Reactivity of Cu(I) nacnac complexes towards \([\text{Cp}^*\text{Ru}(\eta^5-\text{E}5)]\) \(\text{(E = P, As)}\)

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ABSTRACT

The reactivity of the nacnac Cu(I) compound \([L^2\text{Cu}()\text{MeCN}]\) \((2)\) \((L^2 = \{\{\text{C}_6\text{H}_5\text{Me}_2-2,6\}\text{C}(\text{Me})_2\text{CH}\})\) towards complexes containing aromatic cyclo-\(\text{E}_5\) ligands \((\text{E = P, As})\) was investigated. The copper complex was reacted with \([\text{Cp}^*\text{Ru}(\eta^5-\text{E}5)]\) \((\text{E = P (1a-Ru), As (1b-Ru)}\), yielding the heterometallic complexes \([\{\text{Cp}^*\text{Ru}(\mu\eta^5-\text{E}5)\}L^2\text{Cu}]\) \((\text{E = P (3a), As (3b)}\). These neutral and molecular complexes represent rare examples of the coordination of group 11 metal complexes to cyclo-\(\text{E}_5\) units and are also rare examples of the coordination compounds of 1a-\(\text{Ru}\) and 1b-\(\text{Ru}\). They were fully characterized by crystallographic and spectroscopic methods and compared to related compounds.

GRAPHICAL ABSTRACT

Introduction

The conversion of white phosphorus and yellow arsenic is an active research topic. Decades of extensive studies have led to the formation of a plethora of polypnictogen \((\text{E}_n)\) ligand complexes \((\text{E = P, As})\).[1] Of special interest are complexes with cyclo-\(\text{E}_5\) ligands which possess a special aromatic character. Such ligands were realized for \(n = 3-6\) as end-decks or middle-decks.[2] The cyclo-\(\text{E}_5\) ligand is present in the ferrocene analog pentaphosphaferrrocene or pentaarsaferrocene \([\text{Cp}^*\text{Fe}(\eta^5-\text{E}5)]\) \((\text{E = P (1a-Fe), As (1b-Fe)}\,[3] \text{Scheme 1})\). These compounds were the subject of numerous research topics: The reactivity of 1a-\(\text{Fe}\) and 1b-\(\text{Fe}\) towards electrophiles, nucleophiles and their redox behavior,[3] and further their use as a building block for coordination polymers and spherical aggregates[4] was extensively studied. Similar complexes containing a cyclo-\(\text{E}_5\) ligand are known for its heavier analogue ruthenium.[2k,5] The chemistry of \([\text{Cp}^*\text{Ru}(\eta^5-\text{E}5)]\) \((\text{E = P (1a-Ru), As (1b-Ru)}\), Scheme 1) is less explored. Recently, our group reported the iodination of \([\text{Cp}^*\text{M}(\eta^5-\text{E}5)]\) \((\text{M = Fe, Ru; E = P, As})\),[6] which leads in the case of 1a-\(\text{Fe}\) and 1a-\(\text{Ru}\) to the formation of a tripodaly cyclo-\(\text{P}_7(\text{PL}_2)_3\) ligand coordinating to a \({\text{Cp}^*\text{M}}\) fragment which represents a MP_{6} core resembling the nortricyclane structure of \(P_{7}^3\). (A, Scheme 1). Interestingly, a different outcome is realized by the reactions of the arsenic compounds 1b-\(\text{Fe}\) and 1b-\(\text{Ru}\). While the reaction of 1b-\(\text{Fe}\) with iodine leads to the formation of a di-cationic Fe-As triple decker complex with a cyclo-\(\text{As}_5\) unit, the reaction of 1b-\(\text{Ru}\) leads to three different products: a mono-cationic Ru-As triple decker complex, a Ru complex with a planar \(\mu\eta^4-\text{As}_4\text{I}_4\) middle deck with a four-point star structural motif (B, Scheme 1), and \([\{\text{Cp}^*\text{Ru}_2\text{As}_8\}]\). These results clearly show a different reactivity between the phosphorus and the arsenic compounds and also the impact of the metal center.

Furthermore, there are efforts to investigate the reactivity of \(\beta\)-diminato M(I) complexes towards cyclo-\(\text{E}_n\) complexes. Roeshly et al. reported the reaction of \([\text{L}^1\text{Al}]\) \((\text{L}^1 = \{\{(\text{C}_6\text{H}_5\text{H}_{2})\text{Pr}_{2}-2,6\}\text{C}(\text{Me})_2\text{CH}\})\) with \([\text{Cp}^*\text{Fe}(\eta^5-\text{P}_5)]\) leading to \([\{\text{Cp}^*\text{Fe}(\mu\eta^5-\text{P}_5)\}L^1\text{Al}]\) (C, Scheme 1) containing an envelope-shaped \(\text{P}_5\) ring.[7] Recently, we reported the reactivity of Cu(I) nacnac complexes towards polypnictogen compounds, i.e. \([\text{Cp}^*\text{Fe}(\eta^5-\text{E}5)]\) \((\text{E = P, As})\), which leads to...
the formation of the heterobimetallic compounds 
\[(\text{Cp}/\text{C}_3\text{Fe})_2(\eta^5:2:1-E_5)(\text{L}_2\text{Cu})(\text{E} = \text{P}, \text{As}) \text{ and } \{(\text{Cp}/\text{C}_3\text{Fe})_2(\eta^5:2:1-E_5)(\text{L}_2\text{Cu})_2\}(\text{E} = \text{P}, \text{As})\). Such products are examples of the coordination of a group 11 metal by aromatic cyclo-En ligands. In this study, we varied the ring size of the \[\{\text{CpRM(cyclo-En)}\}\] complex and the metal (M = Fe, n = 5; M = Co, n = 4; M = Ni, n = 3). It turned out that the \[\eta^2\] coordinating E-E bonds are elongated but still intact. Now the question arose as to what would happen when changing the metal to its higher homolog ruthenium by maintaining the cyclo-En unit. In the following, we report on the reactivity of \[\{\text{L}_2\text{Cu(MeCN)}\}\] (dmp = 2,6-dimethylphenyl) towards \[\{\text{Cp}/\text{C}_3\text{Ru}(\eta^5-E_5)\}(\text{E} = \text{P}(\text{1a-Ru}), \text{As}(\text{1b-Ru}))\], resulting in the formation of the new heterometallic compounds \[\{(\text{Cp}/\text{C}_3\text{Ru})(\eta^5:2-E_5)(\text{L}_2\text{Cu})\}(\text{E} = \text{P}(\text{3a}), \text{As}(\text{3b}))\).

**Results and discussion**

The reaction of \[\{\text{Cp}/\text{C}_3\text{Ru}(\eta^5-E_5)\}\] (dmp = 2,6-diisopropylphenyl) (1a-Ru, As (1b-Ru)) with \[\{\text{L}_2\text{Cu(MeCN)}\}\] (2) leads to the formation of \[\{(\text{Cp}/\text{C}_3\text{Ru})(\eta^5:2-E_5)(\text{L}_2\text{Cu})\}(\text{E} = \text{P}(\text{3a}), \text{As}(\text{3b}))\).

The \[31\text{P}^\text{1H}\] NMR spectrum of 3a in C\text{D}_8 at room temperature indicates a sharp singlet at \[\delta = 58.3 \text{ ppm} (\omega_{1/2} = 13 \text{ Hz})\]. One would expect at least three different phosphorus signals. Even though the low temperature of 193 K is not enough to freeze the ongoing dynamic behavior of 3a, the \[31\text{P}^\text{1H}\] NMR spectrum still indicates a singlet which is broadened (\[\omega_{1/2} = 166 \text{ Hz}\]). Therefore, this highly dynamic behavior in solution of 3a reflects either the tumbling of the \{\text{L}_2\text{Cu}\} fragment around the cyclo-P\text{S} ring or a dissociation-reassociation process of the \{\text{L}_2\text{Cu}\} fragment. Based on the results for \[\{(\text{Cp}/\text{C}_3\text{Fe})(\mu,\eta^5:2:1-P_3)(\text{L}_2\text{Cu})\}\] which show that its dynamic motion consists of an \[\eta^1 \rightarrow \eta^2 \rightarrow \eta^1\] walk of the two \{\text{L}_2\text{Cu}\} fragments around the cyclo-P\text{S} ring, we propose a similar behavior for the ruthenium complex. The \[^1\text{H}\] NMR spectra of 3a and 3b (C\text{D}_8, r.t.) reveal a full set of signals for the nacnac ligand and a sharp signal for the Cp\text* ligand. In the LIFDI-MS spectra of 3a and 3b, the corresponding molecular ion peaks are detected. The molecular structure of 3a and 3b reveals a dinuclear complex in which the \{\text{L}_2\text{Cu}\} fragment is bonded in an \[\eta^2\] fashion side-on to the \{\text{Cp}/\text{C}_3\text{Ru}(\eta^5-E_5)\}\) unit (Figure 1). The \{\text{L}_2\text{Cu}\} fragment is almost perpendicular to the E\text{S} plane (dihedral angle: 3a: 82.46(3); 3b: 96.15(3)°). The Cu-E distances are 2.2916(8)/2.2844(8) Å for 3a and 2.3996(10)/2.3921(11) Å for 3b. Four of the E-E distances are in the range between a single[10]
and a double bond (Table 1). The \( \eta^2 \)-coordinated E-E distances are elongated (2.2327(10) Å (3a) and 2.4292(10) Å (3b)). All these values are in accordance with the reported complexes \([\text{Cp}^* \text{Fe}) (\mu_\eta^1\eta^2 \text{E}_5) (\text{L}^2 \text{Cu})]\). These compounds are rare examples of the reactivity of the ruthenium analogues of pentaphospha- and pentaarsaferrocene. Their structural characterization shows that the coordinated E-E bond of the cyclo-E₅ ligands are still intact. \(^{31}\)P \(^{1}\)H NMR investigations for 3a reveal a dynamic behavior in solution. Therefore, the reactivity of Cu(I) nacnac compounds is not affected by the choice of the metal center (Fe or Ru) and also the nature of the cyclo-E₅ ring shows the same reactivity.

### Conclusion

In summary, it was shown that the reactivity of copper nacnac compounds towards complexes containing a cyclo-E₅ lig-and results in the synthesis of the heterometallic complexes \([\text{Cp}^* \text{Ru}) (\mu_\eta^1\eta^2 \text{E}_5) (\text{L}^2 \text{Cu})]\). These compounds are rare examples of the reactivity of the ruthenium analogues of pentaphospha- and pentaarsaferrocene. Their structural characterization shows that the coordinated E-E bond of the cyclo-E₅ ligands are still intact. \(^{31}\)P \(^{1}\)H NMR investigations for 3a reveal a dynamic behavior in solution. Therefore, the reactivity of Cu(I) nacnac compounds is not affected by the choice of the metal center (Fe or Ru) and also the nature of the cyclo-E₅ ring shows the same reactivity.

### Experimental section

#### General materials and method

All manipulations were performed to the rigorous exclusion of oxygen and moisture using standard Schlenk techniques on a dual manifold Schlenk line with Argon or N₂ inert gas or a glove box filled with nitrogen containing a high-capacity recirculator or a glove box filled with nitrogen containing a high-capacity recirculator (<>). All solvents were degassed and purified by standard procedures. A moisture in the inert gas were removed by passing it through a drying column filled with Cu/MgSO₄ catalyst as well as concentrated H₂SO₄ and orange gel, respectively. All solvents were degassed and purified by standard procedures. All NMR spectra were recorded using deuterated benzene-\( \text{d}_6 \) or toluene-\( \text{d}_8 \) dried (over Na/K or CaH₂), refluxed for three hours and then distilled under inert atmosphere. The compounds \([\text{Cp}^* \text{Ru}) (\mu_\eta^1\eta^2 \text{E}_5) (\text{L}^2 \text{Cu})]\) were prepared according to literature procedures.

Mass spectrometry was performed using a Jeol AccuTOF GCX LIFDI mass spectrometer provided by the MS department of the University of Regensburg. The observed fragment ions were assigned according to the mass/charge (m/z) ratio and the corresponding isotope pattern. Elemental analyses (CHN) were performed by the department of central analyses of the University of Regensburg on a Versa micro cube and a MT5 micro scale device. \(^{1}\)H and \(^{31}\)P NMR spectra were recorded on a Bruker Avance III HD 400 (\(^{1}\)H: 400.13 MHz, \(^{31}\)P: 161.98 MHz) spectrometer at the NMR department of the University of Regensburg. The chemical shifts are reported in ppm relative to external TMS (\(^{1}\)H) or \(85\% \) H₃PO₄ (\(^{31}\)P). The chemical shifts \( \delta \) are given in parts per million [ppm] and coupling constants \( J \) in [Hz].

### Single-crystal X-ray crystallography

The X-ray diffraction experiments were performed on either a SuperNova DualFlex diffractometer ( Rigaku ) equipped with a TitanS2 CCD detector, or a XtaLAB Synergy R, DW system ( Rigaku ) equipped with a HyPix Arc 150° detector. All measurements were performed at 123 K. Data collection and reduction were performed with CrysalisPro (12) (171.41.90a, 2020 (3a, 3b)). For the compounds 3a and 3b, a Gaussian absorption correction based on Gaussian integration over a multifaceted crystal model was applied. Using Olex2, the structures were solved by direct methods with ShelXT and refined by the full-matrix least-squares method against \(F^2\) in anisotropic approximation using ShelXL. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in the calculated positions using the riding on pivot atom model. Figures were created with Olex2.

CCDC-2120088 (3a) and CCDC-2120089 (3b) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

### Synthesis of \([\text{Cp}^* \text{Ru}) (\mu_\eta^1\eta^2 \text{P}_5) (\text{L}^2 \text{Cu})]\) (3a)

\([\text{Cp}^* \text{Ru}) (\mu_\eta^1\eta^2 \text{P}_5) (\text{L}^2 \text{Cu})]\) (3a) crystallized as orange needles, suitable for X-ray structure analysis. Crystalline yield: 20 mg (51, 0.026 mmol); \(^{1}\)H NMR (C₆D₆, 300 K): \( \delta \) [ppm] = 7.32 (d, 4H, \( \text{H}_{\text{meta}} \)), 7.19 (t, 2H, \( \text{H}_{\text{para}} \)), 7.19 (t, 2H, \( \text{H}_{\text{para}} \)), 4.74 (s, 1H, \( \text{H}_g \)), 2.10 (s, 12H, \( \text{ortho-Me} \)), 1.56 (s, 6H, \( \text{ortho-Me} \)), 1.10 (s, 15H, \( \text{Cp}^* \)); \(^{1}\)H NMR (tol-\( \text{d}_8 \), 193 K): \( \delta \) [ppm] = 7.34 (d, 4H, \( \text{H}_{\text{meta}} \)), 7.23 (t, 2H, \( \text{H}_{\text{para}} \)), 4.69 (s, 1H, \( \text{H}_g \)), 2.08 (s, 12H, \( \text{ortho-Me} \)), 1.49 (s, 6H, \( \text{ortho-Me} \)), 0.99 (s, 15H, \( \text{Cp}^* \)); \(^{31}\)P \(^{1}\)H NMR (C₆D₆, 300 K): \( \delta \) [ppm] = 58.33 ppm (s, 5P); \(^{31}\)P \(^{1}\)H NMR (tol-\( \text{d}_8 \), 193 K): \( \delta \) [ppm] = 54.84 ppm (s, 5P).

| Table 1. Comparison of selected atomic distances and angles in 3a, 3b, 3a-Fe and 3b-Fe (E = P, As; \( \phi \) = angle between E₅ plane and E-Cu-E plane). |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Compound       | 3a              | 3b              | 3a-Fe           | 3b-Fe           |
| \( \delta \text{[Cu-E]} \) [Å] | 2.2844(8) 2.2916(8) | 2.3921(11) 2.3996(10) | 2.2820(7) 2.2859(7) | 2.4002(7) 2.4255(7) |
| \( \delta \text{[E-E]} \) [Å]  | 2.1301(10) - 2.1384(10) | 2.3400(10) - 2.3475(10) | 2.1172(3) - 2.1326(11) | 2.3251(9) - 2.3425(8) |
| \( \delta \text{[E1-E2]} \) [Å] | 2.2237(10) | 2.4292(10) | 2.2100(10) | 2.4039(6) |
| \( \phi \) [°] | 82.46(3) | 96.15(3) | 83.43(2) | 94.29(2) |
LIFDI-MS (toluene): m/z (%) = 759.98 (29.19, [M⁺]), 1130.10 (100, [(Cp³Ru)(P₃)(L²Cu)]); EA calculated for C₃₁H₄₀CuN₂RuP₅: C: 48.98, H: 5.30, N: 3.69, found [%]: C: 48.93, H: 5.28, N: 3.63.

**Synthesis of [(Cp³Ru)(μη³:2-As₂)(L²Cu)] (3b)**

[(Cp³Ru(η⁵-As₂))](1b) (20 mg, 0.03 mmol, 1 equiv.) and [L²Cu(MeCN)] (13.4 mg, 0.03 mmol, 1 equiv.) were dissolved in Et₂O and stirred for 1 hour at room temperature. The reaction mixture was filtered over diatomaceous earth and transferred into a double Schlenk (with 1 mL of toluene on the other side). The solvent was reduced by slow evaporation at -30°C. Compound [(Cp³Ru)(μη³:2-As₂)(L²Cu)] (3b) crystallized as orange needles, suitable for X-ray structure analysis. Crystalline yield: 15 mg (47%, 0.015 mmol).

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**Funding**

This work was supported by the Deutsche Forschungsgemeinschaft within the project Sche 384/40-1.

**Author contributions**

M. Haimerl performed the experimental work. Prof. M. Scheer acted as supervisor, raised the funding and directed the project. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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