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ARTICLE

Cobalt-Based Metallo-Mesoionic Carbene Gold Complexes with Antiproliferative Effects

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D. Menia,[a] F.R. Neururer,[a] K. Wurst,[a] P. Lippmann,[b] I.V. Esarev,[b] M. Seidl,[a] I. Ott,[b]* M. Podewitz,[c]* S. Hohloch[a]* and B. Bildstein[a]*

We report the facile synthesis of new gold(I) carbene complexes based on a mesoioinic cobaltocenylidene metallocarbene via a fluorinative desilylation reaction. The carbene is characterized by a variety of spectroscopic methods, revealing the lowest HEP value reported for a MIC so far, indicating them to be highly electron donating. The properties of the new class of metallo mesoionic carbenes is further investigated, revealing also exceptionally low TEP values. Electrochemical studies also suggest the cobaltocenium moiety to be further reducible. In addition, the cell growth inhibitory effects of the new metallocarbene complexes were explored in cancer cells and bacteria. The combination of electrochemical activity, exceptional electron donating properties and their putative application in medicinal chemistry, makes these new metallo-MICs a highly interesting new class of ligands.

Introduction

Undoubtfully, not many ligands have changed the chemical landscape as much as N-heterocyclic carbenes did.[1,2] Since their first exploration by Wanzlick and Öfele,[3] over the isolation of the first free carbenes[4] to the recent decade, they have played a crucial role in the development and application of organometallic chemistry.[1,2,5] It is therefore no surprise that over the years a plethora of subclasses emerged, ranging from classical *n*NHC to remote NHC[6,7] and cyclic alkyl/aryl carbenes[8] to abnormal or mesoionic carbenes.[6,7,9–12] Especially in the past two decades, the latter have emerged from laboratory curiosities to a valuable and important subclass of NHCs.[7,9,13] This is partly related to the development of MICs based on ubiquitously accessible triazoles (so-called triazolylidenes)[9–11,13] as well as to their unique electronic properties rating them as strongly electron donating carbenes. Given the modular approach of NHC synthesis, the donating abilities of the NHC ligands can be tuned quite easily. However, this approach requires the synthesis of new ligands, changing in most cases also the steric properties of the flanking groups. Thus, redox-active NHCs have emerged in the literature.[14,15,16] These allow the tuning of the electronic structure of the NHC/MIC ligand by simple oxidation/reduction without the need of tedious synthetic remodeling. This has been achieved whether by the introduction of redox active groups into the backbone of the ligand (e.g. chinones or ferrocenes)[14,16] or by the introduction of redox-active wingtip groups, in most cases ferrocene or cobaltocene(ium) groups.[17] However, in all these cases the redox-active group is not integral part of the NHC framework but covalently linked to it. Contrasting this, in 2018 we have reported the synthesis of a purely metallocene-based mesoionic carbene termed 1-cobaltocenylidene **1a'** with a gold(III) central metal.[18] This carbene differs from previous redox-active carbenes, as the carbene carbon is direct part of the redox-active group. However, this original synthesis lacked

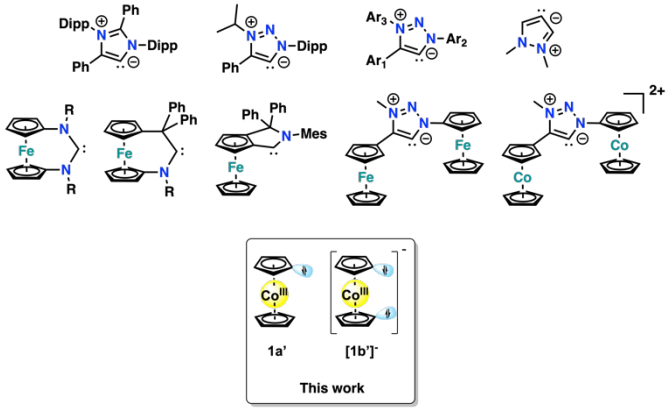

Figure 1: Selected overview of mesoionic carbenes (first row) and metallo-NHC/MIC ligands (middle row) known to the literature compared to the examples reported here. The first two examples of the first row, correspond to the examples, which are known to also exist in their free form.

[a] Department of General, Inorganic and Theoretical Chemistry
University of Innsbruck,
Innrain 80 – 82, 6020 Innsbruck, Austria
E-mail: Stephan.Hohloch@uibk.ac.at; Benno.Bildstein@uibk.ac.at
[b] P. Lippmann, Dr. I.V. Esarev, Prof. Dr. I. Ott
Institute of Medicinal and Pharmaceutical Chemistry
Technische Universität Braunschweig
Beethovenstraße 55, 38106 Braunschweig, Germany
E-Mail: ingo.ott@tu-braunschweig.de
[c] Prof. Dr. M. Podewitz
Institute of Materials Chemistry
Technische Universität Wien
Getreidemarkt 9, 1060 Wien, Austria
E-Mail: maren.podewitz@tuwien.ac.at
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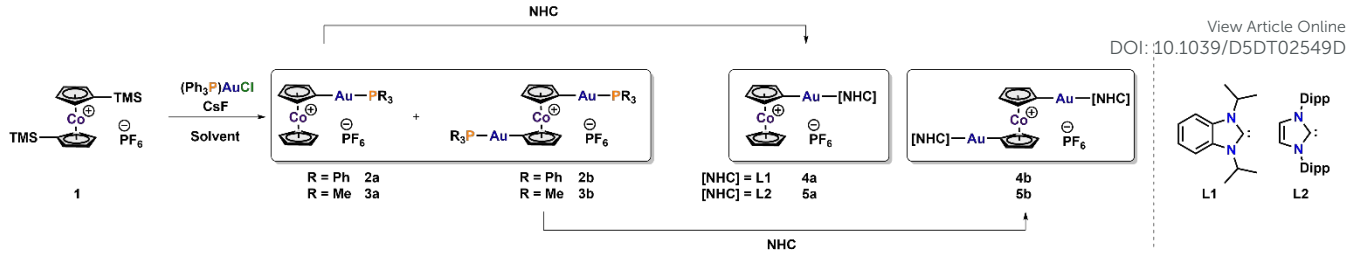

Scheme 1: Synthetic procedure towards monometallic and bimetallic 1- and 1,1' metallated cobaltocenylidene complexes of gold(I).

of variability and only 1- but no 1,1'-cobaltocenylidenes were accessible via this route.[18] Furthermore, the reaction only proceeded from the 1-diazoniumcobaltocenium bis-hexafluorophosphate di-cation, which is tedious to prepare in a four step synthesis and can only be stored at low temperatures for prolonged time.[19] Finally, the reaction starts from an Au(I) source, but an Au(III) complex is finally isolated. Thus, we aimed to expand the synthesis to a more versatile and direct approach. Here we demonstrate the simple synthetic accessibility of 1- and 1,1'-cobaltocenylidenes making use of a fluorinative desilylation reaction starting from readily accessible 1,1'-trimethylsilylcobaltocenium hexafluorophosphate **1**.[20] A library of gold(I) complexes is reported and their redox, electronic as well as antiproliferative properties are explored.

Results and Discussion

Starting from readily accessible bis-TMS-cobaltocenium hexafluorophosphate $[(Cp^{TMS})_2Co][PF_6]$ **1**,[20] we envisioned that in the presence of fluoride donors C-Si bond cleavage would occur, which would allow trapping of the desired cobaltocenylidene species **2a** or **2b** using gold(I) precursors. Indeed we found that after mixing CsF, **1** and $(PPh_3)AuCl$ (3 eq) in acetonitrile, complexes **2a** and **2b** were obtained after chromatographic separation using an activated aluminum oxide column as air and moisture stable yellow solids. Interestingly, the product distribution between **2a** and **2b** is highly solvent dependent. While in acetonitrile **2a** is the main product and **2b** is a minor product, which can be isolated in 40 and 11 % yield respectively, in THF **2b** becomes the main product and can be isolated in 45 % yield, while **2a** is only accessible in yields of 20%. However, the reaction only proceeds well if 3 equivalents of $(PPh_3)AuCl$ are used, while lower amounts of the gold reagent lead to a high amount of hydrolysis with unsubstituted cobaltocenium hexafluorophosphate being the major product of the reaction. To further investigate the reaction mechanism for the formation of the desired cobaltoceneylidene complexes, we performed the reaction in wet solvents, which almost exclusively lead to the isolation of the protonated cobaltocenium salts. Furthermore, changing the fluoride source was also found to be detrimental to the formation of the cobtaltoceneylidene complexes. Thus, we propose that the high concentration of gold(I) and the low-soluble fluoride source is needed to keep the concentration of the transient cobaltoceneylidene species as low as possible, while also trapping it as fast as possible. However, a full mechanistic investigation of this reaction is still outstanding. Furthermore, the reaction also works with other gold(I) precursors such as $(PMe_3)AuCl$, however chromatographic separation of the corresponding trimethylphosphine complexes **3a** and **3b** was impossible. Formation of the new cobaltocenylidene complexes **2a** and **2b** is evident by several spectroscopic features. For the successful formation of **2a** from **1** the first indication is given by the observation of an "asymmetric" spin system in which one Cp ligand is completely protonated (δ ^{1}H = 5.52 ppm) while the other retains the typical AA'BB' coupling pattern (Figure S1).[18] The expected *pseudo*-triplets appear at 5.76 and 5.42 ppm and are drastically shifted compared to **1** in which the Cp-proton are overlayed to one multiplet at 5.72 ppm. [20] This coupling pattern is retained in **2b** for both Cp-rings, but the signals are shifted to 5.61 and 5.32 ppm (Figure S6). Furthermore, for both, **2a** and **2b**, the typical phenyl protons are observed between 7.72 and 7.38 ppm. The presence of the triphenylphosphine moiety is also unambiguously indicated by the observation of a ^{31}P NMR resonance at 42.9 and 43.0 ppm for **2a** and **2b**, respectively (Figure S5/S10). Although the ^{13}C carbene resonance was not directly observed via one dimensional NMR spectroscopy (Figure S2/S7), ^{1}H-^{13}C HMBC experiments showed a cross peak at 5.76 / 120.0 and 5.42 / 120.0 ppm in **2a** (Figure S4) and at 5.61 / 118.0 and 5.32 /118.0 ppm in **2b** (Figure S9), which

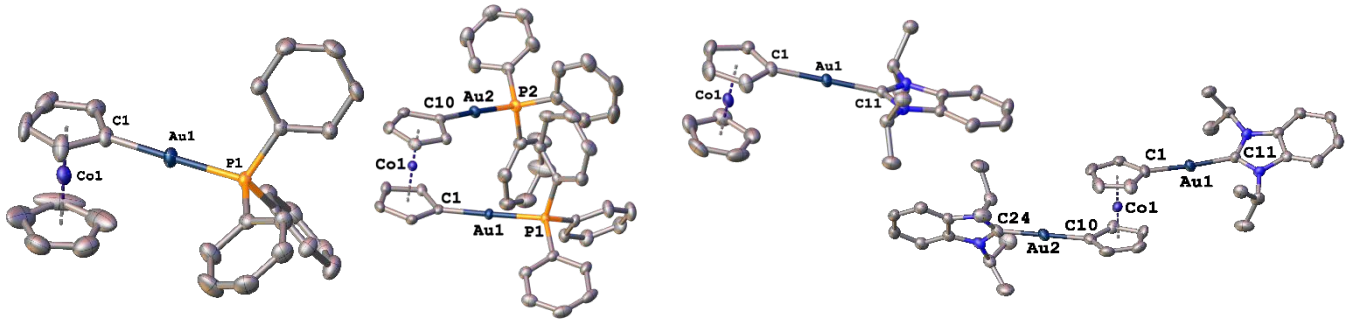

Figure 2: Molecular structures of complex **2a**, **2b**, **4a** and **4b** (f.l.t.r). Hydrogen atoms, counter ions and lattice solvent molecules have been omitted for clarity. Ellipsoids are shown at a probability level of 50%.

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unambiguously belong to the cobaltocenylidene carbon atom. Final proof for the successful 1- and 1,1'-metalation in **2a** and **2b** was given by X-ray diffraction analysis (Figure 2, S71/72). The carbon gold distances Au1-C1 and Au2-C10 are 2.038(3) Å in complex **2a** and 2.070(2) / 2.034(2) in complex **2b**. Compared to classical gold(I) NHC complexes, such as (IPr)AuCl (C1-Au1 1.94 Å),[21] (CAAC)AuCl (C1-Au1 1.98 Å), [22] and even (MIC)AuCl (C1-Au1 1.97 Å), [23] these distances are significantly longer, but comparable to cationic $[(IPr)Au(PPh_3)]^+$ (2.04 Å).[24] The P1-Au1 / P2-Au2 distances are comparable at 2.2941(8) Å in **2a** and 2.2964(5) / 2.2831(6) in **2b** and similar to $[(IPr)Au(PPh_3)]^+$ (2.29 Å). The Au1-Au2 distance in **2b** is 4.047(1) Å, which rules out any direct aurophilic Au-Au interactions in the complex.[25] Although we weren't able to completely separate the trimethylphosphine complexes **3a** and **3b** chromatographically from each other, unambiguous proof of their synthesis was given by X-ray diffraction analysis (Figure S73/74). Notably, while in **2b** a torsion angle of 57.705(2)° was found between the two gold atoms, for **3b** a torsion angle of 147.679(2)° was noted, resulting in a Au1-Au2 distance of 7.509(1) Å.

The isolation of gold(I) complexes furthermore allowed now the determination of the Huynh Electronic Parameter (HEP).[26] Exchange of the triphenylphosphine ligands in **2a** and **2b** works well by simple addition of the free NHC ligands and gives access to the desired carbene complexes **4a** and **4b** in the case of NHC = BenziPr (**L¹**, Scheme 1) and **5a** and **5b,** if IPr (**L²**, Scheme 1) is used. Successful ligand exchange is indicated by ^{31}P NMR which shows no phosphine resonance anymore. In contrast, the ^{15}N NMR spectra show a resonance at 244.8, 244.8, 244.8 and 244.9 ppm (Figure S26/S35/S44/S50) indicative of the (benz)imidazolylidene ligands in **4a**, **4b**, **5a** and **5b**.[27] Unambiguous proof for successful phosphine-NHC exchange is the appearance of a new singlet in the ^{13}C NMR spectra of the new complexes at 193.7 / 194.4 ppm for **4a** / **4b** (Figure S28/S31) and at 193.0 / 193.9 ppm for **5a** / **5b** (Figure S40/S46) respectively. Via the formula recently reported by Huynh ([Pd] = 1.19[Au] – 45, with [Pd] and [Au] = chemical shift of carbene resonance in ppm), [28] the HEP parameter of **4a** and **4b** can be calculated at 185.5 and 186.3 ppm, even exceeding the highest HEP value of **Pyry-C** (Figure 4),[29] which was reported at 184.0 ppm, making **1a'** and **[1b']⁻** (see Figure 1 or Figure 4 for their structures) the most donating MIC ligand reported so far.[30] To set these values into more context, typical 2-imidazolylidenes

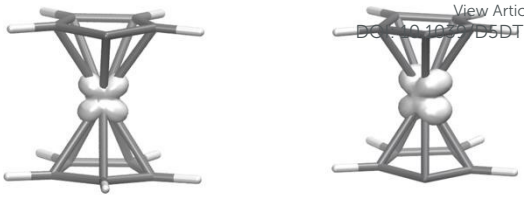

Figure 3: Spin density calculated the TPSSh functional for **[1a]⁻** and **[1b]²⁻**.

such as IPr, IMes, substituted benzimidazolylidenes and imidazolidines appear in the range of 180.1 – 176.6 ppm, triazolylidenes (MIC) have been reported between 181.2 – 179.5 ppm and even the more donating 4-imidazolylidenes display values in the range of 181.9 ppm. Thus, the new 1 and 1,1'-cobaltocenylidenes belong to the most donating MICs reported so far and have (based on their HEPs) similar donor properties compared to Dielmann's electron rich phosphines.[31] The results from the HEP analysis are also in line with the calculated TEP parameters of the cobaltocenylidene moiety being 2037.1 cm^{-1} for the 1-cobaltocenylidene ligand **1a'**[18] and 1996.8 cm^{-1} for each carbene carbon of the 1,1'-cobaltocenylidene **[1b']⁻**. The X-ray structures of the complexes **4a**, **4b**, **5a** and **5b** show the expected linear coordination geometries for gold(I) NHC/MIC complexes (Figure 2 for **4a**, **4b**; Figure S77 (**5a**) and S78 (**5b**)). The gold-cobaltocenylidene distances Au1-C1 and Au1-C10 are similar to the phosphine complexes **2,3a** and **2,3b** (*vide supra*) in the range between 2.016(6) – 2.025(3) Å, while the gold (benz)imidazolylidene ligands lie in between 2.022(2) – 2.041(6) Å and are comparable to $[(IPr)Au(PPh_3)]^+$.[24] Given the redox-active nature of the cobaltocene(ylidene) moiety we were further interested in their electrochemical properties. The phosphine complexes **2a** and **2b** show a reversible one-electron reduction at –1.55 and –1.82 V *vs.* $Fc/[Fc]^+$ (Figure S65 & S 68), while the NHC congeners **4a,b** and **5a,b** display reduction potentials of –1.68, –2.05, –1.75 and –2.05 V *vs.* $Fc/[Fc]^+$. The lower reduction potentials of the NHC complexes **4** and **5** compared to **2**, are in line with the higher donor strengths of the NHC ligands compared to phosphines. Unfortunately, we have not been able to chemically isolate any of these reduced complexes, but the values of the reduction potentials strongly speak for a cobalt-centred reduction process (Figure 3).[32] To further elucidate the electronic structure of the new carbenes **1a'** and **[1b']⁻** (Figure 1 and 4) we turned to

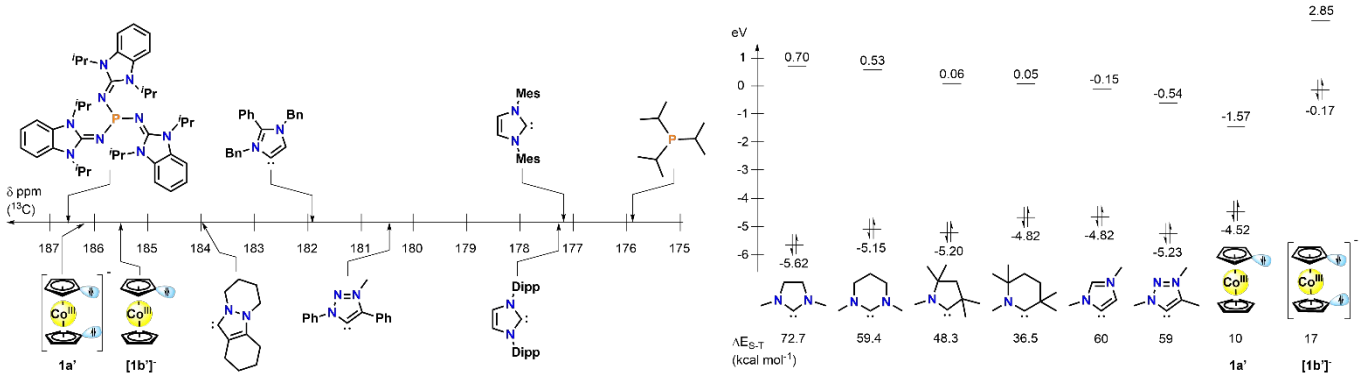

Figure 4: Structures of the free (reduced) carbenes (top); Comparison of HEP parameter of different NHC, MIC and phosphine donors with **1a'** and **1b'** (bottom left) and HOMO-LUMO gaps for different NHC/ligands including the (reduced) carbenes presented here (bottom, left).

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computational investigations. Computational investigations with Density Functional Theory (PBE0/def2-TZVPP/D3BJ//BP86/def2-TZVPP/D3BJ in implicit polar solvent, see SI for details) show that both complexes, **2a** and **2b**, adopt a singlet state with the according triplet state energies are over 100 kJ mol^{-1} higher in energy (compare Table S3 and Figure S79 and S80). Once reduced, the ground state of the species becomes a doublet, while the energy to the quartet state is 31.5 kJ mol^{-1} (7.5 kcal mol^{-1}) and 6.7 kJ mol^{-1} (1.6 kcal mol^{-1}, Table S3). To compare this data to other (mesoionic) carbenes (see Figure 4), the HOMO-LUMO gap in the free carbenes were calculated with B3LYP/def2-TZVPP and amounted to be 2.954 eV and 3.024 eV in the isolated ligands **1a'** and **[1b']**$^{-}$. Calculating the singlet-triplet energy gaps in **1a'** and **[1b']**$^{-}$ with the same methodology yields, 44.0 kJ mol^{-1} (10.5 kcal mol^{-1}) and 72.2 kJ mol^{-1} (17.3 kcal mol^{-1}) in favour of the singlet state. Since the reduced complexes are not chemically accessible, we computationally determined the TEP parameters of the reduced cobaltocenylidene ligands. In line with the reduction of the cobalt centre (and the enhancement of the electron density at the carbene moiety), the TEP parameters decreases from 2037.1 cm^{-1} in **1a'** to 2015.2 cm^{-1} in **[1a']**$^{-}$, and 1996.8 cm^{-1} (for each carbene carbon atom) in **[1b']**$^{-}$ to 1974.8 cm^{-1} in **[1b']**$^{2-}$. This proves that upon reduction the cobaltocene(II)-ylidene ligands become even stronger donors and would thus belong to the most donating carbenes reported so far.

Finally, we performed preliminary investigations regarding the potential of these new MIC gold(I) complexes as prospective anticancer or antibacterial drug candidates. Due to their high stability and strong effects against cancer cells, gold NHC complexes have attracted increasing interest in inorganic medicinal chemistry.[33,34] Given the fact that both gold(I) NHC[33,35] as well as cobaltocene(ium) supported complexes[36] have been shown to be quite potential against various tumorous and pathogenic cells,[33,37] we envisioned the new complexes to be highly active. The growth inhibitory effects of the complexes were evaluated in several tumor cell lines, a non-tumor reference cell line, and two bacterial strains (Table 1). Complexes **2a, 2b,** and **4a-5b** generally triggered strong cytotoxic effects in MCF-7 (breast cancer), HT-29 (colon cancer) and A549 (lung cancer) cell lines with IC_{50} values in the low micromolar or submicromolar concentration range. Complexes **4a** and **5a** triggered stronger effects in these cancer cell lines than in the Vero-E6 non-tumor cell line (African green monkey kidney cells), which is a promising result regarding possible tumor selectivity. Interestingly, the cobaltocene derivatives with attached NHC complexes **5a** and **5b** triggered significantly stronger activity than a recently studied ferrocenyl-based NHC gold(I) complex in both cancer and non-tumor cells. [38] As for the antibacterial activity, the complexes were generally very low active or inactive against the Gram-negative *E. coli* bacteria, however, with the exception of **5b** all complexes demonstrated moderate to very strong activity against the Gram-positive *B. subtilis* strain. The exceptionally strong activity of **4b** and **5a** against *B. subtilis* and almost 100-fold selectivity of these two complexes in comparison to the results obtained with *E. coli* is noteworthy. Preference for Gram-positive bacteria over Gram-negative ones is a common effect of many gold compounds and can be attributed to the high sensitivity of Gram-positive bacteria towards gold-based thioredoxin reductase (TrxR) inhibitors.[33,39] For a recently reported cobaltoceniumethynyl gold(I) complex we had confirmed strong TrxR inhibition,[40] indicating that inhibition of this essential enzyme is also a likely mechanism of action for the complexes of this report. Regarding, structure-activity-relationships for cytotoxic effects in cancer cells, there was a clear trend of the NHC ligands to increase bioactivity compared with the phosphine ligands. Importantly, the introduction of cobaltocene core to the gold NHC unit tends to generally increase cytotoxic and antibacterial effect, as observed when comparing to Auranofin. Thus, complex **5a** was the most active complex against the investigated tumor cells. In summary, complex **5a** emerged as the most promising compound of this study with strong and selective cell growth inhibitory effects against tumor cells as well as Gram-positive *B. subtilis.*

Conclusion

In conclusion, we have reported the versatile and simple access to new gold(I) complexes based on mesoionic 1- and 1,1'-cobaltocenylidene mesoionic carbene ligands, These carbenes were found to be among the most donating MIC ligands reported so far and their donor properties can be even enhanced if the cobalt(III) centre is further reduced to cobalt(II).

Table 1. Biological results: cytotoxic effects against cancer cells (MCF-7, HT-29, A549) and one non-tumor cell line (Vero-E6) as well as antibacterial activity against one Gram-negative (*E. coli*) and one Gram-positive (*B. subtilis*) bacterial strains. All effects are expressed as IC_{50} values and are given in µM unit (± standard deviation) from 3 independent experiments or from a single experiment (*); ciprofloxacin, auranofin served as positive controls for antibacterial and anticancer tests, respectively.

	MCF-7	HT-29	A549	Vero-E6	*E. coli*	*B. subtilis*
Ciprofloxacin·HCl	n.d.	n.d.	n.d.	n.d.	0.021 (0.003)	0.15 (0.01)
Auranofin	2.2 (0.1)	3.0 (0.8)	3.6 (0.8)	2.2 (0.6)	n.d.	n.d.
2a	4.4 (0.9)	3.8 (1.0)	3.7 (1.4)	5.8 (0.5)	>50	8.6 (1.2)
2b	1.2 (0.2)	1.9 (0.6)	1.6 (0.2)	1.8 (0.1)	>50	18.1 (0.3)
4a	0.25 (0.10)	0.48 (0.15)	0.13 (0.08)	1.58 (0.41)	>50	5.3 (1.1)
4b	0.14 (0.13)	0.12 (0.04)	0.15 (0.01)	0.13 (0.02)	21.7 (5.7)	0.26 (0.02)
5a	0.3 (0.3)	0.3 (0.3)	0.3 (0.3)	1.0 (0.1)	27.5 (4.3)	0.30 (0.03)
5b	1.8 (0.2)	2.1 (0.1)	0.6 (0.2)	5.7 (0.2)	>50	>50
5b	1.8 (0.2)	2.1 (0.1)	0.6 (0.2)	5.7 (0.2)	>50	>50

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The biological evaluation highlighted complexes **4b** and **5a** as highly active regarding cytotoxicity and Gram-positive selective antibacterial activity. Future work will focus on the implementation of these new, redox-active carbenes in switchable processes, especially in catalysis and on further evaluating the mechanism and essay of their biological activity.

Acknowledgements

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Notes and references

‡ Supporting information contains all ^{1}H, ^{13}C, ^{31}P and 2D NMR spectra, IR and UV-Vis data as well as further information regarding X-ray crystallography and computational investigations and antiproliferative testing. Deposition numbers 2314980 (**2a**), 2314979 (**2b**), 2476574 (**3b**), 2314982 (**4a**), 2314981 (**4b**), 2314983 (**5a**) and 2314984 (**5b**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformations-zentrum Karlsruhe Access Structures service. The authors have cited additional references within the Supporting Information.[41]

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University of Innsbruck
Institute for General, Inorganic, and Theoretical Chemistry
Centre for Chemistry and Biomedicine

assoz. Prof. Dr. Stephan Hohloch

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Innsbruck, 17. December 2025

Dear Editor.

Dear Referees,

All data is available free of charge from our side if requested. NMRs, IR and cyclic voltammograms have been included (plotted) into the Supporting Information. Raw data is stored on the university servers and can be accessed via us if necessary.

Crystallographic data (CIF-files) have been uploaded to the CCDC and can be obtained via the CCDC homepage using the CCDC numbers assigned in the Supporting Information. Raw data and frames are stored on the university servers and can be accessed via us if necessary.

We thank you for your consideration,

S. Hohloch

assoz. Prof. Dr. Stephan Hohloch (on behalf of all authors)

Innrain 80-82 | A-6020 Innsbruck
Telefon +43 (0) 512 / 507 – 57035
Sekretariat: Fr. Boch, Tel.: +43 (0) 512 / 507 – 57001
E-Mail Stephan.Hohloch@uibk.ac.at | Internet https://www.uibk.ac.at/en/aatc/ag-hohloch/

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