analysis

DSC and TG analysis were performed on an 822e Mettler Toledo and TGA/SDTA 851e Mettler Toledo instruments respectively at a heating rate of 5 °C/min under nitrogen in the range of 80–500 °C. To investigate the catalytic performance of the phenanthroline derivative copper(I) complexes for the thermal decomposition of AP, specific amounts of the complexes and AP were mixed and ground in a certain weight ratio for DSC analysis.



#### Synthesis of the compounds

#### General synthetic procedure of complexes

For complexes C2 and C4-6, a solution of the corresponding ppl derivative ligand (1 eq) in CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to a solution of  $[Cu(CH_3CN)_4]X$  (X =  $^{-}BF_4$  or  $^{-}PF_6$ ) (1 eq) in a mixture of acetonitrile /  $CH_2Cl_2$  (1:1). The reaction mixture was stirred for 30 minutes at room temperature. Then, a CH<sub>2</sub>Cl<sub>2</sub> solution of (Oxydi-2,1-phenylene) bis(diphenylphosphine) (POP) (1 eq) was added and stirred for 90 minutes at room temperature. For bimetallic complex C7, a solution of  $[Cu(CH_2CN)_4]PF_6$  (2 eq), in a mixture of acetonitrile /  $CH_2Cl_2$  (1:1), was added dropwise to a solution of pyrazino[2,3-f][4,7] phenanthroline (ppz) ligand (1 eq) in CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was stirred for 30 minutes at room temperature. Then, a POP (2 eq) solution in CH<sub>2</sub>Cl<sub>2</sub> was added and stirred for 90 minutes at room temperature. For all complexes, the volatiles were removed in vacuum and the crude product was purified by crystallization using  $CH_2CI_2$  / Hexane mixture at -20 °C. For additional experimental details, 2D NMR and assignment data see the ESI.

**Complex C2**. Isolated as a yellow powder in 85% yield (151.6 mg, 0.15 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = 9.47 (d, J = 8.3 Hz, 2H), 9.04 (s, 2H), 8.83 (d, J = 4.8 Hz, 2H), 7.81 (dd, J = 8.3, 4.8 Hz, 2H), 7.40–6.85 (m, 26H), 6.72 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl3, 298 K):  $\delta$ /ppm = 158.4 (d, J<sub>C-P</sub> = 6.1 Hz), 151.6, 145.6, 144.3 (t, J<sub>C-P</sub> = 2.1 Hz), 139.7, 134.6, 134.4, 133.2, 133.1, 133.0, 132.2, 130.7, 130.5, 130.3, 129.2, 129.0 (t, J<sub>C-P</sub> = 4.8 Hz), 128.4, 126.4, 125.4, 124.0 (d, J<sub>C-P</sub> = 14.9 HZ), 120.6. <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = -73.5 (J<sub>F-P</sub>: 712 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = -10.4 (s), -144.3(J<sub>P-F</sub>: 712 Hz). HRMS (ESI): m/z [M]<sup>+</sup> for C<sub>50</sub>H<sub>36</sub>CuN<sub>4</sub>OP<sub>2</sub>: calc: 833.1660; found: 833.1606.

**Complex C4.** Isolated as a yellow powder in 89% yield (75.9 mg, 0.15 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm =9.58 (d, J = 8.1 Hz, 2H), 9.02 (d, J = 4.7 Hz, 2H), 7.98 (dd, J = 8.1, 4.7 Hz, 2H), 7.49–6.98 (m, 26H), 6.78 (m, 2H), 4.61 (c, J = 7.1 Hz, 4H), 1.52 (t, J = 7.1 Hz, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = 164.3, 158.5, 152.8, 145.1, 145.0, 139.4, 135.1, 134.5, 133.1 (t, J<sub>C-P</sub> = 8.2 Hz), 132.3, 130.4, 130.3, 129.2, 129.0 (t, J<sub>C-P</sub> = 4.8 Hz), 127.2, 126.9, 125.4, 123.8 (t, J<sub>C-P</sub> = 15.2 Hz), 120.6, 63.4, 14.2. <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = -154.0 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ / ppm = -10.4 (s). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ / ppm =-0.63 (s). HRMS (ESI): m/z [M]<sup>+</sup> for C<sub>56</sub>H<sub>44</sub>CuN<sub>4</sub>O<sub>5</sub>P<sub>2</sub>: calc: 977.2083; found: 977.2020.

**Complex C5.** Isolated as a yellow powder in 86% yield (105.9 mg, 0.11 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = 9.52 (d, J = 8.2 Hz, 1H), 9.50 (d, J=8.2 Hz, 1H), 8.85 (s, 1H), 8.81 (d, J=4.8 Hz, 1H), 8.78 (d, J=4.8 Hz, 1H), 7.81 (dd, J=8.1, 4.8 Hz, 1H), 7.70 (dd, J=8.1, 4.9 Hz, 1H), 7.34–6.99 (m, 26H), 6.82 (m, 2H), 4.56 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm=158.6 (t, J<sub>C-P</sub>=6.0 Hz), 151.1, 150.9, 150.4, 145.3, 144.3, 140.1, 138.6, 134.9, 134.5, 133.2, 133.1 (t, J<sub>C-P</sub>=8.1 Hz), 132.2, 130.6 (d, J<sub>C-P</sub>=9.3 Hz), 130.3, 129.6 (d, J<sub>C-P</sub>=10.5 Hz), 129.0, 126.6, 126.5, 126.0, 125.4, 124.0 (t, J<sub>C-P</sub>=15.0 Hz), 120.5, 43.0. <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = -153.6 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = -0.63 (s). HRMS (ESI): m/z [M]<sup>+</sup> for C<sub>52</sub>H<sub>28</sub>CuN<sub>6</sub>OP<sub>2</sub>: calc: 887.1878; found: 887.1826.

**Complex C6.** Isolated as a brown powder in 80% yield (101.9 mg, 0.10 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = 9.47 (d, *J* = 8.3 Hz, 2H), 9.04 (s, 2H), 8.82 (m, 2H), 7.80 (dd, *J* = 8.2, 4.8 Hz, 2H), 7.34–6.69 (m, 28H,). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = 158.5, 157.8, 151.5, 146.0, 144.3, 139.7, 134.5, 133.7, 133.0, 132.3, 130.9, 130.7, 130.6, 130.4, 130.3, 129.3, 128.9, 128.4, 126.4, 125.3, 125.2, 124.0, 123.8, 123.7, 122.9, 120.5, 120.0. <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = -153.8 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = -153.8 (s). <sup>31</sup>P{<sup>1</sup>H}

298 K):  $\delta$ /ppm = -10.4 (s). <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = -0.69 (s). HRMS (ESI): m/z [M]<sup>+</sup> for C<sub>52</sub>H<sub>36</sub>CuN<sub>4</sub>OP<sub>2</sub>S: calc: 889.1381; found: 889.1444.

**Complex C7**. Isolated as a red crystalline material in 90% yield (224.2 mg, 0.14 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = 9.76 (d, J = 8.4 Hz, 2H), 9.66 (s, 2H), 8.51 (d, J = 4.7 Hz, 2H), 7.96 (dd, J = 8.4, 4.8 Hz, 2H), 7.39–7.28 (m, 24H), 7.08-6.97 (m, 12H), 6.88 (t, J = 7.5 Hz, 8H), 6.73 (m, 4H), 6.64 (m, 8H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = 158.5 (t, J<sub>C-P</sub> = 5.8 Hz), 150.8, 148.4, 141.1, 139.9, 135.9, 134.6, 133.9 (t, J<sub>C-P</sub> = 8.4 Hz), 132.4, 132.1 (t, J<sub>C-P</sub> = 7.8 Hz), 131.0, 129.9 (dt, J<sub>C-P</sub> = 155.6, 17.6 Hz), 129.8, 129.7 (t, J<sub>C-P</sub> = 5.0 Hz), 128.7 (t, J<sub>C-P</sub> = 4.6 Hz), 127.8, 127.2, 125.4, 123.5 (t, J<sub>C-P</sub> = 15.6 Hz), 120.6. <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = -152.7 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ /ppm = -0.78 (s). HRMS (ESI): m/z [M]<sup>+2</sup> for C<sub>86</sub>H<sub>64</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>2</sub>P<sub>4</sub>: calc: 1434.2572; found: 1434.2527, m/z [MBF<sub>4</sub>]<sup>+</sup> for C<sub>86</sub>H<sub>64</sub>BCu<sub>2</sub>F<sub>4</sub>N<sub>4</sub>O<sub>2</sub>P<sub>4</sub>: calc: 1523.2588; found: 1523.2534.

Deposition Number 2042067 (for **C7**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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# **Conflict of Interest**

The authors declare no conflict of interest.

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