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Synthesis and characterization of organomercury(II) and -lead(IV) compounds with aryl substituents bearing functional groups

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I. Organometallic linkers – State of the art

One of the common methods used in the crystalline frameworks design is the *directional bonding* approach.[1] In order to construct a framework with a certain architecture, metal containing units with predefined bite angles are combined with ligands with two or more donor atoms that have angles between the directions of the lone pairs between 0 and 180° (Figure 1). An additional factor that influences the framework architecture is the stoichiometric ratio of the precursors.

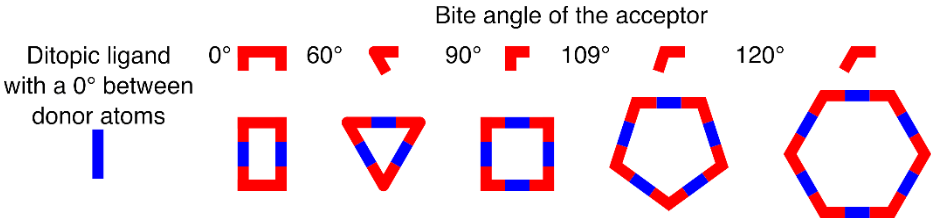


Figure 1. 2D convex polygons obtained *via* self-assembly from a ditopic donor (blue) and various acceptors (red). Figure adapted from Cook and Stang.[1]

When a linear linker is used with a 0° node a 2+2 rectangle is obtained. Using the same linker, acceptors bite angle is larger and adequate stoichiometry, more and more sophisticated structures are obtained, *e.g.* 3+3 triangle with 60° acceptors, 4+4 square with a 90° acceptors, 5+5 pentagon with 109° acceptors, 6+6 hexagon with 120° acceptors.[1]

Using linkers or nodes with more than 2 donor or acceptor sites with non-planar arrangements, interesting topologies can be obtained. For example, a ditopic subunit with angles of 80-90° mixed with a 90° tritopic subunit gives trigonal bipyramid.

Relevant for the aim of the thesis are tetratopic tetrahedral linkers. These parts in combination with tetrahedric or linear spacers give 3D adamantoid networks (Figure 2 and Figure 3).[2–4]

The use of organic linear or tetrahedral linkers/nodes was well established in the last 30 years. Using these linkers preparation and characterization of a significant number of MOFs (**M**etal-**O**rganic **F**rameworks) was reported.[5–7] By contrast, the development of organometallic linkers was nascent due to particularities in their synthesis and their properties as well as the higher costs.[8,9] Most of the results in the field were published in the last 20 years.[8,9] Since the 90s, every year novel species as well as improvements of the existing preparation methods were reported. For example the yield of $(4\text{-}NC_5H_4)_2Hg$ [abbreviated $(4\text{-}py)_2Hg$ along this thesis] from 12%[10] in 2009 to 42% in 2016.[11]

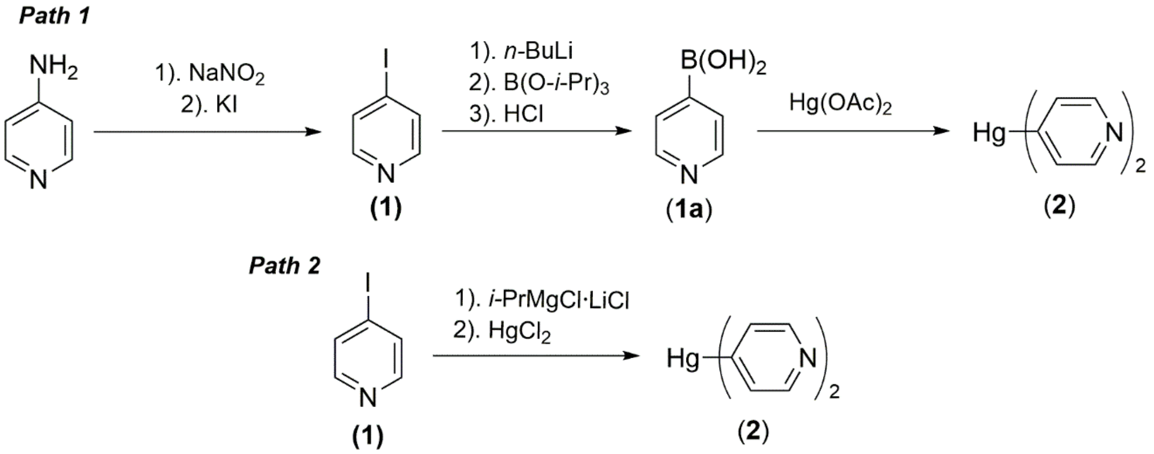
II. Organomercury(II) chemistry

II.2. Original contribution to organomercury(II) chemistry

This Chapter presents the original contributions brought within the performed research aiming in the development of new synthesis methods for existing and new linear and tetrahedral organometallic linkers.

II.2.1. $(4\text{-py})_2Hg$ (2) - a versatile organometallic linear building block for supramolecular chemistry

Via the literature method[10] first the boronic acid **1a** needs to be obtained and later a reaction with mercury(II) acetate is required to give **2** (Scheme 18, *path 1*). On the other hand, **2** could be obtained in a one-pot synthesis *via* the Turbo Grignard reagent (*i*-PrMgCl·LiCl), with one step less (Scheme 18, *path 2*).

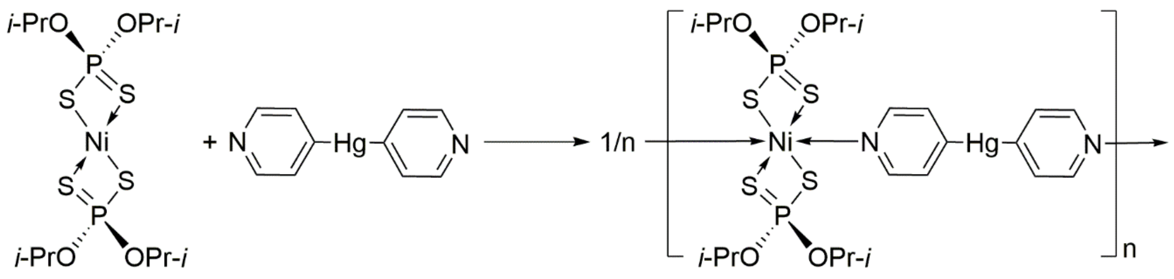


Scheme 18. Synthesis of $(4\text{-py})_2Hg$ (**2**) *via* boronic acid (*path 1*)[10] and Turbo Grignard reaction (*path 2*).[11]

II.2.1.1. Synthesis of $[\{Ni(dipdtp)_2\}\{(4\text{-py})_2Hg\}]_n$ (3)

The compound $(4\text{-py})_2Hg$ (**2**) was used as supramolecular linker to obtain a handful of coordination polymers.[11,100] On top of the similar interactions that 4,4′-bipy linker can have with nodes the extra metal in the middle of the linker gives rise to a new net of possible interactions like Hg···N, Hg···O, π···Hg or π-π.[100]

When solutions of $(4\text{-py})_2Hg$ (**2**) in methanol and $[Ni(dipdtp)_2]$ (**3a**) in dichloromethane were mixed instant precipitation follows suggesting a very fast reaction that produced the new heterobimetallic coordination polymer $[\{Ni(dipdtp)_2\}\{(4\text{-py})_2Hg\}]_n$ (**3**) as an insoluble polymer (Scheme 20).



(**3a**) (**3**)

Scheme 20. Synthesis of the coordination polymer [{Ni(dipdtp)$_2$}{(4-py)$_2$Hg}]$_n$ (**3**).

II.2.1.3. Single crystal X-ray structure of [{Ni(dipdtp)$_2$}{(4-py)$_2$Hg}]$_n$ (3)

The structure of [{Ni(dipdtp)$_2$}{(4-py)$_2$Hg}]$_n$ (**3**) was established by single-crystal X-ray diffraction.[100] It was found to be linear 1-D coordination polymer. The repeating coordination entity in the crystal of **3** is shown in Figure 6.

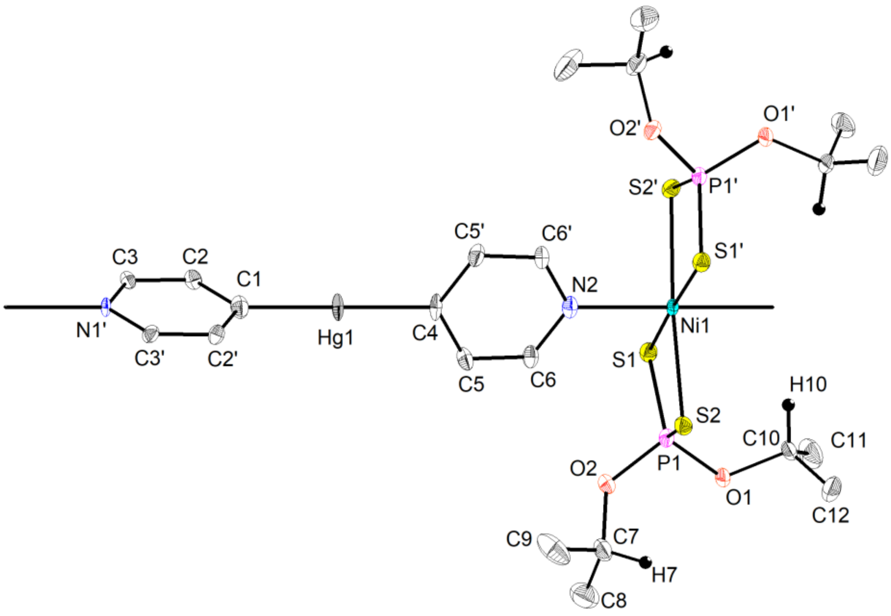
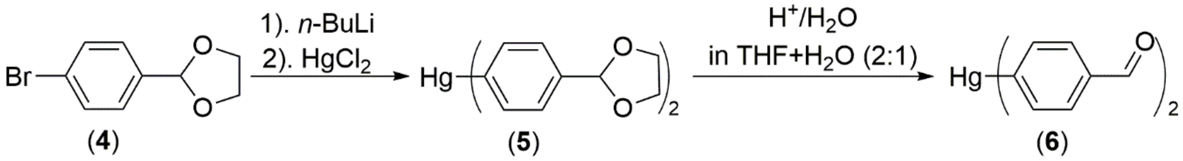


Figure 6. Repeating coordination entity in the crystal of **3** (only methine hydrogen atoms of the isopropyl groups are shown) Thermal ellipsoids are drawn at 40% probability [symmetry equivalent atoms (1–x, y, 1.5–z) are given by “prime”].

II.2.2. Starting materials (4-6) and di(4-imino)arylmercury(II) derivatives (7-10)

II.2.2.2. Synthesis of compounds 4-6

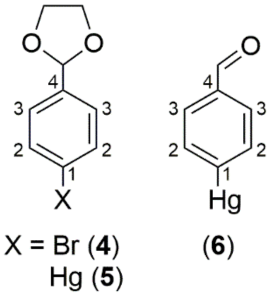
In the first step, the 4-bromobenzaldehyde was protected with ethylene glycol in refluxing toluene in a Dean-Stark apparatus in the presence of *p*-toluenesulfonic acid (Scheme 21).[106,107] After refluxing for 3-5 h and the collection the required amount of eliminated water, the solvent was removed and the remaining oily product was purified by distillation at reduced pressure resulting in a colorless oil, with a yield of about 90%. This colorless oil (**4**) was treated with *n*-BuLi at −78 °C and then with solid $HgCl_2$ in 1:2.5 molar ratio to give **5** in excellent yield (97%) without the formation of the RHgCl. Compound **6** was obtained by catalytic hydrolysis of the protecting group with *p*-toluenesulfonic acid in a THF:H_2O = 2:1 mixture.



Scheme 21. Synthesis of **5** and **6**.

II.2.2.3. Structural characterization of compounds 4-6 by NMR spectroscopy

These compounds were characterized in solution by NMR spectroscopy to determine their structure and purity. For compounds **4**, **5**, and **6** the ^{1}H, ^{13}C, and ^{199}Hg (for **5** and **6**) were measured in $CDCl_3$, at ambient temperature.



Scheme 22. The numbering scheme for compounds **4-6**.

The ^{1}H NMR spectrum of compound **4** (Figure 9) comprises of two doublets in the aromatic region at δ 7.51 and 7.35 ppm corresponding to H-3 and H-2, a singlet at δ 5.77 ppm for the methine proton [$CH(OCH_2)_2$] and a multiplet at δ 4.03 ppm for the methylene [$CH(OCH_2)_2$] protons.

Compound **5** exhibits a similar spectrum (Figure 10), with somewhat more deshielded chemical shifts at δ 7.56 ppm and 7.45 ppm for the H-3 and H-2 protons, δ 5.82 ppm for the $CH(OCH_2)_2$ proton, and the multiplet in the range δ 4.21–4.00 ppm for the methylene [$CH(OCH_2)_2$] protons. Interestingly, only for the doublet resonance at δ 7.45 ppm, we could observe Hg-H satellites with a visible $^3J_{HgH}$ coupling constant of 45.4 Hz, partially overlapped by the resonance of *meta* protons.

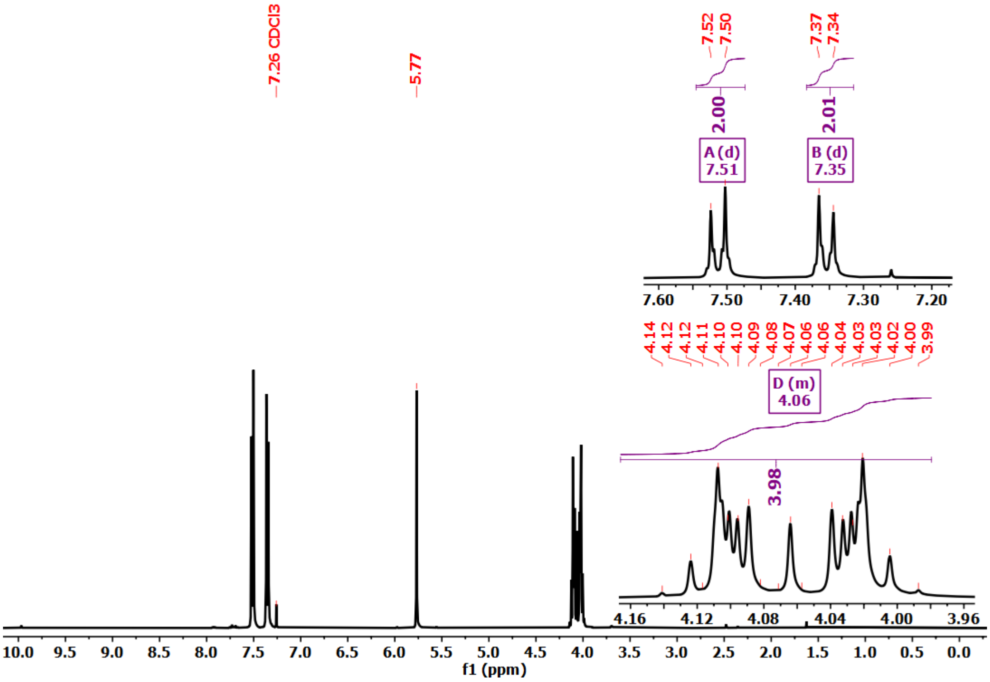


Figure 9. The ^{1}H NMR spectrum of compound **4** in CDCl$_3$.

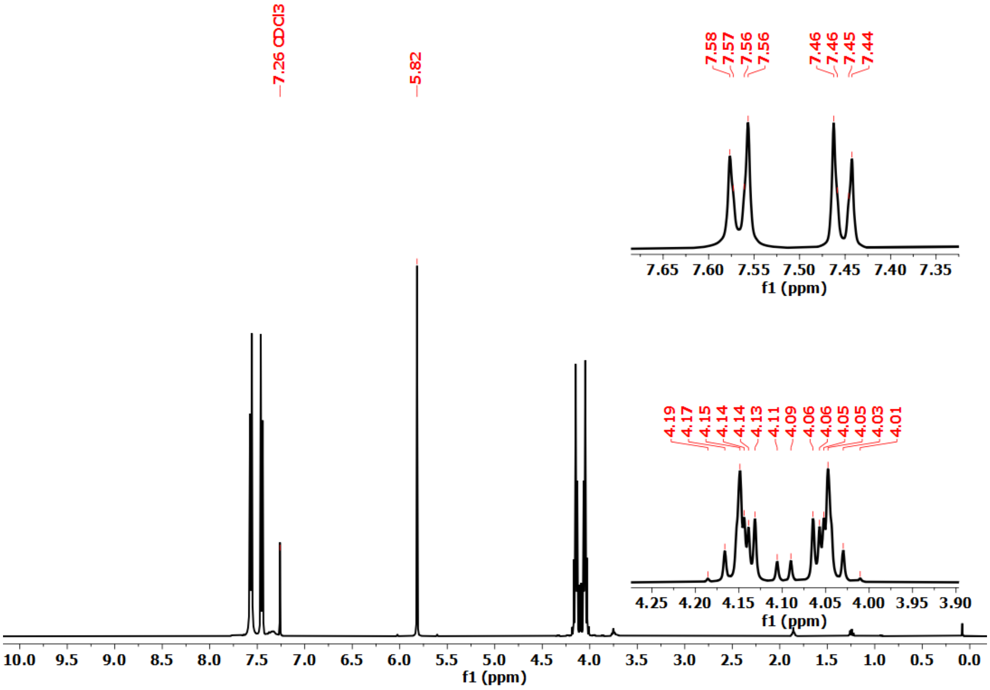


Figure 10. The ^{1}H NMR spectrum of compound **5** in CDCl$_3$.

The ^{1}H NMR spectrum of **6** (Figure 11) becomes simpler after removing the protecting group, with only 3 resonances corresponding to the formyl group at δ 10.02 ppm, the H-3 at δ 7.96 ppm, and H-2 protons at δ 7.64 ppm in CDCl$_3$. The Hg-H ($^3J_{HgH}$) satellites are visible as broad resonances with a coupling constant of 47.5 Hz.

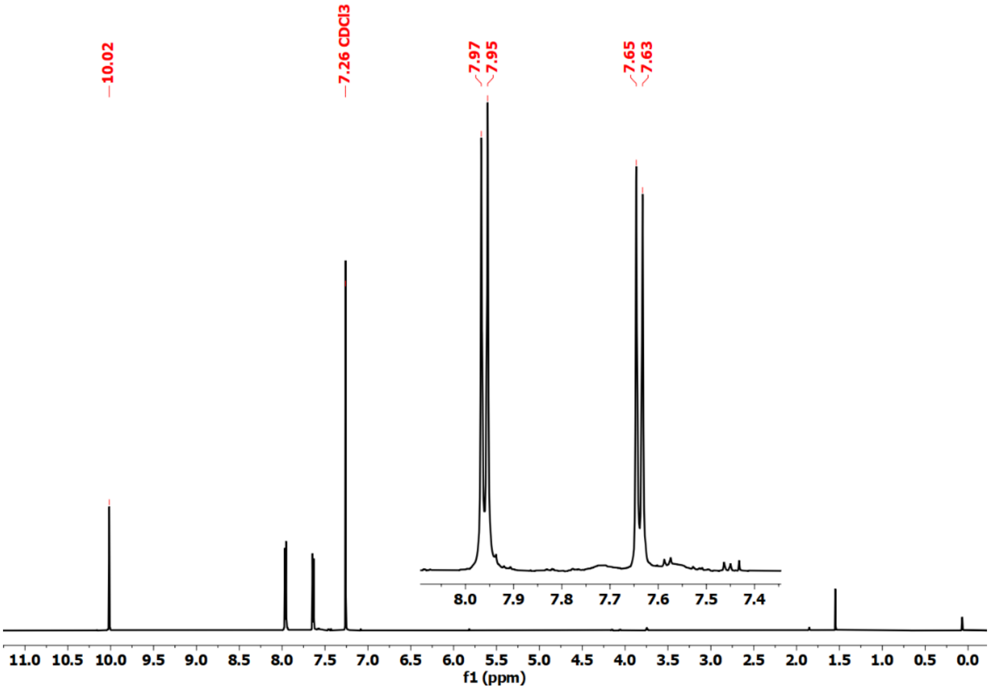


Figure 11. The ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

The organomercury(II) **5** and **6** exhibit distinctive resonances in the ^{199}Hg{^{1}H} NMR spectra (Figure 17), *i.e.* a sharp signal at δ −751.9 ppm for compound **5** in $CDCl_3$, and a broad signal at δ −813.6 ppm for compound **6** in the same solvent, in good agreement with literature data reported for other diarylmercury(II) compounds with electron-withdrawing groups in position 4 on the aromatic ring.[57] Interestingly when the ^{199}Hg{^{1}H} NMR spectrum of **6** was measured in DMSO-d_6 a sharp resonance at δ −908.8 ppm was observed, with a chemical shift difference of about 100 ppm compared to the value obtained in $CDCl_3$ solution. This is in close agreement with the literature data,[57] where one can find a slight deshielding of 80-150 ppm when changing the solvent from $CDCl_3$ to DMSO-d_6.[57,108,109]

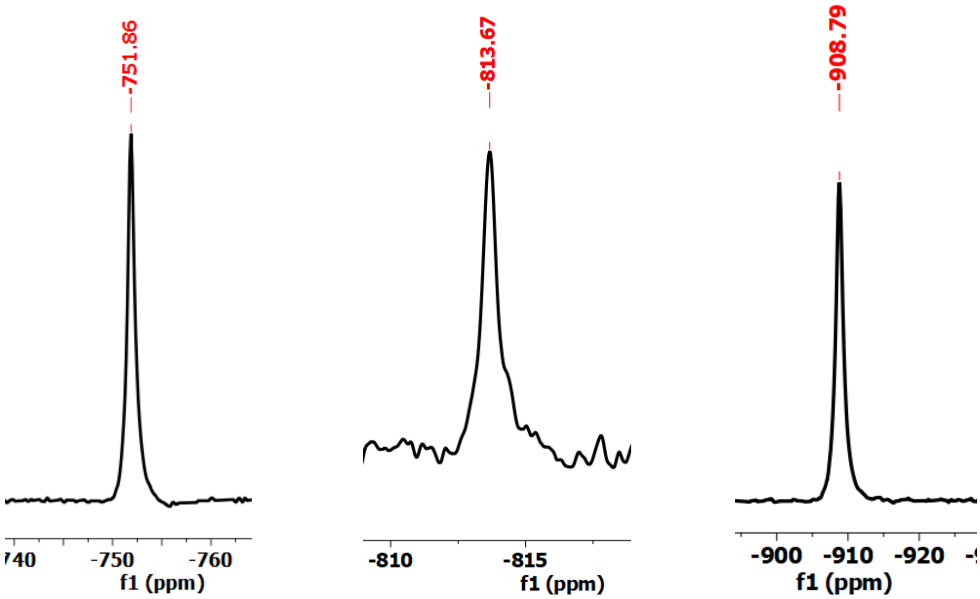


Figure 17. The ^{199}Hg{^{1}H} NMR spectra of **5** in $CDCl_3$ (*left*), **6** in $CDCl_3$ (*middle*), and **6** in DMSO-d_6 (*right*).

II.2.2.4. Characterization of compounds 5 and 6 by mass spectrometry

In organomercury(II) chemistry there is a specific fragmentation pattern as described earlier[88–91] resulting in two main peaks besides the molecular peak, *i.e.* the $[RHg]^+$ and the $[R_2 + H]^+$, the later obtained from the recombination of the aryl fragments.

In the APCI+ mass spectrum for compound **5** (Figure 18) two intense peaks were observed at *m/z* 299.12747 (calculated: 299.12779) corresponding to $[M - Hg + H]^+$ (or $[R_2 + H]^+$) and being the base peak (relative intensity 100%), and *m/z* 501.09848 (calculated: 501.09841) (relative intensity 27%) for $[M + H]^+$. Some low-intensity peaks were also observed and were assigned to other fragments, *i.e.* *m/z* (relative intensity, %): 211.07 (4) $[M - Hg - C_4H_7O_2]^+$, 255.10 (24) $[M - Hg - C_2H_3O]^+$, 457.07 (2) $[M - C_2H_3O]^+$.

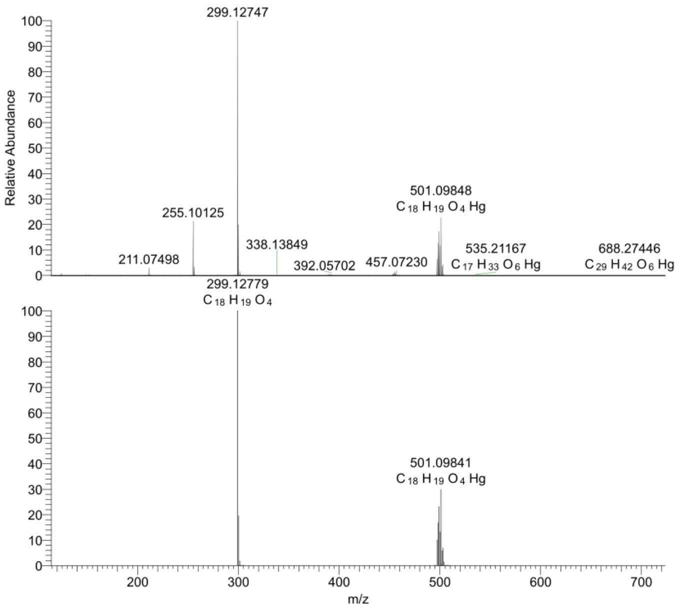


Figure 18. The APCI+ mass spectrum of **5** (*top* – observed; *bottom* – simulated).

II.2.2.5. Single crystal X-ray structure of $[4\text{-}(O{=}CH)C_6H_4]_2Hg$ (6)

The molecular structure of **6** was established by single-crystal X-ray diffraction and a representation, with the atom numbering scheme, is shown in Figure 20. Selected interatomic distances and bond angles in the molecular structure of **6** are listed in Table 6.[107]

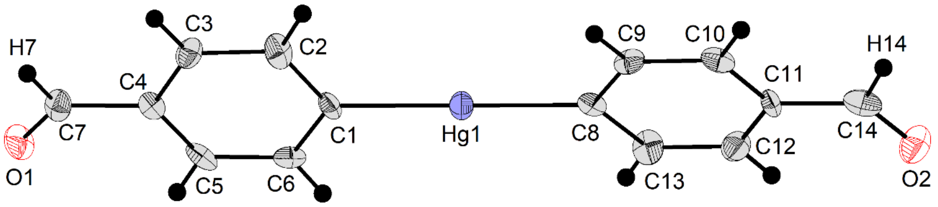
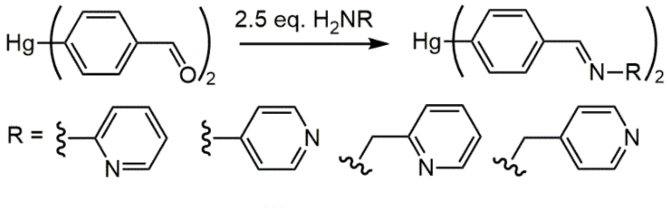


Figure 20. Thermal ellipsoid representation (40% probability) of the molecular structure of [4-(O=CH)$C_6H_4]_2Hg$ (**6**).

II.2.2.6. Synthesis of compounds 7-10

Compounds **7-10** were obtained from **6** *via* condensation reactions with the corresponding amine (Scheme 23).[107] The resulting water from the reaction was absorbed by the 4 Å molecular sieves present in the reaction vessel. All reactions were complete; however, the products are slightly water-sensitive thus some of the products decomposed back to the starting materials. To remove any starting material the obtained colorless solids were washed with anhydrous CH_2Cl_2 and MeCN.

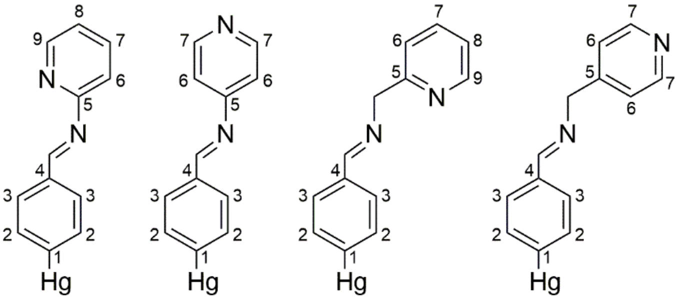


(7) **(8)** **(9)** **(10)**

Scheme 23. Synthesis of compounds **7**−**10**.

II.2.2.7. Structural characterization of compounds 7-10 by NMR spectroscopy

For compounds **7-10** the expected number of resonance signals with expected patterns were obtained in the NMR spectra in $CDCl_3$. The assignment of the proton and carbon resonances was carried out with the help of COSY, HSQC, and HMBC 2D NMR techniques according to the numbering scheme shown in Scheme 24.



(**7**) (**8**) (**9**) (**10**)

Scheme 24. The numbering scheme for compounds **7-10**.

For compound **7** the obtained pattern helps in the assignment of the resonances (Scheme 24). For H-2 we can even observe some ^{1}H-^{199}Hg coupling; however, due to overlap with resonances assigned to H-6 and H-7 protons, the coupling constant could not be exactly determined and thus was given with a standard deviation ($^{3}J_{HgH}$ 46±4 Hz). As expected, all the resonances are observed in their optimal chemical shift range with the expected multiplicity making an easy assignment for the pyridine ring protons and the phenyl ring protons(Figure 23). The remaining imine proton (−C*H*=N−) could be easily assigned to the most deshielded resonance at δ 9.16 ppm, as expected.

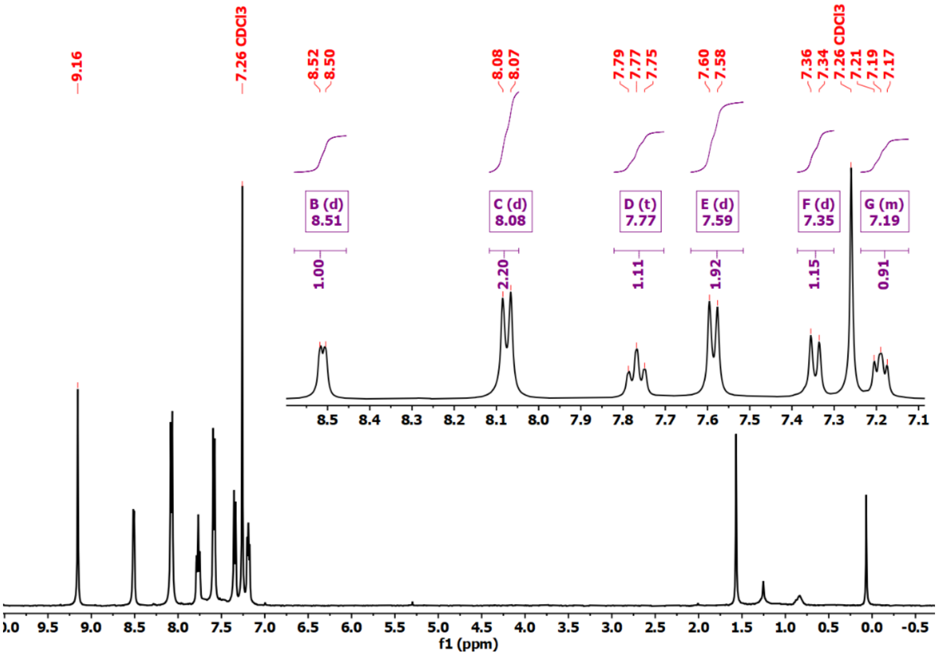


Figure 23. The ^{1}H NMR spectrum of compound **7** in $CDCl_3$.

In the $^{199}Hg\{^{1}H\}$ NMR spectra for compounds **7-10** a resonance is visible in the interval of δ (−800)-(−750) ppm, in $CDCl_3$ (Figure 31), in accordance with the literature results reported for $Hg(C_6H_4X\text{-}4)_2$ (where X = CH_3, OCH_3, F, Br, Cl, CF_3) compounds.[57] Interestingly the lowest value was observed at δ −786.58 ppm for **8** and the highest at δ −765.22 ppm for **9**. An explanation for this difference could be the Hg-imine interaction which is observed for **9** in the solid state as established by single-crystal X-ray diffraction and discussed in more detail in chapter II.4.2.9.

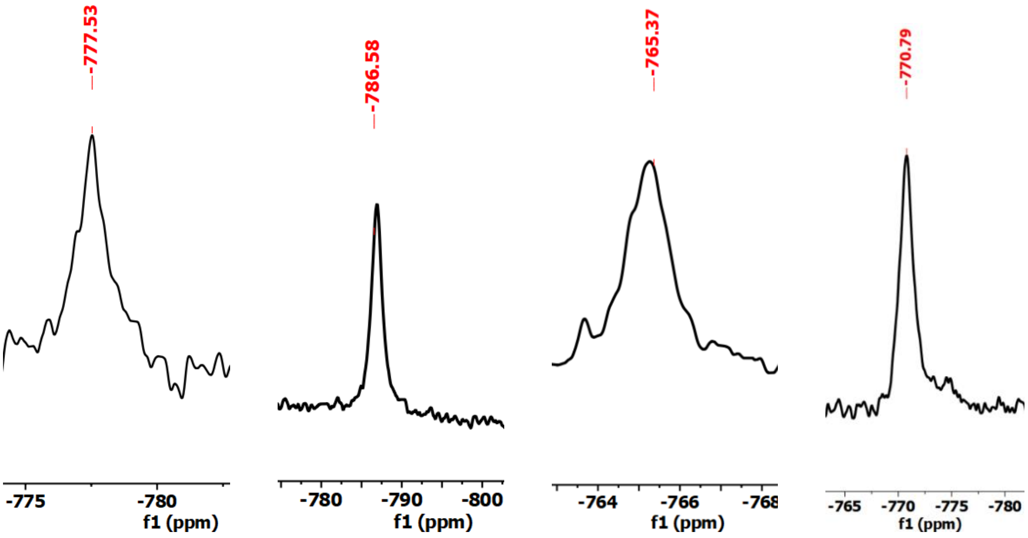


Figure 31. The ^{199}Hg{^{1}H} NMR spectra of **7** (*left*), **8** (*middle left*), **9** (*middle right*), and **10** (*right*) in $CDCl_3$.

II.2.2.9. Single crystal X-ray structure of [(*E*)-4-(4′-pyN=CH)C_6H_4]$_2$Hg·3H_2O (8·3H_2O) and [(*E*)-4-(2′-pyCH_2N=CH)C_6H_4]$_2$Hg (9)

Single crystals of compounds **8** and **9** were obtained from solutions in CH_2Cl_2 and $CHCl_3$, respectively, by slow evaporation of the solvent in open atmosphere.

The molecular structure of [(*E*)-4-(4′-pyN=CH)C_6H_4]$_2$Hg·3H_2O (**8**·3H_2O), with the atom numbering scheme, is depicted in Figure 36. (the disordered water molecules are not shown), and selected interatomic distances and bond angles are listed in Table 8. As for compound **6**, the Hg−C bond lengths are in agreement with the literature data range (2.06-2.15 Å)[110] for diarylmercury(II) compounds.

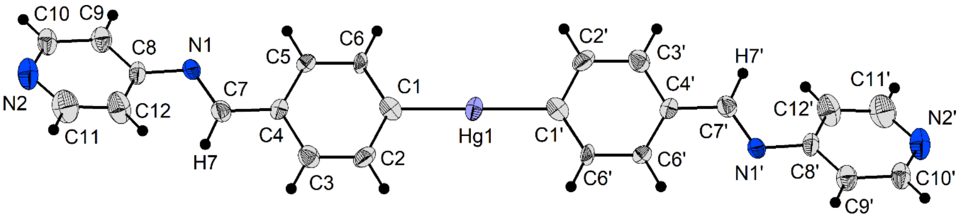


Figure 36. The molecular structure of [(*E*)-4-(4′-pyN=CH)C_6H_4]$_2$Hg·3H_2O (**8**·3H_2O), with thermal ellipsoids drawn at 40% probability.[107]

The molecular structure of [(*E*)-4-(2′-pyCH_2N=CH)C_6H_4]$_2$Hg (**9**), with the atom numbering scheme, is depicted in Figure 40 and selected interatomic distances and bond angles are listed in Table 8. Again, the geometry of the Ar_2Hg skeleton was found to be planar as in the molecule of the related compound **8**, but however the pyridine rings are switched almost orthogonal with respect to the plane of the Ar_2Hg backbone (for dihedral angles, see Figure 12), thus giving a hook-like structure.

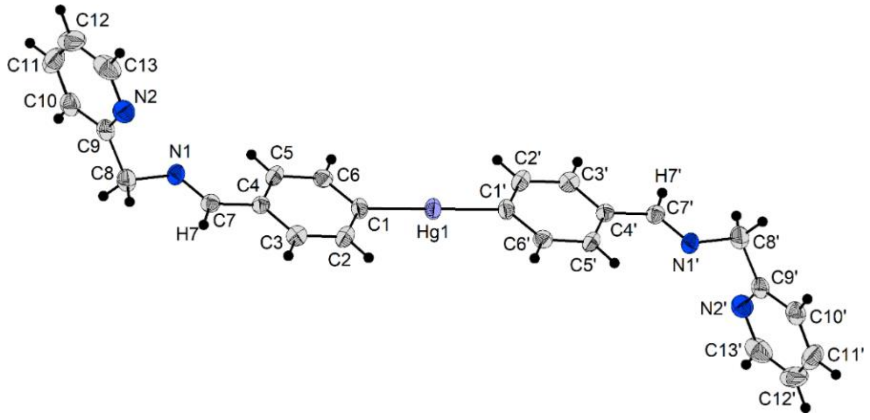


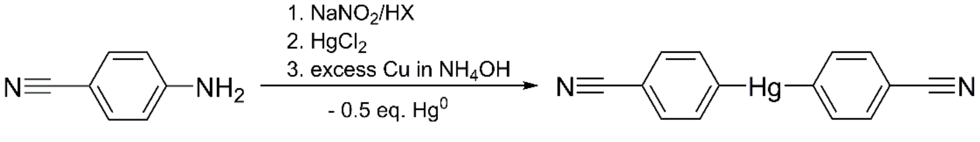
Figure 40. The molecular structure of [(*E*)-4-(2′-pyCH_2N=CH)C_6H_4]$_2$Hg (**9**), with thermal ellipsoids drawn at 40% probability.[107]

In contrast to the related compound **8**, no Hg···π or other interactions between heavy atoms are present in the crystal of **9**.

II.2.3. [4-(N≡C)C_6H_4]$_2$Hg (11) - a potential organometallic, linear neutral linker for coordination polymer networks

II.2.3.1. Synthesis of [4-(N≡C)C_6H_4]$_2$Hg (11)

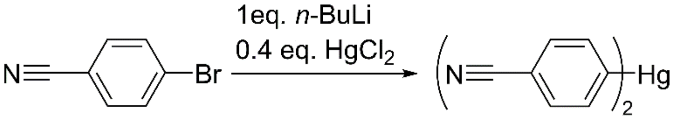
Compound **11** was already reported in the literature[40] as a useful reagent for transmetallation of the organic substituent from mercury(II) to platinum(II) (Scheme 25).



(**11**)

Scheme 25. The Nesmeyanov's method for the synthesis of **11**.

The metalation of 4-bromobenzonitrile was a problematic endeavor due to the side reaction that can occur at the nitrile group. This is well discussed in the literature.[116] The tetrahedral tecton [4-(N≡C)C_6H_4]$_4$Si was first synthesized in moderate yield,[117] by a temperature-controlled reaction in anhydrous THF, at −100 °C. This method was adapted for the synthesis of compound 11(Scheme 26).

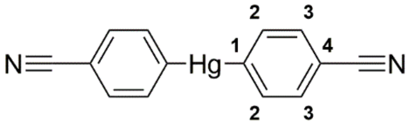


(**11**)

Scheme 26. Synthesis of [4-(N≡C)C_6H_4]$_2$Hg (**11**).

II.2.3.2. Structural characterization of compound 11 by NMR spectroscopy

Compound **11** has a lower-than-normal solubility in common organic solvents. To check the purity of the isolated compound, a ^{1}H NMR spectrum was taken in $CDCl_3$ (Figure 44). However, for its full characterization by ^{1}H, ^{13}C and ^{199}Hg NMR spectroscopy, a solution in DMSO-d_6 was utilized. The numbering scheme used for NMR assignments in this case is shown in Scheme 27.



Scheme 27. Numbering scheme for compound **11**.

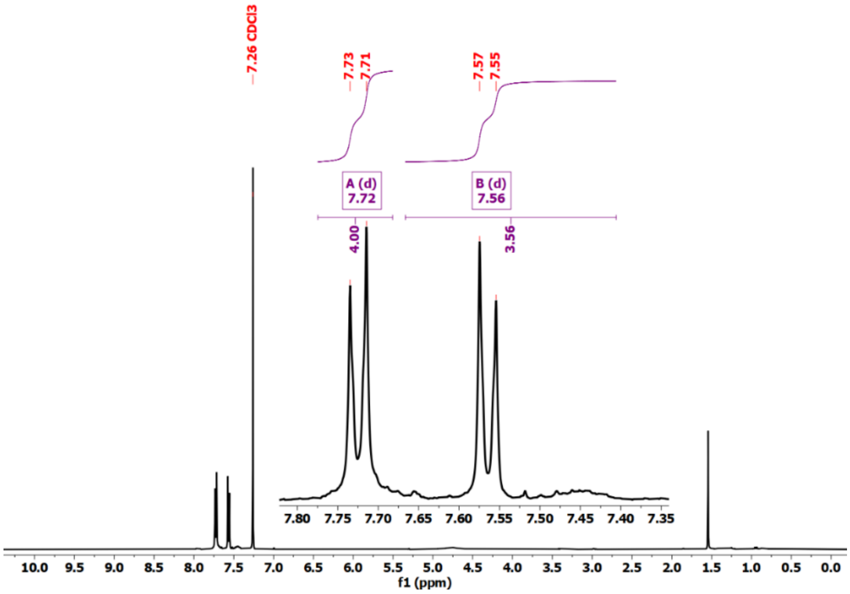


Figure 44. The ^{1}H NMR spectrum of compound **11** in $CDCl_3$.

In the ^{1}H NMR spectrum in $CDCl_3$ two, well-defined, doublets are visible, with no impurities (Figure 45). Some Hg coupling is visible; however, it is not well defined.

In the ^{199}Hg{^{1}H} NMR spectrum in DMSO-d_6 the ^{199}Hg resonance was observed at δ −934.5 ppm (Figure 46), with a value in the range of ^{199}Hg chemical shifts for other diarylmercury(II) compounds reported in the literature.[57]

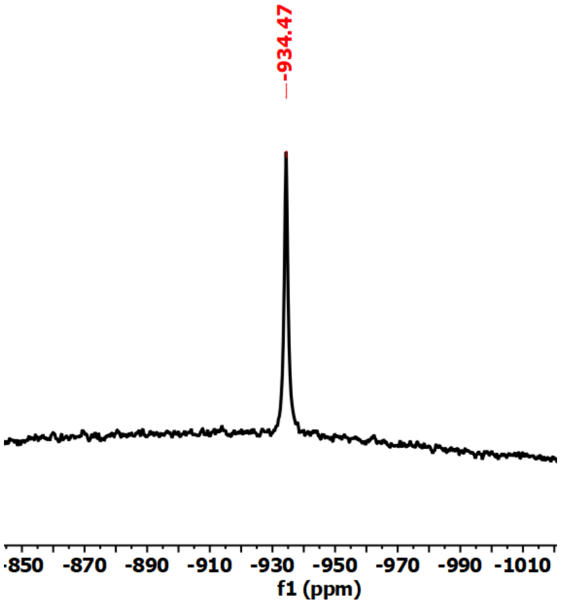


Figure 46. The ^{199}Hg{^{1}H} NMR spectrum of compound **11** in DMSO-d_6.

II.2.3.3. Single crystal X-ray structure of $[4\text{-}(N{\equiv}C)C_6H_4]_2Hg$ (11)

Single crystals of **11** were obtained from both acetone and acetonitrile *via* slow evaporation. The C−Hg bond lengths and the C−Hg−C bond angle (Table 10) observed in the molecular structure of **11** (Figure 48) are unspectacular and are in the range of those reported for other diarylmercury(II) compounds.

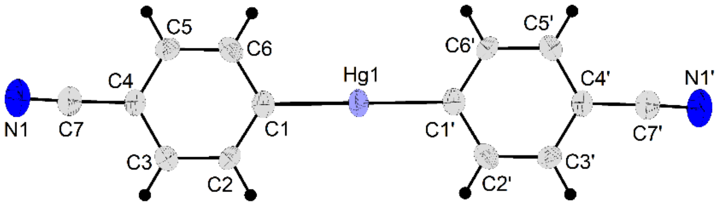


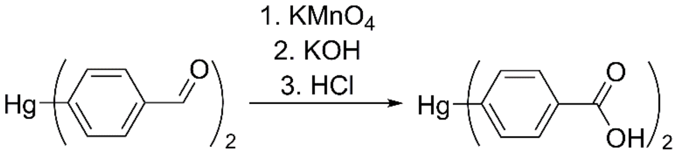
Figure 48. ORTEP structure of compound **11** [symmetry equivalent atoms (–x, –y, –z) are given by “prime”].

II.2.4. [4-{HO(O)C}$C_6H_4]_2$Hg (13) - a precursor of potential organometallic, linear anionic linker for coordination polymer networks

II.2.4.1. Synthesis of [4-{HO(O)C}$C_6H_4]_2$Hg (13) and its potassium salt (14)

This subchapter focuses on the results obtained in the synthesis and characterization of [4-{HO(O)C}$C_6H_4]_2$Hg (**13**). The first synthetic approach attempted was the methyl oxidation in the (4-Me$C_6H_4)_2$Hg (**12**), the second is based on the hydrolysis of the nitrile groups in [4-(N≡C)$C_6H_4]_2$Hg (**11**) and, lastly, the oxidation of the formyl group of [4-(O=CH)$C_6H_4]_2$Hg (**6**).

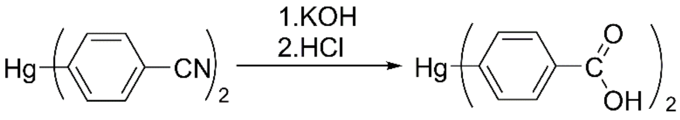
Compound **6** was subjected to the general, moderate oxidation method in an acetone-water 1:1 mixture with $KMnO_4$ as oxidant (Scheme 31). Compound **13** was obtained in a very good yield.



(**6**) (**13**)

Scheme 31. Synthesis of **13** *via* oxidation of **6**.

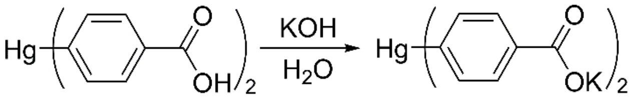
In parallel, another method was investigated for the synthesis of **13**. This method was based on literature data[122] via the hydrolysis of nitrile groups of [4-(N≡C)$C_6H_4]_2$Hg (**11**) (Scheme 32).



(**11**) (**13**)

Scheme 32. Synthesis of **13** *via* hydrolysis of **11**.

Indeed, the work-up of the reaction mixture for **13**, due to presence of basic conditions, afforded the isolation of [4-(KOOC)C_6H_4]$_2$Hg (**14**). Compound **14** can be also obtained by the reaction of a suspension of the free acid derivative **13** in water with aqueous solutions of KOH (Scheme 33).

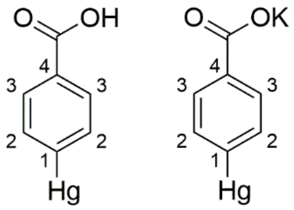


(**13**) (**14**)

Scheme 33. Synthesis of **14** *via* deprotonation of **13** with KOH.

II.2.4.2. Structural characterization of compounds 13 and 14 by NMR spectroscopy

In the ^{1}H NMR spectrum of **13**, a broad signal is visible at δ 12.76 ppm for the acidic proton and two doublet resonances at δ 7.91 and δ 7.71 ppm for the H-3 and H-2 protons (Figure 54). In the ^{199}Hg NMR spectrum, a singlet resonance is observed δ −863.8 ppm in accordance with the literature result of a resonance at δ −800 ppm for Ph_2Hg[57] with a less than 100 ppm deshielding for (4-$CF_3C_6H_4$)$_2$Hg (Figure 56).



(**13**) (**14**)

Scheme 34. ^{1}H and ^{13}C NMR numbering scheme for compounds **13** and **14**.

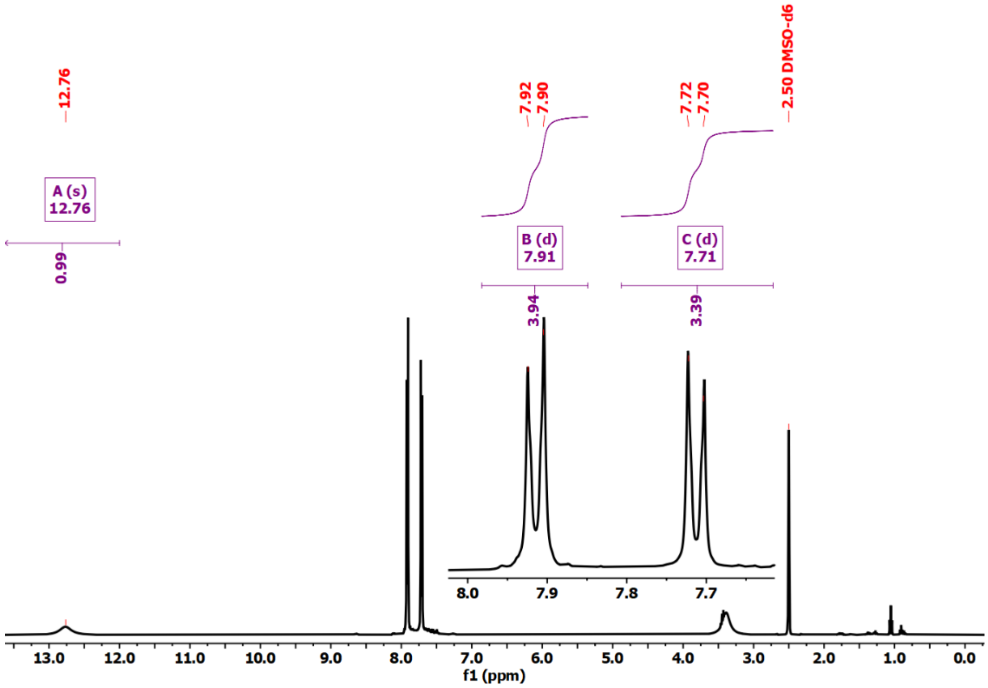


Figure 54. The ^{1}H NMR spectrum of compound **13** in DMSO-d_6.

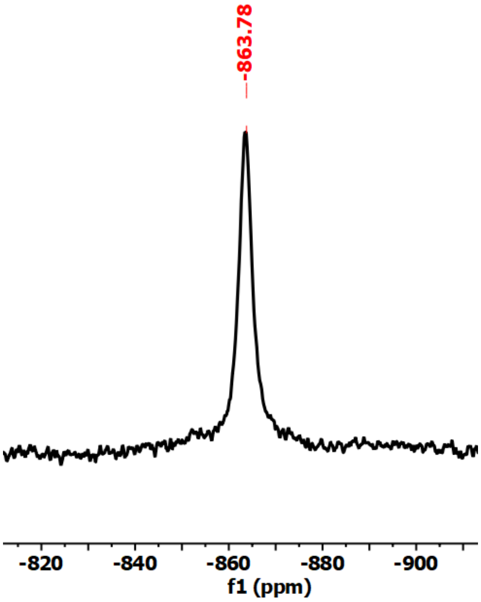


Figure 56. The $^{199}Hg\{^{1}H\}$ NMR spectrum of compound **13** in DMSO-d_6.

Compound **14** is soluble only in water; thus, its ^{1}H and ^{13}C NMR spectra were measured in D_2O. In the ^{1}H NMR spectrum of the potassium salt **14** the two doublets are visible (Figure 57), while five singlet resonances with intensities as expected, are observed in its ^{13}C NMR spectrum (Figure 58).

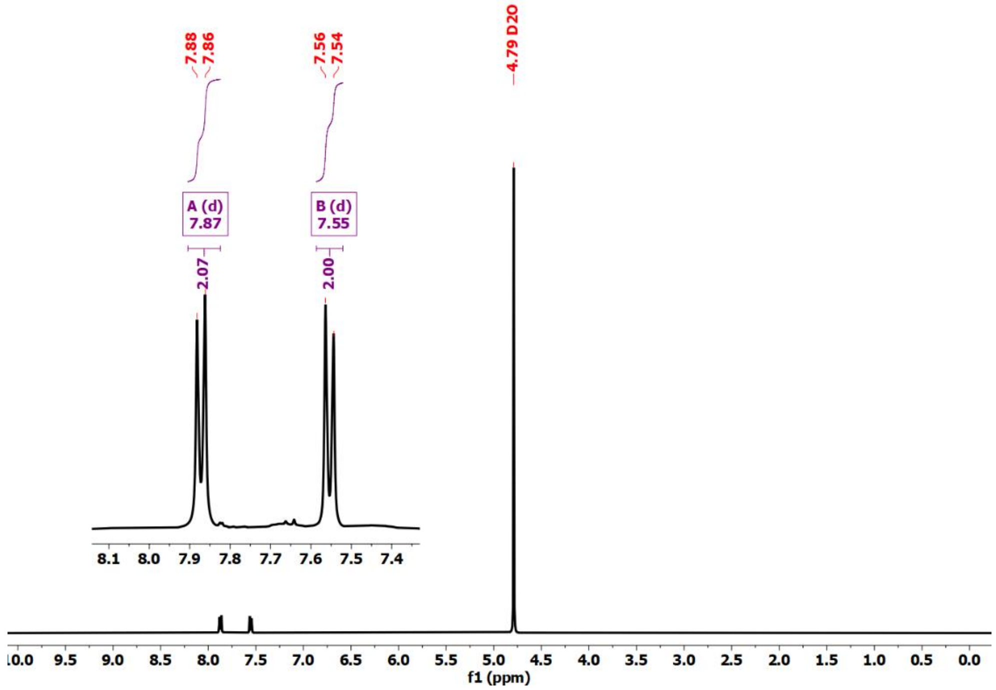


Figure 57. The ^{1}H NMR spectrum of compound **14** in D_2O.

The $^{199}Hg\{^{1}H\}$ NMR spectrum of compound **14** in D_2O exhibits a singlet resonance at −855.2 ppm, with less than 10 ppm deshielding compared with the chemical shift (δ −863.8 ppm) of the resonance in the corresponding **13** derivative, as shown in Figure 59.

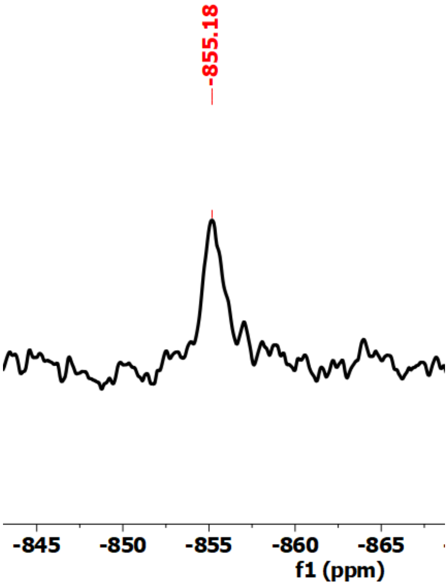


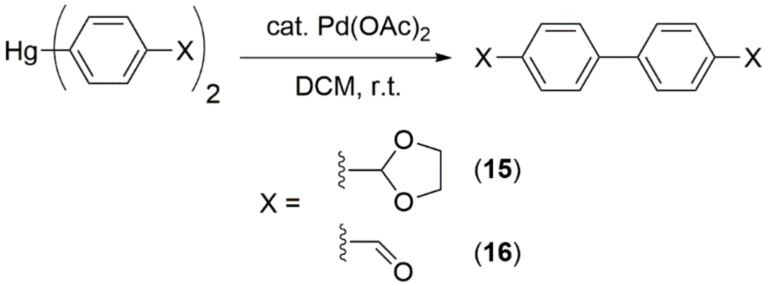
Figure 59. The $^{199}Hg\{^{1}H\}$ NMR spectrum of compound **14** in D_2O.

II.2.5. Coordination *vs* transmetallation *vs* C−C homocoupling reactions

When organometallic linkers are used to connect metal cations or metal centers from particular inorganic or organometallic nodes the possibility of transmetallation must be taken into consideration. Organomercurials were used as transmetallating reagents due to their tendency to transfer one or even two organic groups to other transition metals or metalloids.[123,124] They are mostly used to transfer aryl groups to Pt,[40,125] Au,[123,125,126] and Te,[64] etc.[126–133] Some examples exist in the literature where organomercurials are used as starting material to obtain organic compounds[134,135] in the presence of catalytic rhodium,[136] palladium,[137–140] platinum[141] or copper reagents.[142,143] In these cases is generated either a homocoupled product (R−R) or heterocoupled derivative (R−R′).[138]

II.2.5.1. Synthesis of [4-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_2$ (15) and [4-(O=CH)C$_6$H$_4$]$_2$ (16) as homocoupling products

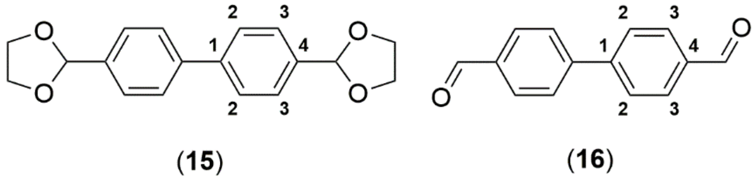
Both [[4-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_2$Hg (**5**) and [4-(O=CH)C$_6$H$_4$]$_2$Hg (**6**) were mixed in dichloromethane, at room temperature, with a catalytic amount of palladium(II) acetate (Scheme 35). These reaction mixtures were worked up after stirring overnight, protected from light, and the main products were isolated in good yields.



Scheme 35. Homocoupling reactions affording [4-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_2$ (**15**) and [4-(O=CH)C$_6$H$_4$]$_2$ (**16**).

II.2.5.2. Spectroscopic characterization of compounds 15 and 16 by NMR spectroscopy

In these reactions, the two main products were the homocoupling products Ar−Ar. The atom numbering schemes used for NMR resonance assignments are shown in Scheme 36.



Scheme 36. The numbering scheme for compound **15** and **16**.

In the case of both compounds, the corresponding number of resonances were observed with the expected multiplicities. Compound **16** was already reported in the literature thus the obtained results could be compared with the literature data.[145,146] These obtained results (for ^{1}H NMR see Figure 61 and Figure 62) were compared with the ones published in the meantime by Garago *et al*. in 2020.[150]

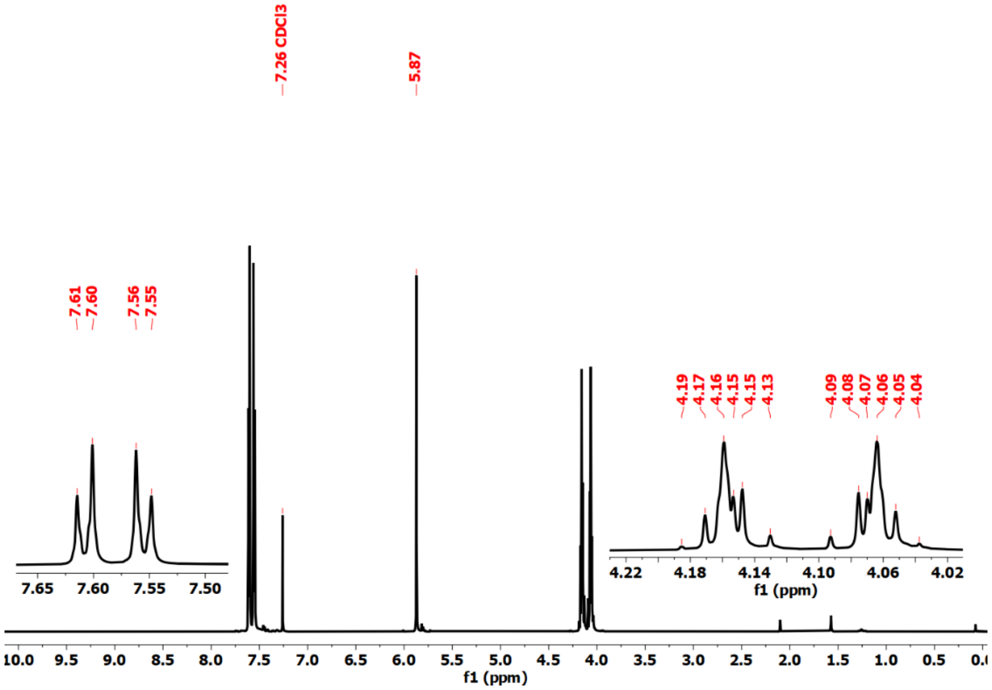


Figure 61. The ^{1}H NMR spectrum of **15**, in CDCl$_3$.

Interestingly for **15,** all resonances are more deshielded then for the diarylmercury(II) precursor **5** or even the aryl bromide **4**. The resonance for H-3 protons appeared at δ 7.61 ppm in the case of **15**, whereas equivalent resonances were observed at δ 7.56 ppm for **5** and at δ 7.51 ppm in the case of the aryl bromide **4**. The same order of magnitude can be observed for the resonances of aliphatic $-\mathrm{C}H(\mathrm{OCH_2})_2$ protons, *i.e.* values of δ 5.87 ppm, 5.82 ppm, and 5.77 ppm for **15**, whereas equivalent resonances were observed at δ 7.56 ppm for **15**, **5** and aryl bromide **4**, respectively.

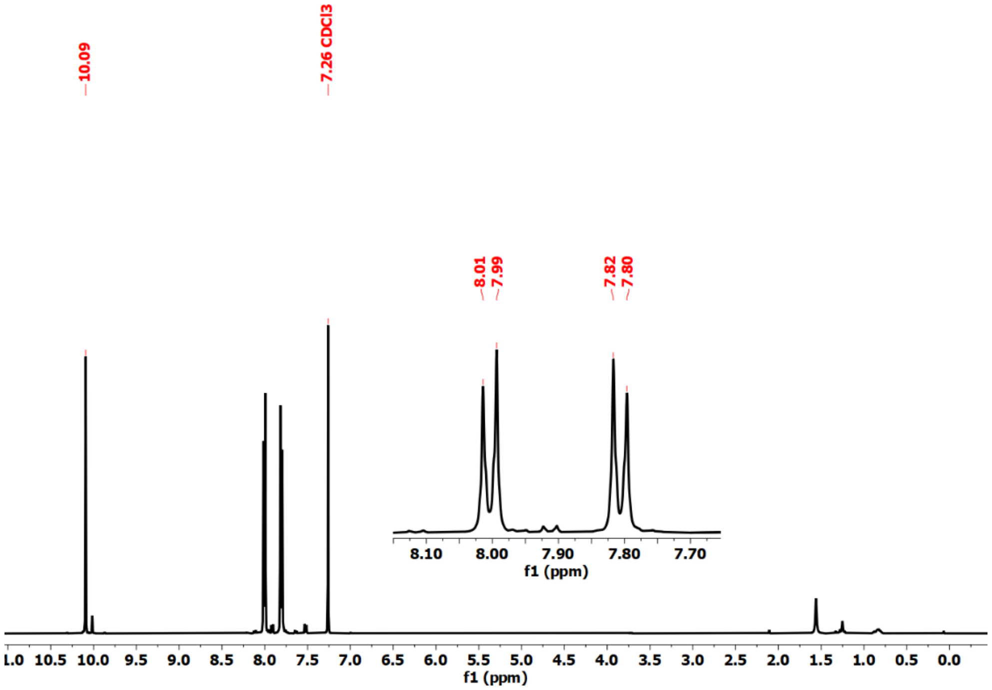


Figure 62. The ^{1}H NMR spectrum of **16**, in $CDCl_3$.

Compound **16** has the expected number of resonances following the pattern observed before whereas the pure organic product exhibits more deshielded resonances then the diarylmercury(II) compound **6**.

II.2.5.4. Single crystal X-ray structure of $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_2$ (15) and $[4\text{-}(O{=}CH)C_6H_4]_2$ (16)

Four independent molecules can be observed in the crystal structures of **15** (numbered as **15a**, **15b**, **15c** and **15d**) connected by intermolecular C–H···O interactions ranging from 2.31 to 2.51 Å, well under the 2.7 Å value for the sum of the Van der Waals radii of of the corresponding atoms (Σr_{vdW}(O,H) 2.70 Å).[103] The ORTEP representation of molecule **15a** is depicted in Figure 67.

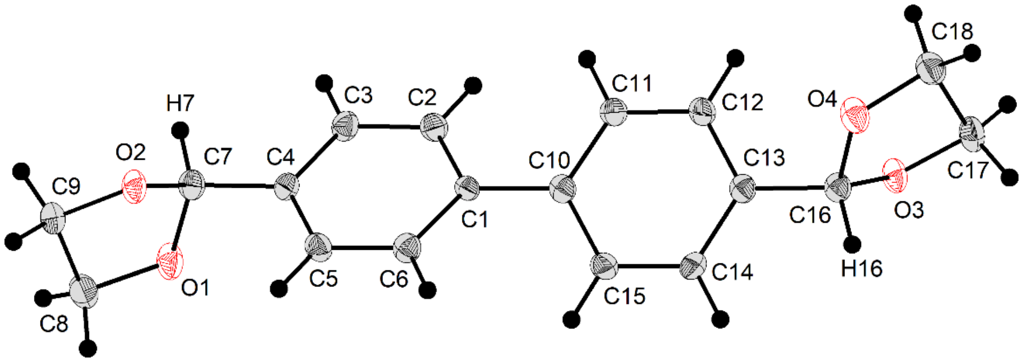


Figure 67. Thermal ellipsoid representation (40% probability) of the molecular structure of $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_2$ (**15a**).

The molecular structure of **16** is depicted in Figure 69. The lack of the mercury atom in **16** eliminated the possibility of intermolecular Hg···O interactions, as observed in the crystal **6**; thus the main interactions are $C{-}H_{\mathrm{carbonyl}}\cdots O$ hydrogen bonds [$C(14b){-}H(14b)_{\mathrm{carbonyl}}\cdots O(1)$ 2.44 Å] resulting in a chain polymer (Figure 70).

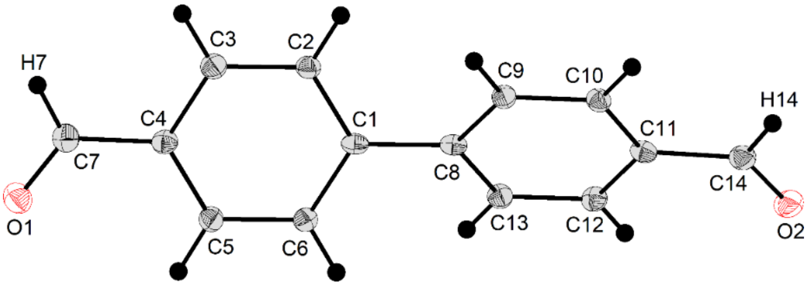
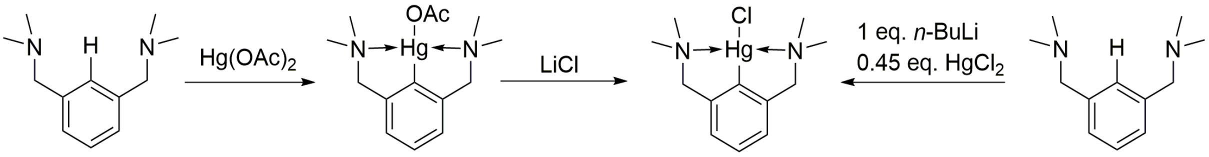


Figure 69. Thermal ellipsoid representation (40% probability) of the molecular structure of $[4\text{-}(O{=}CH)C_6H_4]_2$ (**16**).

II.2.6. Potential organometallic nodes – RHgX [R = 2,6-$(Me_2NCH_2)_2C_6H_3$; X = OAc (17), Cl = (18)]

II.2.6.1. Synthesis of [2,6-$(Me_2NCH_2)_2C_6H_3$]HgOAc (17) and [2,6-$(Me_2NCH_2)_2C_6H_3$]HgCl (18)

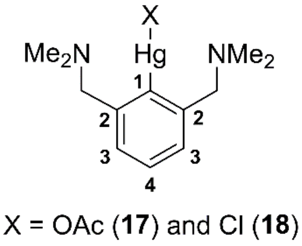
The direct mercuration of the hydrocarbon with mercury(II) acetate resulted in [2,6-$(Me_2NCH_2)_2C_6H_3$]HgOAc (**17**) in a one-step reaction with good yield (Scheme 38). The chloride (**18**) was obtained by the literature method[152] employing the organolithium reaction with $HgCl_2$ and also by an exchange reaction with LiCl.



Scheme 38. Synthesis of compounds [2,6-$(Me_2NCH_2)_2C_6H_3$]HgX [X = OAc (**17**), Cl (**18**)].

II.2.6.2. Structural characterization of compounds 17 and 18 by NMR spectroscopy

The atom numbering scheme for the NMR resonances assignment for **17** and **18** is shown in Scheme 40. The ^1H and ^{13}C NMR spectra of both compounds are almost identical (see Figure 72 to Figure 75).



Scheme 40. ^1H and ^{13}C NMR numbering scheme for compounds 17 and **18**.

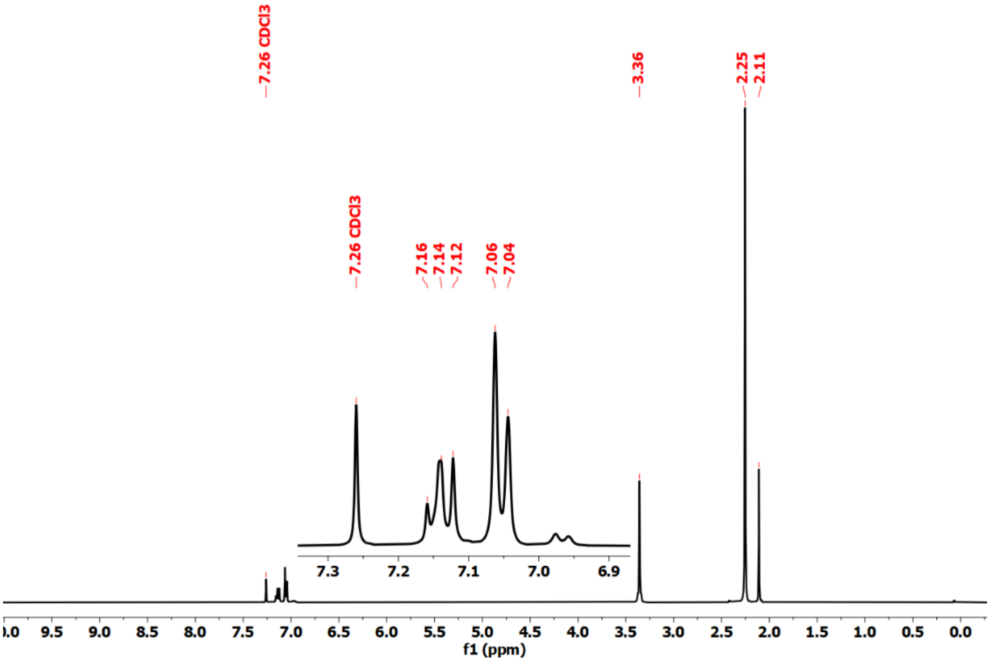


Figure 72. The ^{1}H NMR spectrum of compound **17** in $CDCl_3$.

A huge difference could be observed in the ^{199}Hg NMR chemical shifts observed for the two compounds (Figure 76).

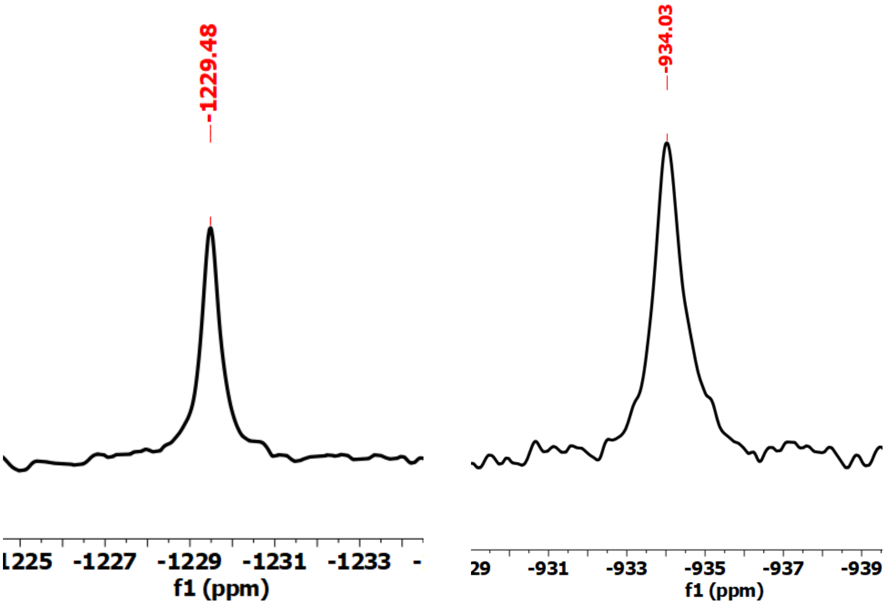


Figure 76. The $^{199}Hg\{^{1}H\}$ NMR spectra of compounds **17** (left) and **18** (right) in $CDCl_3$.

II.2.6.3. Single crystal X-ray structure of [2,6-$(Me_2NCH_2)_2C_6H_3$]HgOAc (17) and [2,6-$(Me_2NCH_2)_2C_6H_3$]HgCl (18)

For both **17** and **18** single crystals were obtained *via* slow evaporation of pentane (**17**) and diethyl ether or acetone (**18**) solutions, and their molecular and crystal structures were established by single-crystal X-ray diffraction.

For both compounds **17** and **18** the C−Hg−O and C−Hg−Cl bonds have an almost perfect linear arrangement with a deviation less than 5° in all cases (C–Hg–O 178.3(2)° for **17**, and C–Hg–Cl 179.4(6) / 176.7(5)° for molecules **18A** / **18B**). Also both nitrogen atoms are strongly coordinated to the Hg atom as expected for *N,C,N*-pincer type ligands(Figure 77).

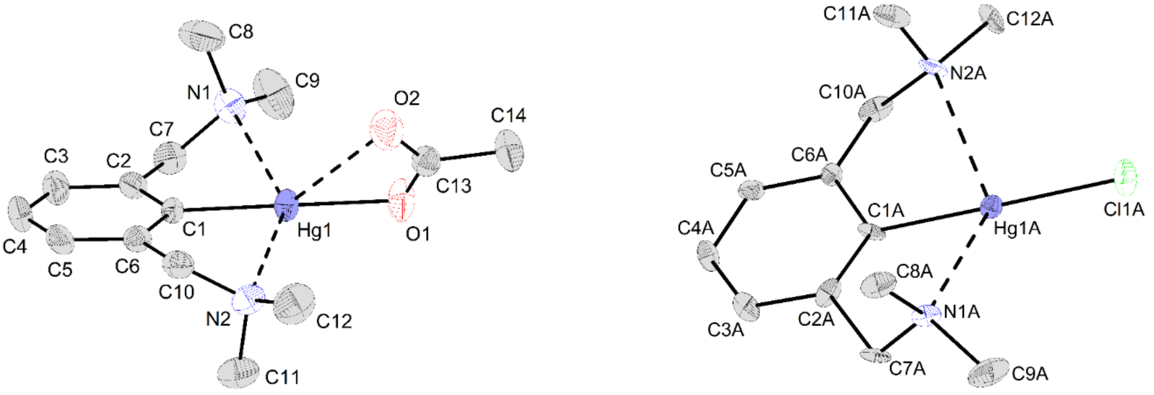


Figure 77. ORTEP structure of compounds **17** (*left*) and **18** (*right*), with 50% probability.

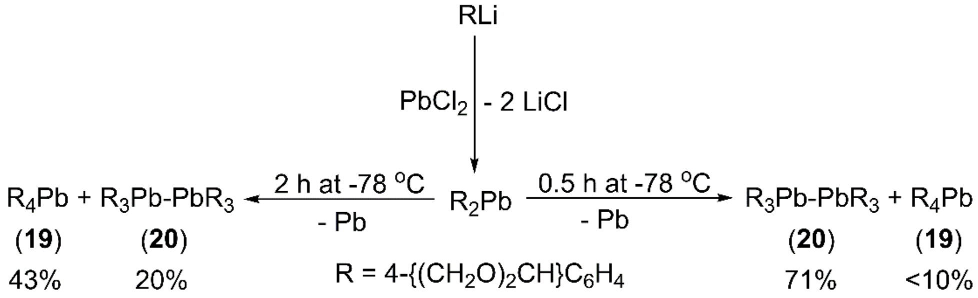
III. Organolead(IV) chemistry

III.2. Original contributions to organolead(IV) chemistry

A series of new tetraorganolead(IV), R_4Pb, and a diplumbane, $R_3Pb{-}PbR_3$, bearing aryl rings with functional groups in *para* position, were synthesized as potential tetrahedral or prismatic organometallic tectons to be used as starting materials in the preparation of 3D coordination polymers.

III.3.1. Synthesis of compounds $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_4Pb$ (19), $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_6Pb_2$ (20), $[4\text{-}(N{\equiv}C)C_6H_4]_4Pb$ (21), $[4\text{-}(O{=}CH)C_6H_4]_4Pb$ (22) and $[4\text{-}\{HO(O)C\}C_6H_4]_4Pb$ (23)

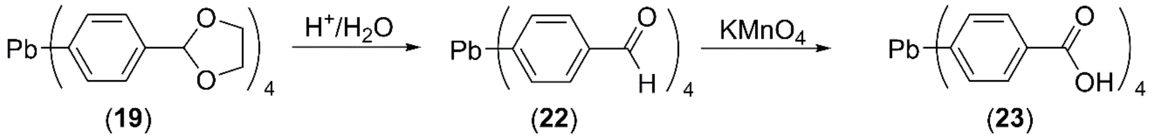
The dioxolane proligand $Br\text{-}4\text{-}C_6H_4CH(OCH_2)_2$ (**4**) was reacted with *n*-BuLi, at low temperature, and the resulting organolithium derivative was treated with $PbCl_2$ to obtain $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_4Pb$ (**19**) (Scheme 41). The reaction was carried out and worked up similarly to **5**; however, the expected compound **19** was obtained only in a moderate yield of 43%. This resulted in an in-depth analysis of the side-products. Surprisingly, about 20% of the total Pb was recovered as a diplumbane species, $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_6Pb_2$ (**20**), and less than 10% (cumulated) as $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_2Pb(n\text{-}Bu)_2$ and $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_3Pb(n\text{-}Bu)$, respectively, in total (percentages calculated from the ^1H NMR spectrum, recorded in $CDCl_3$ for a crude reaction mixture).



Scheme 41. Synthesis of compounds **19** and **20**.

Compound [4-(N≡C)C_6H_4]$_4$Pb (**21**) was obtained from the corresponding aryllithium reagent and the lead(II) chloride. The obtained crude product was fractionally crystallized from various solvents to the desired product in acceptable yield (36%, calculated based on Pb).

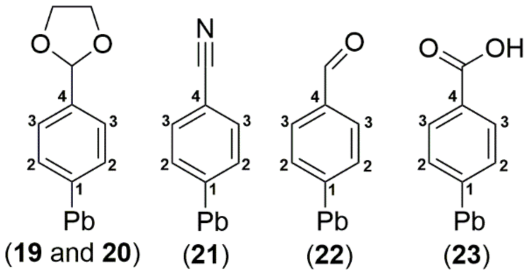
Compounds [4-(O=CH)C_6H_4]$_4$Pb (**22**) and [4-{HO(O)C}C_6H_4]$_4$Pb (**23**) were obtained by the methods previously discussed for **3** and **14**. Using the dioxolane **19**, the protecting groups were removed in a THF/H_2O mixture with *p*-TolSO$_3$H and purified by recrystallization from a CH_2Cl_2/hexane solution of the crude material. The obtained solid was washed with acetone to remove unreacted starting materials to afford [4-(O=CH)C_6H_4]$_4$Pb (**22**). The acid [4-{HO(O)C}C_6H_4]$_4$Pb (**23**) was obtained in good yield by the mild oxidation of the aldehyde **22** (Scheme 42) in a water/acetone mixture using $KMnO_4$ as oxidizing agent.



Scheme 42. Synthesis of compounds **22** and **23**.

III.3.1.1. Spectroscopic characterization of compounds 19-23 by NMR spectroscopy

The assignments of the resonances for compounds **19-23** in the ^{1}H, ^{13}C, and ^{207}Pb NMR spectra were made according to the numbering scheme depicted in Scheme 43.



Scheme 43. Numbering scheme for compounds **19-23**.

In the ^{1}H NMR spectra of the compounds **19-23** (Figure 83), ^{207}Pb satellites were observed only the ortho (H-2) and the meta aromatic protons (H-3). It should be mentioned here that the magnitude of the $^{2}J(^{1}\text{H}-^{207}\text{Pb})$ and $^{1}J(^{13}\text{C}-^{207}\text{Pb})$ coupling constants are extremely useful in the assignments of the resonances observed in the ^{1}H NMR and ^{13}C{^{1}H} NMR spectra, respectively.

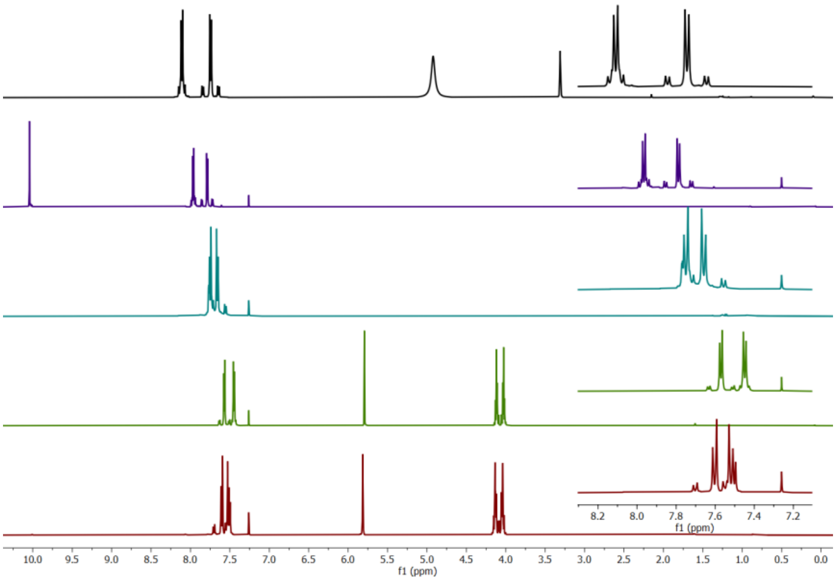


Figure 83. ^{1}H NMR spectra of compounds **19-22** in $CDCl_3$ and **23** in MeOH-d_4 (**19** bottom, **23** top).

The ^{207}Pb{^{1}H} NMR spectra (Figure 85) were recorded for compounds **19**, and **21-23**. All results are in accordance with literature values of 180 ± 20 ppm for R_4Pb (where R is an aryl group) compounds.[184,202,203] The highest value for the chemical shift of the ^{207}Pb resonance was obtained for **19** at δ −171.6 ppm, followed by δ −176.1 ppm for **21**, δ −181.7 ppm for **20**, and δ −186.7 ppm for **23**.

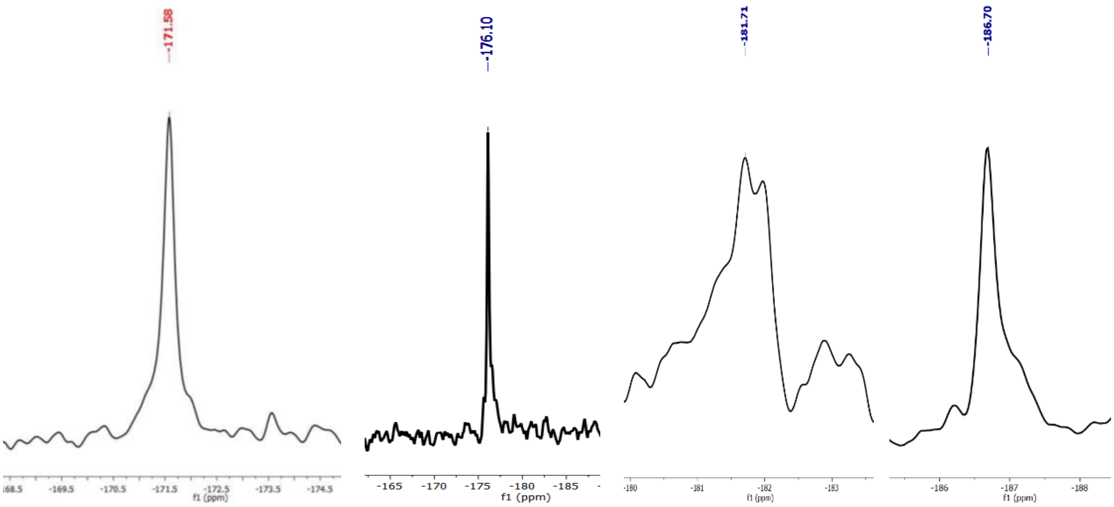


Figure 85. ^{207}Pb{^{1}H} NMR spectra of compounds **19** (left), **21**, and **22** (middle left and right) in $CDCl_3$, and **23** in MeOH-d_4 (right).

The molecular structures of compounds **19** and **20** are shown in Figure 87.

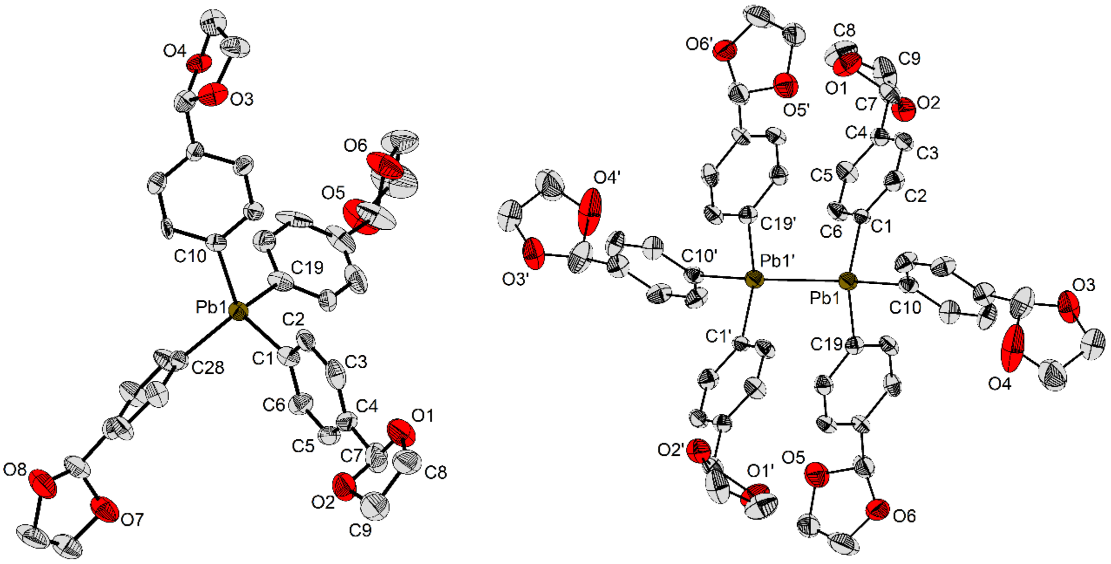


Figure 87. Thermal ellipsoid representation (40% probability) of the molecular structure of **19** (*left*) and **20** (*right*).

III.3.1.4. Single crystal X-ray structure of compounds 21 and 22

The single crystal structure of **21** (Figure 92) has a slightly distorted tetrahedra with C-Pb-C angles in the interval of 105-112° as seen in Figure 92. The C-Pb bonds as seen in Table 13 are below the value of 2.22 Å associated with the sum of covalent radii for Pb-C single bond.[210] The C-N (see Table 13) bonds are also less than the value associated with the C≡N triple bond of 1.4 Å.[210] Selected interatomic distances and bond angles are presented in Table 13.

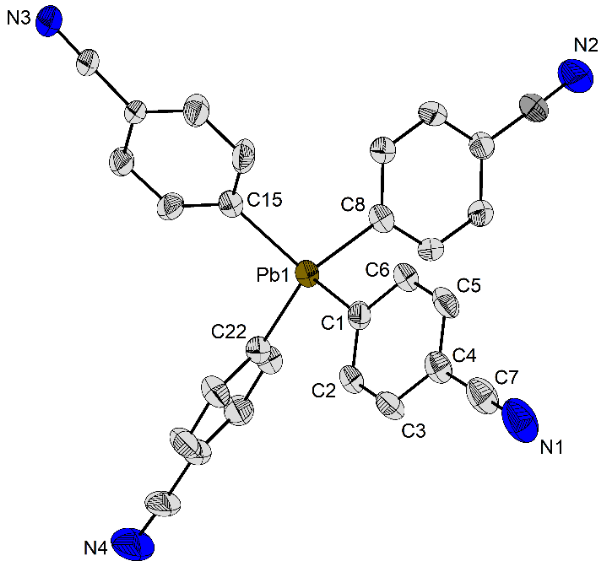


Figure 92. Thermal ellipsoid representation of the molecular structure of compound **21** (40% probability).

As already discussed for compounds **19-21**, compound **22** has a distorted tetrahedral geometry around the Pb atom with bond values and angles in the expected region.

The molecular structure of compound **23** is presented on Figure 95.

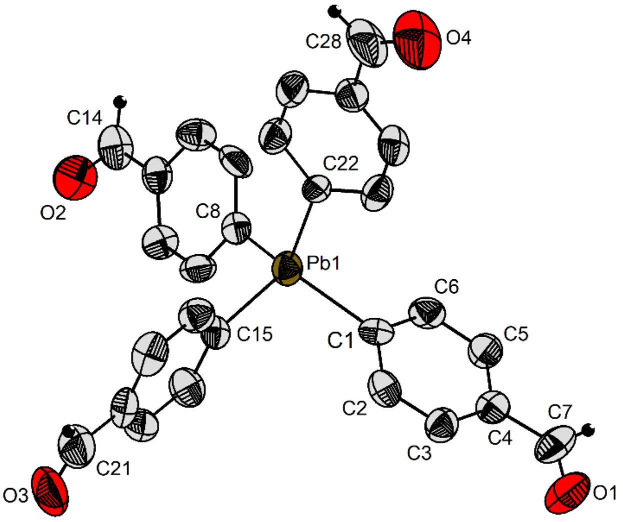


Figure 95. Thermal ellipsoid representation of the molecular structure of compound **22** (40% probability).

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