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Author: Dijkman, T.F. van
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Chapter 7

Summary, Conclusions and Outlook
Chapter 7

7.1. Summary

7.1.1. Introduction

For almost a century ethene has been known to affect climacteric plants in both desirable and undesirable ways. Unfortunately many of the food crops humanity relies on for nutrition are such climacteric plant species and significant quantities of food are lost to ethene-induced spoilage during transport and storage. In order to respond to rising ethene concentrations and prevent spoilage, detection of ethene at the low range of biologically relevant concentrations is required which poses a technological challenge.

Ethene is a highly diffusive, relatively unreactive molecule and therefore difficult to detect. Further complicating the detection of ethene is the fact that biologically relevant concentrations of ethene are extremely low with threshold concentrations that typically vary between 10 ppb and 1000 ppb. Our current ability to monitor ethene at the required low concentrations relies on the use of techniques like gas chromatography and photoacoustic detection. Both techniques require large and expensive equipment and are poorly suited for applications in shipping and transport. Clearly, there is a need for smaller, more cost-effective alternatives that are suitable for transport with the produce.

A useful source of inspiration for the development of novel sensors is the mechanism of detection of ethene in nature where ethene is bound by copper(I)-containing transmembrane proteins such as ETR-1 inducing responses to small quantities of ethene. A suitable class of copper complexes that can be employed in a similar role is found in the copper(I) hydridotrispyrazolylborate complexes, which have been used to model biologically relevant systems such as hemocyanin.

Such copper(I) compounds have also been used as sensitizer molecules to detect ethene in a carbon nanotube-based device. The carbon nanotube-based system in particular showed promise for the sensitive detection of ethene but failed to provide sufficient sensitivity and stability. The aim of the work described in this thesis was to explore the chemistry of potentially useful copper(I) hydridotrispyrazolylborate complexes and to employ them as sensitizers for highly sensitive ethene sensors based on graphene.

In Chapter 1 an introduction into the horticultural relevance of ethene is provided. This is followed by a summary of the techniques that represent the
The dppbz complex was found to emit a bright cyan luminescence, whereas the other complexes showed only weak luminescence upon irradiation with UV-light. Time-resolved luminescence experiments showed that the bright cyan emission of the dppbz complex is due to phosphorescence while the PPh₃ and dppe complexes show mainly fluorescence, a difference that is attributed to the conformational stiffness of the dppbz complex. The excited state of the dppbz complex was modelled using TD-DFT (B3LYP/6-31G) and found to be best described as a mixed triplet state composed of a metal-to-ligand charge transfer from the copper(I) ion to the dppbz ligand and a ligand-to-ligand charge transfer from the [MPh₂⁺] ligand to the dppbz ligand, \(^3\)MLCT + LLCT.

7.1.3. Naphthyl-substituted hydridotrispyrazolylborate ligands and their copper(I) complexes

For hydridotrispyrazolylborate ligands to be applicable for use in ethene detection a number of requirements must be met: the resulting copper(I) complexes must be air stable; the complexes must be sterically restrictive enough to prevent the undue coordination of as many other ligands as possible and the complexes must interact well with the substrate that generates the current state of the art in ethene detection and few examples of copper(I) and silver(I)-based systems that were examined as ethene detection platforms.

7.1.2. Phosphorescent copper(I) complexes of [MPh₂⁻]⁻

In the process of familiarization with the synthetic chemistry of hydridotrispyrazolylborate ligands a batch of potassium trihydrido(3,5-diphenylpyrazol-1-yl)borate (KMPH₂) was obtained. As the chemistry of copper(I) monopyrazolylborate complexes is relatively unexplored it was decided to prepare a number of copper(I) compounds using this monopyrazolylborate ligand in combination with phosphane co-ligands. The phosphanes used in the investigations described in Chapter 2 are triphenylphosphane, 1,2-bis(diphenylphosphanyl)ethane (dppe) and 1,2-bis(diphenylphosphanyl)benzene (dppbz), ranging from conformationally entirely flexible (PPh₃) to almost entirely rigid (dppbz). The resulting complexes were analyzed using NMR, infrared spectroscopy and X-ray crystallography revealing the expected mononuclear structures for the PPh₃ and dppbz complexes, but an unexpected dinuclear structure for the dppe-containing complex. The formation of disproportionation products was not observed for any of the complexes.
actual signal (e.g. carbon nanotubes or graphene). To satisfy these requirements a pair of ligands was devised incorporating strongly electron-withdrawing trfluoromethyl groups for the stabilization of the copper(I) oxidation state and naphthyl groups capable of pi-stacking $[\text{Tp}^{\text{CF}_{3},n\text{N}]^+}$ ($n = 1$ or 2). The synthesis, physical properties and copper(I) coordination compounds of these ligands is described in Chapter 3.

To examine the influence of the subtle difference between these ligands that arises from the connecting carbon of the naphthyl ring, the ethene and carbonyl copper(I) complexes were prepared and studied using $^1$H and $^{13}$C NMR, infrared spectroscopy and X-ray crystallography. The X-ray crystal structures were obtained of both ethene complexes $[\text{Cu}^{\text{TP}^{\text{CF}_{3},n\text{N}]}}(\text{C}_2\text{H}_4)]$ and of the sodium salt Na$\text{TP}^{\text{CF}_{3},2\text{N}}$. The compound Na$\text{TP}^{\text{CF}_{3},2\text{N}}$ was found to crystallize as a dinuclear complex with bridging aqua ligands; completing the coordination spheres of the octahedrally coordinated sodium ions are nearby fluorine atoms from trfluoromethyl groups of the hydridotrispyrazolyborate ligands. The two copper-ethene complexes were found to have nearly identical coordination pockets. The 1-naphthyl substituents were found to have larger torsion angles with respect to the pyrazole rings than the 2-naphthyl groups. NMR and IR spectroscopy revealed that the electron density on the copper(I) ions varies, with the most electron-poor copper(I) centers being present in the 1-naphthyl substituted complexes. As the bond distances and angles in the coordination pockets containing the ethene and carbonyl ligands are nearly identical the electronic differences must thus be the result of the different conformations of the naphthyl groups.

The sodium salts of the ligands and all the complexes showed distinctly different tendencies to crystallize. The 1-naphthyl substituted complexes were found to be slow to crystallize, forming foams, slowly crystallizing oils and amorphous materials instead. In stark contrast to the tedious crystallizations of the 1-naphthyl substituted compounds the 2-naphthyl substituted species showed a pronounced tendency to crystallize. An important consequence of the different crystallizing behavior of the two ligands and their complexes is an equally pronounced difference in their solubility in most organic solvents. The 1-naphthyl species tend to mix with even the smallest amounts of most solvents to form viscous oils that appear to be miscible in any proportion while the 2-naphthyl substituted ligand and particularly its copper(I) complexes are poorly soluble in most solvents. This difference is caused by the difference in the rotational freedom of the 1-naphthyl and 2-naphthyl groups and allows access
to complexes that are relatively similar in structure but with strongly different solubilities, which might prove useful for future catalysis research.

A downside of the necessary inclusion of trifluoromethyl groups on the pyrazole rings is the limitation it imposes on potential π-stacking interactions of the ligand with carbon materials and the steric bulk of the coordination pocket surrounding the copper(I) center. The trifluoromethyl groups were therefore omitted entirely in favor of di-aryl substituted hydridotrispyrazolylborate ligands. The ligands described in Chapter 4 are symmetrically substituted with either two phenyl rings [Tp_ph2]− or two n-naphthyl groups [Tp_naph]− (n = 1 or 2). The copper(I) complexes of these ligands were found to have varying degrees of oxidative stability in air. Typically in the solid state the ethene and carbonyl complexes were found to decompose only very slowly if at all. In solution however, the complexes rapidly decomposed to form green solutions. The X-ray crystal structures of the ethene complexes [Cu(Tp_ph2)(C2H4)] and [Cu(Tp_naph2)(C2H4)] were obtained, showing the expected tetrahedral coordination cavities with varying degrees of distortion as a result of π-stacking interactions between the complexes. The phenyl-substituted complex revealed interactions between the phenyl rings and the ethene ligand; similar interactions are suspected to occur in the 2-naphthyl complex but the more pronounced distortion resulting from the increased π-stacking interactions obscure this effect.

The difference in the crystallizing behavior of the 1- and 2-naphthyl substituted ligands reported in the Chapter 3 was observed to be even more pronounced in the dinaphthyl-substituted complexes. Whereas the bis(2-naphthyl)-substituted complexes crystallized readily the corresponding 1-naphthyl-substituted complexes did not. As early in the synthetic route towards to the complexes as the synthesis of 3,5-di(1-naphthyl)pyrazole did the tendency to form oils over solids become apparent. The non-crystalline behavior of the 1-naphthyl species is assumed to be the result of the limited rotational freedom of the 1-naphthyl group, an effect that was also clearly visible from the NMR experiments of the ethene complex, showing strong peak broadening in half of the naphthyl resonances. A strong indication that such limited conformational freedom is at least partially due to interactions with the ethene ligands is that the carbonyl complex shows no such peak broadening. Further indications of the presence of polar interactions between the ethene ligands and the hydridotrispyrazolylborate ligands is the unusually large upfield shift observed for the ethene protons on NMR.
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As the dinaphthyl-substituted species should be capable of relatively strong π-stacking interactions with carbon materials the carbonyl complexes on graphene and HOPG were examined using ellipsometry, AFM and STM. It was found that both complexes form multilayered structures on the graphene through what is thought to be a Stranski-Krastanov type mechanism. On STM it was unambiguously confirmed that the 2-naphthyl complex forms clearly ordered monolayer structures. In general it appears that the crystallization on the macro-scale is at least indicative for the type of ordering of the complexes on a graphene surface.

7.1.4. The influence of electronic modification of the ligands in isosteric complexes

A series of hydridotrispyrazolylborate ligands was prepared, with a number of different substituents based on the common template [TpCF3,4-RPh]− (R = NMe2, OMe, H, F, Cl, CF3 or NO2). In Chapter 5 the X-ray crystal structures are described of many of the resulting ethene and carbonyl complexes; the complexes all have nearly identical coordination cavities. The substituents R were selected based on their Hammett σp parameters and their compatibility with the forcing conditions required for the synthesis of the ligands. The resulting ethene and carbonyl complexes were studied using NMR and IR spectroscopy; the properties such as the chemical shifts of the ethene protons and CO-stretching frequencies were found to match nicely to the expectations based on the σp parameters of the substituents. However, a number of anomalous observations occurred such as the unexpectedly high CO-stretching frequency of [Cu(TpCF3,4-NMe2Ph)(CO)] and the unexpectedly low CO-stretching frequency of [Cu(TpCF3,4-NO2Ph)(CO)]. Upon closer inspection it was found that the ligand [TpCF3,4-NO2Ph]− had not formed with the expected structure but had instead formed as an asymmetric ligand with one of the pyrazole rings counter-rotated placing the phenyl-ring in the 3-position. The protons of the resulting ethene complex showed a considerably larger upfield shift than the other complexes. In general it can be concluded that it is possible to create ligands and copper complexes with nearly identical coordination cavities whilst greatly changing their electronic properties. Furthermore it was found that the electron density on the copper(I) centers is linearly correlated with the Hammett σp parameters of the substituents installed on the ligands.
7.1.5. Ethene detection using copper(I) sensitized graphene devices

Copper(I) acetonitrile complexes were synthesized of the ligands described in Chapters 3 and 5 and were deposited onto graphene field-effect transistors by means of a simple dip-coating procedure. The surfaces thus obtained were studied using AFM showing disordered but otherwise flat surfaces. Similar to the observations described in Chapter 4 the complexes appeared to assemble on the graphene surface as thin multilayers of between 2 and 5 monolayers. When exposed to ethene gas the surfaces appeared to diffuse indicating significant mobility of the complexes on the graphene surface.

The GFETs were used in gas-detection experiments with ethene and ethanol (for comparison) and were found to be extremely effective gas sensors with detection limits well below 100 ppb for ethene and 1 ppm for ethanol. The kinetics of the interactions between the gases and the copper(I) complexes were studied and found to correspond well to expectations with considerably higher equilibrium dissociation constants for ethanol than for ethene. A mechanism is proposed that explains the observed type and intensity of the response of the sensors upon exposure to ethene gas and their correspondence with the Hammett σp parameters of the substituents. In the proposed mechanism the “on” state that is formed upon exposure to the analyte gas is composed of the ethene (or ethanol) complex whereas the “off” state consists of a dinuclear species that forms as a result of the rapid dimerization of the mononuclear 16-electron species. Using DFT calculations (ZORA-OPBE/QZ4P) the dipole moments of some of the complexes (R = CF3, H and NMe2) were determined. The values of the calculated dipole moments clearly show that the mononuclear 16-electron species cannot represent the “off” states as their dipole moments approximate those of the “on” state complexes whereas the dinuclear species have dipole moments close to 0 D.

7.2. Conclusions

The aim of the research described in this thesis was the development of small and affordable ethene sensors. The copper(I) complexes that were studied were found to display a remarkable flexibility with respect to properties such as solubility, crystallinity and electron density on the copper(I) center even when the coordination cavity of the copper(I) ion was kept constant. Using the dinaphthyl-substituted ligands the self-assembly of the complexes on graphene was found to conform to known mechanisms producing homogeneous surfaces that are ideal for gas sensing. The ligands and the complexes that were
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synthesized provided the knowledge and materials required to produce a set of GFET devices in which the predictable electronic properties of the complexes was combined with the extraordinary properties of graphene to produce ethene (and ethanol) sensors with excellent sensitivities and detection limits. The ethene sensors described in this work can serve as the stepping stone towards commercially viable devices that can be shipped with produce in order to increase general knowledge and control of ethene concentrations during transport. Hopefully, one day such knowledge will help to eradicate completely the loss of valuable fruits and vegetables in transport and storage.

7.3. Outlook

Research is a field where answers to questions more often than not come in the form of new questions. This is also the case in this thesis where the complexes that were developed for use in an ethene sensor not only generated ethene sensors of great sensitivity and selectivity but also a host of follow-up questions and potential points to fine-tune. A number of such points are addressed below.

The complex [Cu(Mp\textsuperscript{dppbz})] that is described in Chapter 2 was found to be not only brightly phosphorescent but also entirely heteroleptic. Luminescent copper(I) complexes are the focus of some research as they potentially give access to phosphors of much reduced prices and much improved availability compared to the currently available molecules which are typically expensive iridium complexes. A downside of the copper(I) complexes that are being researched is ligand scrambling which results in the formation of unwanted, less luminescent species. The combination of a rigid phosphane with a monanionic pseudo-bidentate ligand like [Mp\textsuperscript{dppbz}] was found to give access to stable heteroleptic complexes. Additionally the anionic ligand allows researchers to forgo optimizing the counterion which otherwise affects crystal packing. In all, the facile synthesis of the ligand and its complexes appears to be a fertile source for the future development of luminescent compounds.

The complexes described in Chapters 3 and 4 comprise naphthyl groups in two orientations. The seemingly small differences between the ligands give rise to a number of unexpectedly large effects on the macroscale. The observed differences in crystal packing in particular offer promise for further use in a variety of applications such as the strong packing effects seen in the 2-naphthyl substituted species, which might aid in the further development of luminescent species such as, potentially, [Cu(Mp\textsuperscript{(2N)}\textsuperscript{dppbz})]. In contrast, the distinct lack of crystal packing that occurred in the 1-naphthyl substituted species can be
exploited when higher solubilities are required as was the case in the dip-coating experiments.

In addition to the different solid-state behavior of the compounds there is the photophysical aspect of using larger aromatic systems which gives access to low-lying excited states. Especially considering the fact that aziridination and cyclopropanation catalysis are expected to proceed via radical mechanisms involving redox chemistry on the copper centers the exploitation of such excited states offers potential for interesting future research in which the catalytically active states can be induced by exposing the catalysts to UV-light. At the very least the influence of light on such reactions should be studied as many of the copper(I) complexes reported in this thesis were found to be at least somewhat luminescent upon UV-irradiation.

With regards to catalysis the complexes in Chapter 5 in particular offer great promise. By combining the trends observed and expected in these complexes with the kinetic information gained in Chapter 6 the way is open for thorough and exploration of the electronic effects of the ligand on copper-catalyzed aziridination and cyclopropanation reactions. The results described in Chapter 5 and 6 showed clearly that occasional deviations from the expected trends exist and the spectrochemical series reported in Chapter 5 should allow for clear discrimination between outliers and actual unexpected chemistry. A possible improvement on the ligands in Chapter 5 would be the inclusion of more sterically hindered groups in the 3-positions and the use of nitro- or cyano-groups instead of the fluorinated groups that were employed to date.

The dip-coating procedure used to prepare the thin layers of the complexes on graphene was found to result in fairly homogeneous layers. The exact influence of factors such as the substrate, the solvent, the concentration of the adsorbing species etc. have not been studied in depth. In a world where work at the nanoscale is fast becoming the norm simple methods for epitaxial growth are likely to be of increasing importance which necessitates their further development. Particularly the use of “capping agents” should be examined. A capping agent would consist of an otherwise non-participating molecule that can stack on top the first monolayer of functional material. This way stabilized monolayers could be grown even when non-two-dimensionally stacking molecules are applied to a flat surface such as graphene.

Finally, the ethene (and ethanol) sensors described in Chapter 6 should be refined and made ready for commercial applications. The devices that were
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described in this thesis were found to have excellent sensitivities to ethene and ethanol. Earlier work on carbon nanotubes reported good selectivity which should be equally good in the GFET devices. The exclusion of the remaining cross sensitivities is a logical point of interest and should be attainable using coatings and reference sensors. Such coatings could consist of thin hydrophobic materials containing embedded catalyst particles to scrub gases like water vapor, nitrogen oxides and carbon monoxide. In the case of other cross-sensitivities such as ethanol a better solution might be to explicitly determine the identity and quantity of these unintentional analytes using multiple different complexes on multiple strips of graphene. The use of more than a single sensor per device allows for the construction of a "nose" in which the detection of more than a single analyte not only improves the accuracy of the results but also adds a wealth of additional information. In addition to ethene such a GFET-nose might provide high-fidelity information regarding concentrations of water-vapor, carbon dioxide, ethanol, ammonia etc. all at the same time from a single, affordable device.

Further, more precise characterization of the exact behavior of the complexes combined with the use of other complexes optimized for interaction with other gases would result in a technology so powerful it should be considered disruptive. It is no stretch of the imagination that GFET-based sensors will one day be found not only in transport of sensitive produce but also in cars, refrigerators, ovens, smoke-detectors, domotics and even smartphones.