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Synthesis and Characterization of Dicarboxylate-bridged and Bisphosphine-substituted Dimolybdenum(II) Complexes as Potential Building Blocks for Supramolecular Coordination Compounds

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*„Zwanghaftes Arbeiten allein würde die Menschen ebenso verrückt
machen wie absolutes Nichtstun. Erst durch die Kombination
beider Komponenten wird das Leben erträglich.“*

Erich Fromm

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Deutsche Zusammenfassung

Durch die Reaktionen des zweikernigen Komplexes $[\text{Mo}_2(\text{NCCH}_3)_{10}][\text{BF}_4]_4$ (**1**) mit dem Linker Tetrabromoterephthalsäure in Acetonitril oder Propionitril können die dimeren Koordinationsverbindungen $[(\text{CH}_3\text{CN})_8\text{Mo}_2(\text{O}_2\text{C}-\text{C}_6\text{Br}_4-\text{CO}_2)\text{Mo}_2(\text{NCCH}_3)_8][\text{BF}_4]_6$ (**2**) und $[(\text{CH}_3\text{CH}_2\text{CN})_8\text{Mo}_2(\text{O}_2\text{C}-\text{C}_6\text{Br}_4-\text{CO}_2)\text{Mo}_2(\text{NCCH}_2\text{CH}_3)_8][\text{BF}_4]_6$ (**3**) hergestellt werden. Der dreiecksförmige Komplex $[(\text{CH}_3\text{CN})_6\text{Mo}_2(m\text{-bdc-F})_3][\text{BF}_4]_6$ (**5**) kann ausgehend von **1** und dem Linker 5-Fluoroisophthalsäure in einem molaren Verhältnis von 1:1 und Acetonitril als Lösungsmittel isoliert werden. Zudem entstehen bei den Reaktionen von **1** mit den Dicarbonsäuren Ferrocendicarbonsäure, 2,5-Thiophendicarbonsäure und Tetrafluoroterephthalsäure die tetrameren Komplexe $[(\text{CH}_3\text{CN})_4\text{Mo}_2(\text{O}_2\text{C}-\text{Fc}-\text{CO}_2)_4][\text{BF}_4]_8$, $[(\text{CH}_3\text{CN})_6\text{Mo}_2(\text{O}_2\text{C}-\text{C}_4\text{H}_2\text{S}-\text{CO}_2)_4][\text{BF}_4]_8$ (**4**) und $[(\text{CH}_3\text{CH}_2\text{CN})_4\text{Mo}_2(\text{O}_2\text{C}-\text{C}_6\text{F}_4-\text{CO}_2)_4][\text{BF}_4]_8$ (**6**). Die Verbindungen **2-6**, welche aufgrund ihrer schwach gebundenen Acetonitrilliganden als Ausgangsverbindungen für die kontrollierte Synthese von Baueinheiten für Metal-organic Frameworks dienen können, werden mittels NMR-Spektroskopie (^1H , ^{11}B , ^{13}C , ^{19}F), IR-Spektroskopie, Elementaranalyse, TG-MS-Messungen und UV-Vis-Spektroskopie charakterisiert. Die molekularen Strukturen der Produkte **2-6** werden mit Hilfe der Röntgeneinkristallstrukturanalyse aufgeklärt.

Der molekulare Ring $[(\text{CH}_3\text{CN})_6\text{Mo}_2(\text{O}_2\text{C}-\text{C}_4\text{H}_6-\text{CO}_2)]_2[\text{BF}_4]_4$ (**7**), welcher durch die äquimolare Reaktion von **1** und 1,1-Cyclobutandicarbonsäure in Acetonitril hergestellt werden kann, reagiert in Propionitril mit 2 Äquivalenten Bis(diphenylphosphino)amin (dppa), 1,2-Bis(diphenylphosphino)ethan (dppe) und Bis(diphenylphosphino)methan (dppm) zu den molekularen Ringen mit der Formel $[(\text{CH}_3\text{CH}_2\text{CN})_4(\text{X})\text{Mo}_2(\text{O}_2\text{C}-\text{C}_4\text{H}_6-\text{CO}_2)]_2[\text{BF}_4]_4$ ($\text{X} = \text{dppa}$ (**8**), dppe (**9**), dppm (**10**)). Die Isolierung der Verbindungen **8-10**, welche anhand von NMR-Spektroskopie (^1H , ^{11}B , ^{13}C , ^{19}F , ^{31}P), IR-Spektroskopie, Elementaranalyse, TG-MS-Messungen, UV-Vis-Spektroskopie und Röntgeneinkristallstrukturanalyse charakterisiert werden, beweist, dass die verbleibenden Acetonitrilliganden von **7** reaktiv bezogen auf weitere Substitutionsreaktionen sind und die anfängliche Ringstruktur beibehalten bleibt. Dies ermöglicht theoretisch eine Synthese von größeren molekularen Anordnungen ausgehend von **7**.

English Abstract

By reacting the dinuclear complex $[\text{Mo}_2(\text{NCCH}_3)_{10}][\text{BF}_4]_4$ (**1**) with the linker tetrabromoterephthalic acid in acetonitrile or propionitrile, the dimeric coordination compounds $[(\text{CH}_3\text{CN})_8\text{Mo}_2(\text{O}_2\text{C}-\text{C}_6\text{Br}_4-\text{CO}_2)\text{Mo}_2(\text{NCCH}_3)_8][\text{BF}_4]_6$ (**2**) and $[(\text{CH}_3\text{CH}_2\text{CN})_8\text{Mo}_2(\text{O}_2\text{C}-\text{C}_6\text{Br}_4-\text{CO}_2)\text{Mo}_2(\text{NCCH}_2\text{CH}_3)_8][\text{BF}_4]_6$ (**3**) can be synthesized, respectively. The triangular-shaped complex $[(\text{CH}_3\text{CN})_6\text{Mo}_2(m\text{-bdc-F})_3][\text{BF}_4]_6$ (**5**) can be isolated starting from **1** and the linking molecule 5-fluoroisophthalic acid in a molar ratio of 1:1 and acetonitrile as solvent. Furthermore, the reactions of **1** and the dicarboxylic acids ferrocenedicarboxylic acid, 2,5-thiophenedicarboxylic acid and tetrafluoroterephthalic acid in different nitrile solvents afford the tetrameric complexes $[(\text{CH}_3\text{CN})_4\text{Mo}_2(\text{O}_2\text{C}-\text{Fc}-\text{CO}_2)_4][\text{BF}_4]_8$, $[(\text{CH}_3\text{CN})_6\text{Mo}_2(\text{O}_2\text{C}-\text{C}_4\text{H}_2\text{S}-\text{CO}_2)_4][\text{BF}_4]_8$ (**4**) and $[(\text{CH}_3\text{CH}_2\text{CN})_4\text{Mo}_2(\text{O}_2\text{C}-\text{C}_6\text{F}_4-\text{CO}_2)_4][\text{BF}_4]_8$ (**6**), respectively. Characterization of compounds **2-6**, which might serve as precursors for the controlled synthesis of building blocks for metal-organic frameworks due to their remaining weakly bound nitrile ligands, is done by NMR spectroscopy (^1H , ^{11}B , ^{13}C , ^{19}F), IR spectroscopy, elemental analysis, TG-MS measurements and UV-Vis spectroscopy. The molecular structures of the products **2-6** are determined by single crystal X-ray diffraction.

The molecular loop $[(\text{CH}_3\text{CN})_6\text{Mo}_2(\text{O}_2\text{C}-\text{C}_4\text{H}_6-\text{CO}_2)]_2[\text{BF}_4]_4$ (**7**), which can be synthesized by reacting **1** and 1,1-cyclobutanedicarboxylic acid in a molar ratio of 1:1 using the solvent acetonitrile, reacts in propionitrile with 2 equivalents of bis(diphenylphosphino)amine (dppa), 1,2-bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)methane (dppm) and leads to the tetrametallic loops of the formula $[(\text{CH}_3\text{CH}_2\text{CN})_4(\text{X})\text{Mo}_2(\text{O}_2\text{C}-\text{C}_4\text{H}_6-\text{CO}_2)]_2[\text{BF}_4]_4$ ($\text{X} = \text{dppa}$ (**8**), dppe (**9**), dppm (**10**)), respectively. The isolation of compounds **8-10**, which are characterized by NMR spectroscopy (^1H , ^{11}B , ^{13}C , ^{19}F , ^{31}P), IR spectroscopy, elemental analysis, TG-MS measurements, UV-Vis spectroscopy and single crystal X-ray diffraction, proves that the remaining acetonitrile ligands of **7** are still reactive concerning further substitution reactions and the initial loop structure is maintained. This enables in theory the synthesis of larger molecular arrays starting from **7**.

List of Abbreviations

°C	Degree Celsius
Atm	Atmosphere
Bdc	Benzene-1,3-dicarboxylic acid, Isophthalic acid
BBP	Bis(bisphosphine)
BPEF	1,1'-Bis(4-pyridylethynyl)ferrocene
BP	Bisphosphine
Bipy	Bipyridine
DAniF	<i>N,N'</i> -Dianisylformamidinate
Dhtp	2,5-Dihydroxyterephthalate
Dmpm	Bis(dimethylphosphino)methane
Dppa	Bis(diphenylphosphino)amine
Dppe	1,2-Bis(diphenylphosphino)ethane
Dppm	Bis(diphenylphosphino)methane
Dppma	Bis(diphenylphosphino)methylamine
Equiv	Equivalent
h	Hour
K	Kelvin
<i>M</i> -bdc-F	<i>m</i> -Fluorobenzenedicarboxylic acid, 5-Fluoroisophthalic acid
MOF	Metal-organic framework
Mdip	5,5'-Methylene-diisophthalate
PCN	Porous coordination network
PW	Paddle-wheel
Py	Pyridine
Pz	Pyrazine
SBU	Secondary Building Unit
Tcom	Tetrakis(4-(carboxyphenyl)oxamethyl)methane
TMA	Benzene-1,3,5-tricarboxylic acid, Trimesic acid
Wt	Weight

Table of Contents

1. Introduction	13
1.1 The Metal-metal Quadruple Bond	13
1.2 Dimetal Cores in Paddle-wheel Complexes	14
1.3 Linking Possibilities of Dimetal Units	16
1.4 Dimolybdenum(II) Paddle-Wheel Complexes as a Source for the Mo ₂ ⁴⁺ Core	19
1.5 [Mo ₂ (NCCH ₃) ₁₀][BF ₄] ₄ as a Dimetal Precursor for the Synthesis of large Molecular Arrays	20
1.6 Dicarboxylate-bridged Coordination Compounds based on protected Dimolybdenum(II) Precursors	22
1.6.1 Molecular Dimolybdenum(II) Dimers	22
1.6.2 Molecular Dimolybdenum(II) Loops	23
1.6.3 Molecular Dimolybdenum(II) Triangles	23
1.6.4 Molecular Dimolybdenum(II) Squares	24
1.7 Bisphosphine Substitution of Dimolybdenum(II) based Systems	25
1.8 Metal-organic Frameworks and Selected Applications	27
1.8.1 Gas Separations in Metal-organic Frameworks based on Adsorption	27
1.8.2 Hydrogen Storage in Metal-organic Frameworks	28
1.8.3 Catalytic Activity of Metal-organic Frameworks	30
2. Objective	32
3. Results – Summaries of Publications	33
3.1 Synthesis and Characterization of Dimeric and Square-shaped Dicarboxylate-bridged Dimolybdenum(II) Coordination Compounds	33
3.2 Synthesis and Characterization of Dimolybdenum(II) Complexes Connected by Carboxylate Linkers	35
3.3 Loop shaped Dicarboxylate-bridged Dimolybdenum(II) Bisphosphine Compounds – A Rational Synthesis	37
3.4 Reprint Permissions	39
3.4.1 Elsevier Article	39
3.4.2 ACS Article	46
3.4.3 RSC Article	47
4. Bibliographic Data of Published Articles	48
4.1 Synthesis and Characterization of Dimeric and Square-shaped Dicarboxylate-bridged Dimolybdenum(II) Coordination Compounds	48

4.2 Synthesis and Characterization of Dimolybdenum(II) Complexes Connected by Carboxylate Linkers	48
4.3 Loop shaped Dicarboxylate-bridged Dimolybdenum(II) Bisphosphine Compounds – A Rational Synthesis	49
5. Summary and Outlook	50
6 References	53
7. List of Publications and Curriculum Vitae.....	57
7.1 List of Publications	57
7.2 Presentation	57
7.3 Curriculum Vitae	58

1. Introduction

1.1 The Metal-metal Quadruple Bond

A large number of M_2^{n+} compounds featuring multiply bonded M_2^{n+} subunits is known in literature. Since d-orbitals or orbitals with a higher quantum number are necessary for the formation of a metal-metal quadruple bond, only transition metals are qualified. Because of symmetry reasons, only five nonzero overlaps between two pairs of d-orbitals occur (Figure 1). A bonding σ -orbital is formed by the positive overlap of the two d_z^2 -orbitals ($d_z^2(1)+d_z^2(2)$) of the two metal centers. As a consequence, the negative overlap of these two orbitals results in an antibonding σ -orbital, $d_z^2(1)-d_z^2(2)$. The positive overlaps of the two d_{xz} - and d_{yz} -orbitals ($d_{xz}(1)+d_{xz}(2)$ and $d_{yz}(1)+d_{yz}(2)$, respectively) of the involved metals lead to two orthogonal π -bonds, whereas the negative overlap of the described orbitals generates the corresponding π^* -bonds ($d_{xz}(1)-d_{xz}(2)$ and $d_{yz}(1)-d_{yz}(2)$, respectively). Concerning the two d_{xy} -orbitals of the two involved metals, a bonding and antibonding (δ and δ^*) combination can be observed ($d_{xy}(1)+d_{xy}(2)$ and $d_{xy}(1)-d_{xy}(2)$, respectively). The $d_{x^2-y^2}$ -orbitals of each metal center mostly contribute to the bonds of the metal and the ligands, thus the impact on the metal-metal bond is negligible.¹

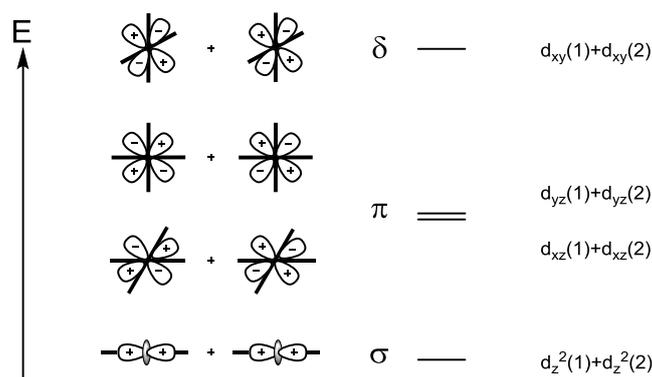


Figure 1. Positive overlaps of d-orbitals and energy levels contributing to the formation of the M-M quadruple bond (A X_4M-MX_4 structure is assumed, the order of the energy levels of the orbitals might change depending on the respective system).¹

1.2 Dimetal Cores in Paddle-wheel Complexes

Complexes featuring the so-called paddle-wheel (PW) structure of the general formula $[M_2(O_2CR)_4]$ (Figure 2) represent a well-studied type of dinuclear compounds, which often serve as precursors for further reaction steps. Each metal center exhibits an octahedral coordination sphere and four bidentate ligands, namely carboxylates, occupy the equatorial positions. A metal-metal bond can arise depending on the applied metal.²

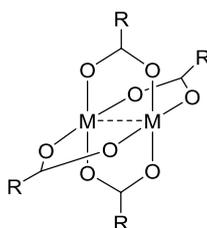


Figure 2. General structure of PW complexes of the general type $[M_2(O_2CR)_4]$.

In general, the most common oxidation states for M_2^{n+} entities are $n = 4, 5$ and 6 . The Mo_2^{4+} core having the formal electron configuration of $\sigma^2\pi^4\delta^2$ is connected by a quadruple bond, which is typically in the range of $2.06\text{--}2.12$ Å. The Rh_2^{4+} moiety is one of the main subunits arising in metal-metal bonded systems and is stabilized by a single bond with typical bond lengths in the range of $2.35\text{--}2.45$ Å. The formal electron configuration of the Rh_2^{4+} entity is $\sigma^2\pi^4\delta^2\delta^*\pi^*4$, whereat eight electrons can be found in binding orbitals and the remaining six electrons in antibonding orbitals. According to the equation $(n_b - n_a)/2$ (n_b = electrons in binding orbitals, n_a = electrons in antibonding orbitals), a bond order of 1 can be derived. The axially substituted compound $[Rh_2(O_2CCF_3)_4][Me_2SO]_2$ ³ serves as a literature known example of a dirhodium PW complex with a representative Rh–Rh length of $2.419(1)$ Å. Dirhenium containing tetracarboxylates are based on Re_2^{6+} cores with an electron configuration of $\sigma^2\pi^4\delta^2$ and therefore stabilized by a quadruple bond, as it is the case for Mo_2^{4+} based systems. Ruthenium is another metal, which forms a metal-metal multiple bond. Due to the electron configuration of $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^3$, a bond order of 2.5 leading to diruthenium tetracarboxylates with an average bond length of around 2.3 Å can be determined. The compound $[Ru_2(O_2CCH_3)_4][thf]_2$ ⁴ for example bears a PW structure and a metal-metal bond length of $2.261(3)$ Å. It is furthermore worth mentioning, as a consequence of redox chemistry, that Re_2^{4+} -, Re_2^{8+} -, Ru_2^{4+} - and Ru_2^{6+} units exist as well under certain conditions, but play a less pronounced role in the chemistry of metal-metal bonded compounds. Table 1 summarizes metals forming M_2^{n+} based carboxylates, their electron configuration and bond orders.^{1,2}

Table 1. Metals forming M_2^{n+} containing tetracarboxylates and their electron configurations and bond orders.²

Metal	<i>n</i>	Electron config.	Bond order
Cr	4	$\sigma^2\pi^4\delta^2$	4
Mo	4	$\sigma^2\pi^4\delta^2$	4
W	4	$\sigma^2\pi^4\delta^2$	4
Tc	6	$\sigma^2\pi^4\delta^2$	4
Re	6	$\sigma^2\pi^4\delta^2$	4
Ru	5	$\sigma^2\pi^4\delta^2(\delta^*\pi^*)^3$	2.5
Os	6	$\sigma^2\pi^4\delta^2(\delta^*\pi^*)^2$	3
Rh	4	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$	1
Pt	6	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$	1

1.3 Linking Possibilities of Dimetal Units

Three general possibilities to assemble metal-metal bonded entities can be distinguished. Depending on the structure of the applied linking molecules, the dimetal units can be connected with an equatorially bridging linker. Dicarboxylates, which feature four oxygen atoms as electron donating units, therefore turned out to be suitable compounds. A second possibility to connect two dimetal moieties occur via an axial linkage. Polynitriles and polypyridyls possessing N-donor atoms are prominent examples of axial linkers. The third way to obtain large molecular arrays based on dimetal units is the combination of both equatorial and axial linkers (Figure 3).^{5,6}

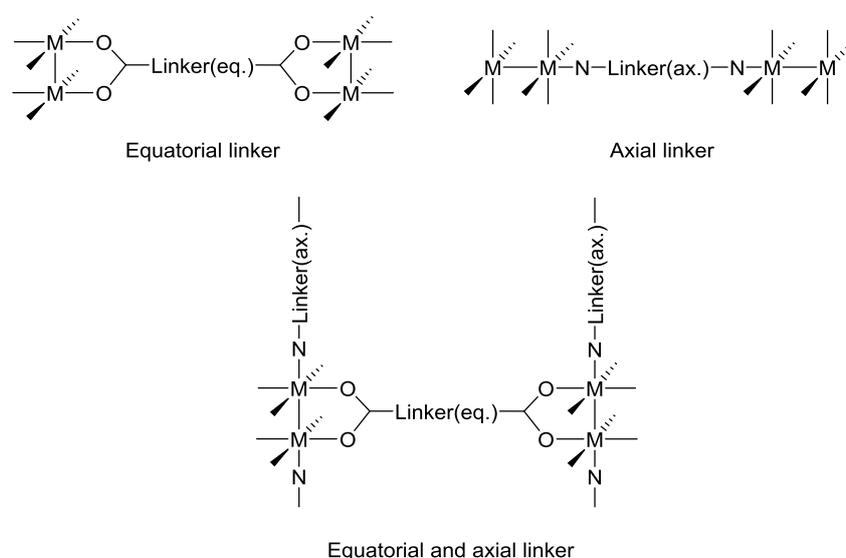


Figure 3. General linking possibilities of dimetal entities.⁵

In general, three types of organic ligands can be distinguished for the synthesis of coordination polymers, namely neutral, anionic and cationic organic ligands. Figure 4 shows examples of all three types, which have been successfully used as linking molecules for generating larger molecular arrays.⁷

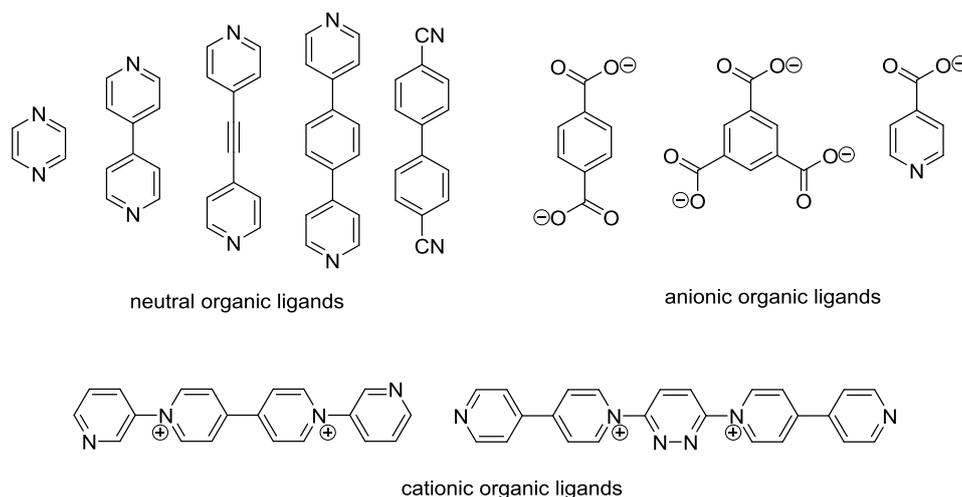


Figure 4. Examples of neutral, anionic and cationic organic ligands.⁷

There is a large amount of literature known complexes serving as examples of all three types of connecting dimetal units shown in Figure 3.^{1,2}

The polymeric compound $[\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_6\text{CH}_3)_4(\text{pz})]_n$ (Figure 5) (pz = pyrazine),⁸ which was synthesized by the reaction of the dinuclear starting material $[\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_6\text{CH}_3)_4]$ and the linker pyrazine using toluene as solvent, is an example of an axially linked metal-metal bonded complex.

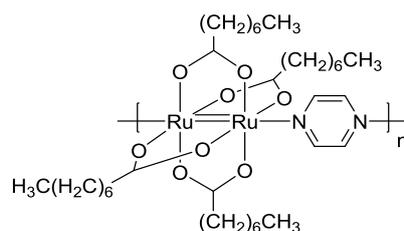


Figure 5. Structure of the axially linked polymer $[\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_6\text{CH}_3)_4(\text{pz})]_n$.

The reaction of the paddle-wheel compound $[\text{Rh}_2(\text{O}_2\text{CC}_7\text{H}_{15})_4]$ with the organometallic linker BPEF (BPEF = 1,1'-bis(4-pyridylethynyl)ferrocene) in a molar ratio of 1:1 and dichloromethane as solvent afforded the axially linked oligomer $[\text{Rh}_2(\text{O}_2\text{CC}_7\text{H}_{15})_4(\text{BPEF})]_n$, which is presented in Figure 6. Crystals suitable for single crystal X-ray diffraction were obtained by diffusion of diethyl ether into a dichloromethane solution of the orange product.⁹

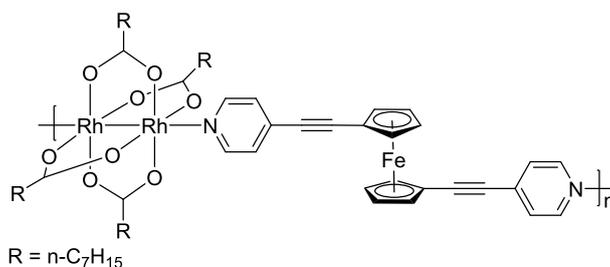


Figure 6. Structure of the axially linked complex $[\text{Rh}_2(\text{O}_2\text{CC}_7\text{H}_{15})_4(\text{BPEF})]_n$.

Both equatorial and axial coordination types are combined in the tetrameric compound shown in Figure 7, in which the nitrogen atom of the pyridine ring axially coordinates to the dirhodium tetracarboxylate complex and the carboxylate functionality coordinates equatorially to another molecule of the dirhodium complex. Starting from the tetracarboxylate dirhodium(II)-tetra-3,5-di-*tert*-butylbenzoate, which was isolated by the reaction of dirhodium tetraacetate and 3,5-di-*tert*-butylbenzoic acid in toluene, and the linker 4-(pyridine-4-yl)benzoic acid in benzene, a molecular square could be obtained. Characterization of the complex was done, amongst others, by means of NMR- and UV-Vis spectroscopy, elemental analysis and mass spectrometry.¹⁰

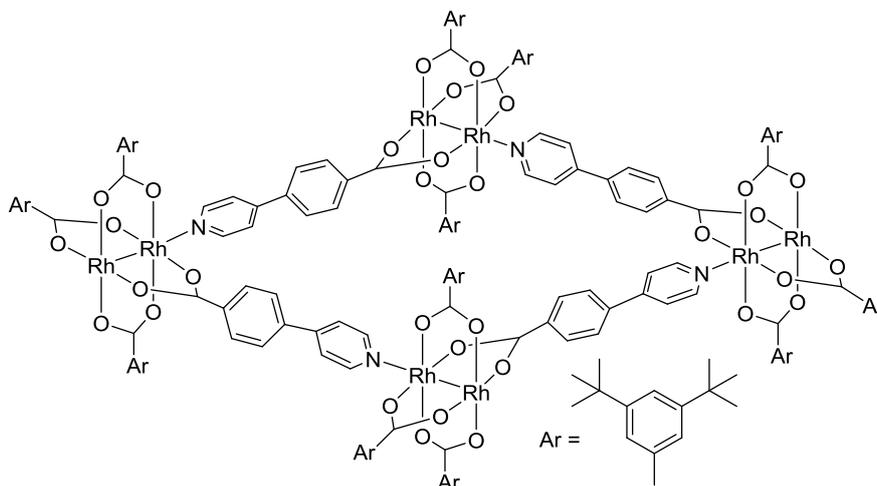


Figure 7. Structure of a molecular square synthesized by the reaction of dirhodium(II)-tetra-3,5-di-*tert*-butylbenzoate and the linker 4-(pyridine-4-yl)benzoic acid.

1.4 Dimolybdenum(II) Paddle-Wheel Complexes as a Source for the Mo₂⁴⁺ Core

In literature, several quadruply bonded dimolybdenum(II) PW complexes of the type shown in Figure 2 or related complexes are described and often used as sources for the Mo₂⁴⁺ core.^{1,11-21} The complex [Mo₂(O₂CCH₃)₄] is often utilized as starting compound for other PW shaped complexes. Starting from the mononuclear complex Mo(CO)₆ and the solvents acetic acid and acetic anhydride the yellow crystalline compound can be synthesized in a yield of up to 60%.²² The ligand exchange reaction of [Mo₂(O₂CCH₃)₄] and formic acid affords the dimolybdenum(II) complex [Mo₂(O₂CH)₄], which was, amongst others, characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction.¹¹

In this context, the well-known dimolybdenum(II) tetracarboxylate [Mo₂(O₂CCF₃)₄] has to be mentioned. Heating of [Mo₂(O₂CCH₃)₄] in trifluoroacetic acid and trifluoroacetic anhydride leads after working up procedures to the yellow product [Mo₂(O₂CCF₃)₄] in a yield of 73%.¹³ Dimolybdenum(II) tetrabenzoate, [Mo₂(O₂CPh)₄], which was isolated by reacting Mo(CO)₆ with benzoic acid, serves as an additional example of dimolybdenum(II) compounds with PW structure.¹⁶ In order to gain insight in typical Mo–Mo and Mo–O bond lengths of dimolybdenum(II) PW complexes, Table 2 summarizes the respective data of the above mentioned literature known examples.

Table 2. Selected bond lengths of quadruply bonded dimolybdenum(II) PW complexes.

Compound	Mo–Mo (Å)	Mo–O (Å)
[Mo ₂ (O ₂ CCH ₃) ₄] ¹²	2.0934(8)	2.107(5)-2.137(4)
[Mo ₂ (O ₂ CH) ₄] ¹¹	2.091(2)	2.072(13)-2.140(13)
[Mo ₂ (O ₂ CCF ₃) ₄] ¹³	2.090(4)	1.97(2)-2.14(2)
[Mo ₂ (O ₂ CPh) ₄] ¹⁶	2.096(1)	2.092(3)-2.131(3)

1.5 [Mo₂(NCCH₃)₁₀][BF₄]₄ as a Dimetal Precursor for the Synthesis of large Molecular Arrays

The synthesis of [Mo₂(NCCH₃)₁₀][BF₄]₄ (**1**) is attributed to *Cotton et al.* Starting from an acetonitrile suspension of [Mo₂(O₂CCH₃)₄] and [Et₃O][BF₄] in dichloromethane, the moisture sensitive and hygroscopic blue complex **1** can be isolated in a scale depending yield of 40-60%.²³ Another way to synthesize **1** is to use an acetonitrile and dichloromethane solution of [Mo₂(O₂CCH₃)₄] and a HBF₄ solution in diethyl ether as starting materials, whereby **1** can be isolated in a yield of 93%.²⁴

The purity of **1** is typically proven by elemental analysis. Thereby, it has to be considered that some of the weakly bound acetonitrile ligands of **1** can be easily removed under reduced pressure during the drying process. Furthermore, ¹H NMR spectroscopy in CD₃CN can be applied to analyze **1**. The corresponding spectrum shows a singlet at 1.96 ppm, which can be explained by the methyl protons of free acetonitrile being released, when **1** is dissolved in CD₃CN.

TG-MS is another method, which helps to investigate the composition and reactivity of **1**. One peak with a maximum at 221 °C appears in the MS curve of acetonitrile (mass 41) indicating that all equatorial acetonitrile ligands of **1** are bound equally and can be, at least partially, replaced by other ligands or substituents. The residual mass of 21.3% can be predominantly explained by elemental molybdenum.

X-ray diffraction crystallography can be used to determine the molecular structure of **1**. Suitable crystals were obtained by the diffusion of dichloromethane into a saturated acetonitrile solution of **1**. The Mo–Mo bond length in **1** is 2.187(1) Å, which is significantly larger compared to other compounds containing the quadruply bonded Mo₂⁴⁺ moiety, such as [Mo₂(O₂CCH₃)₂(NCCH₃)₆][BF₄]₂ and [Mo₂(O₂CCH₂Cl)₂(NCCH₃)₆][BF₄]₂ (2.134(2) and 2.140(2) Å, respectively).²⁵ Each molybdenum center is surrounded by four equatorial acetonitrile ligands. The Mo–N_{eq.} bond length is in the range of 2.113(10)-2.141(9) Å. Axial acetonitrile ligands of **1** are weaker bound, which is reflected in a longer Mo–N_{ax.} bond length (2.600(13) Å). Figure 8 shows the simplified structure of **1**.²³

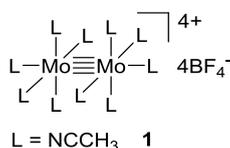


Figure 8. Simplified structure of **1**.

In order to build up larger coordination compounds, complex **1** has been reacted with several dicarboxylic acids earlier, and the resulting structures, such as the molecular dimer $[(\text{CH}_3\text{CN})_8\text{Mo}_2(\text{O}_2\text{C}-\text{CO}_2)\text{Mo}_2(\text{NCCH}_3)_8][\text{BF}_4]_6$ (**I**), the molecular loops $[(\text{CH}_3\text{CN})_6\text{Mo}_2(\text{O}_2\text{C}-\text{C}_4\text{H}_6-\text{CO}_2)]_2[\text{BF}_4]_4$ (**II**) and $[(\text{CH}_3\text{CN})_6\text{Mo}_2(\text{O}_2\text{C}-\text{CH}_2\text{CH}_2-\text{CO}_2)]_2[\text{BF}_4]_4$, the triangular-shaped compound $[(\text{CH}_3\text{CN})_6\text{Mo}_2(m\text{-bdc-OH})]_3[\text{BF}_4]_6$ (**III**) and the tetrameric square $[(\text{CH}_3\text{CN})_6\text{Mo}_2(\text{O}_2\text{C}-\text{C}_6\text{F}_4-\text{CO}_2)]_4[\text{BF}_4]_8$ (**IV**), have been determined by means of single crystal X-ray diffraction (Figure 9).^{26,27}

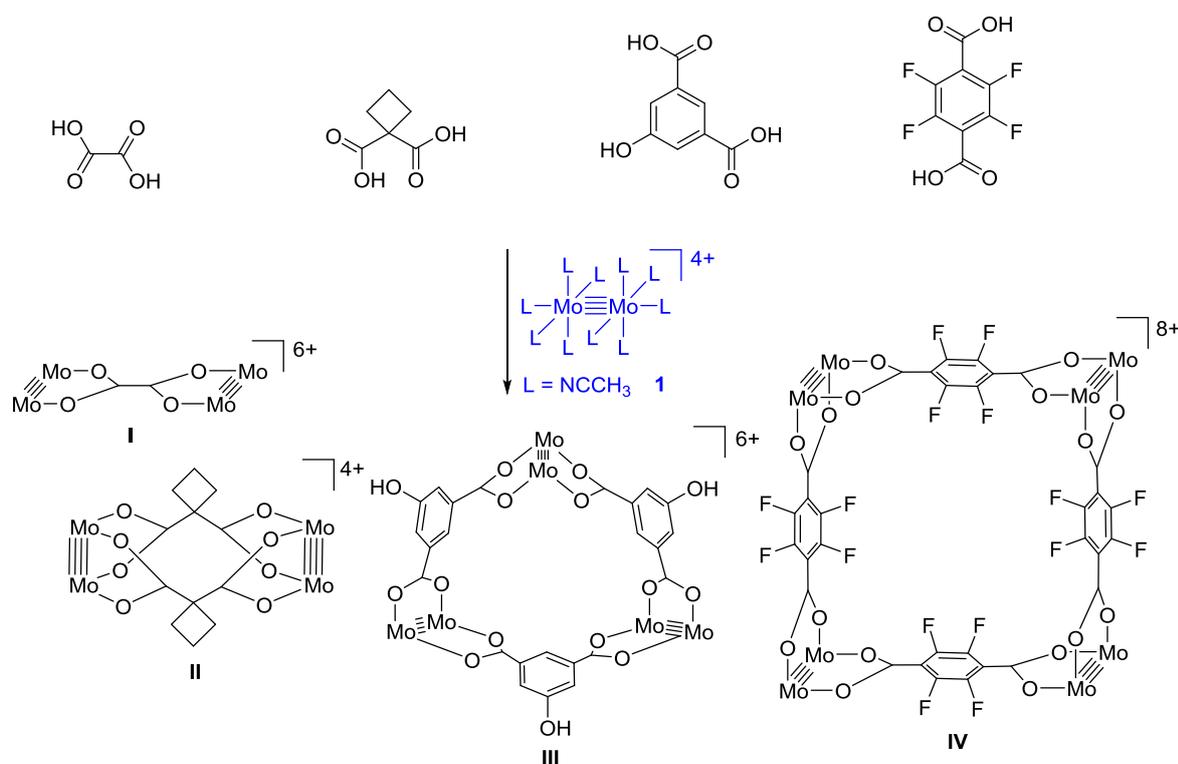


Figure 9. Structures of the dicarboxylic linkers and the molecular structures of the products resulting from the reactions with **1**, respectively. Nitrile ligands and BF₄ counterions are omitted for clarity, respectively.

1.6 Dicarboxylate-bridged Coordination Compounds based on protected Dimolybdenum(II) Precursors

Cotton and his coworkers have synthesized and characterized a large amount of dicarboxylate-bridged dimolybdenum(II) coordination compounds with different structural motifs. Thereby, Mo_2^{4+} precursors with strongly bound bridging ligands, such as *N,N'*-dianisylformamidinate (DAniF), served as a source for the dimetal unit entailing the advantage to elude side reactions. Furthermore, these starting materials fulfill a template function, since the DAniF ligands cannot be replaced and only the remaining weakly bound ligands are accessible for substitution reactions. Thus, the structure of the applied precursor, together with the structure of the linking molecule, determines the final molecular structure of the isolated products. On the other hand, the final products are restricted concerning further substitution reactions for building up larger molecular arrays, since all possible coordination sites are blocked.^{1,2,5,6,27-29}

1.6.1 Molecular Dimolybdenum(II) Dimers

The simplest way to obtain a larger coordination compound is the reaction of two Mo_2^{4+} units with one linking molecule leading to dimers with the general formula $([\text{Mo}_2]_2\text{L})$. By using $(\text{DAniF})_3\text{Mo}_2^+$ complexes and 180° dicarboxylic linkers of the type $\text{O}_2\text{C-X-CO}_2$ as starting materials, a plurality of complexes of the form $[(\text{DAniF})_3\text{Mo}_2(\text{O}_2\text{C-X-CO}_2)\text{Mo}_2(\text{DAniF})_3]$ could be isolated.³⁰⁻³³

The complex $[(\text{DAniF})_3\text{Mo}_2(\text{O}_2\text{C-CO}_2)\text{Mo}_2(\text{DAniF})_3]$, which was synthesized together with a series of other similar compounds in *Cotton's* group by reacting $[\text{Mo}_2(\text{DAniF})_3\text{Cl}_2]$ with the tetrabutylammonium salt of oxalic acid in dichloromethane with a yield of 54%, serves as an example of that structural motif. Figure 10 illustrates the general structure of the formed dimolybdenum(II) dimers and shows some examples of applied organic linkers.³³

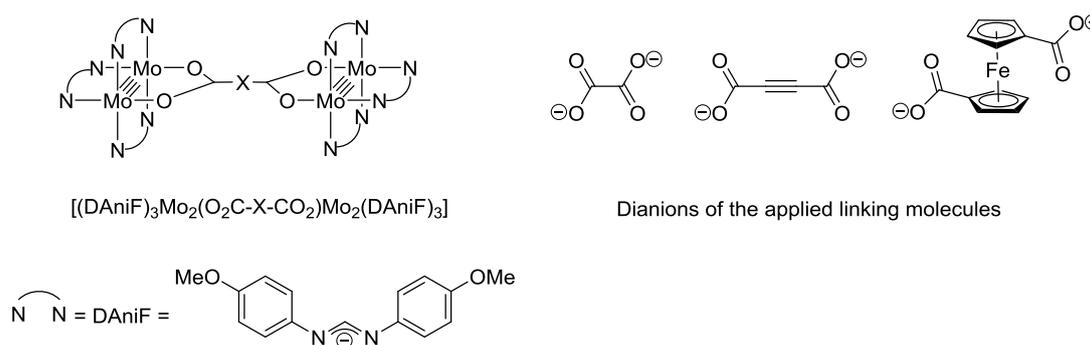


Figure 10. General structure of a molecular dimer synthesized by *Cotton* et al. and examples of used linkers.³³

1.6.2 Molecular Dimolybdenum(II) Loops

By reacting Mo_2^{4+} entities and suitable bent dicarboxylic linking molecules in a molar ratio of 1:1, molecular loops represented by the formula $([\text{Mo}_2]\text{L})_2$ can be formed. That structural type is characterized by a double linkage of two Mo_2^{4+} units by two linkers. Therefore, the dimolybdenum(II) precursor needs two accessible coordination sites. Starting from *cis*- $[\text{Mo}_2(\text{DAniF})_2(\text{NCCH}_3)_4][\text{BF}_4]_2$ and the tetraalkylammonium salts of linkers, a variety of molecular loops of the form *cis*- $[(\text{DAniF})_2\text{Mo}_2(\text{O}_2\text{C-X-CO}_2)]_2$ were isolated (Figure 11).^{1,34,35}

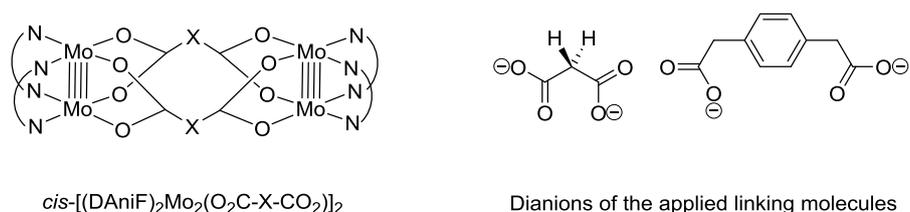


Figure 11. General structure of a molecular loop and examples of used linkers.³⁵

1.6.3 Molecular Dimolybdenum(II) Triangles

A third structural type is that of molecular triangles, abbreviated by the formula $([\text{Mo}_2]\text{L})_3$. In this case, three Mo_2^{4+} entities are connected by three linking molecules to form a triangular-shaped complex. Though the formation of molecular triangles based on 180° linkers is unlikely, since the geometry supports dimeric or tetrameric structures, the isolation of trimers was successful using that type of linker, which can be explained by thermodynamic reasons. The compound *cis*- $[(\text{DAniF})_2\text{Mo}_2(\text{O}_2\text{C-C}_6\text{H}_{10}\text{-CO}_2)]_3$ ³⁶ is an example of that structural motif (Figure 12). Again, the precursor *cis*- $[(\text{DAniF})_2\text{Mo}_2(\text{NCCH}_3)_4][\text{BF}_4]_2$ was reacted with the tetrabutylammonium salt of the linker *trans*-1,4-cyclohexanedicarboxylic acid (molar ratio 1:1) in an acetonitrile solution.^{1,37-39}

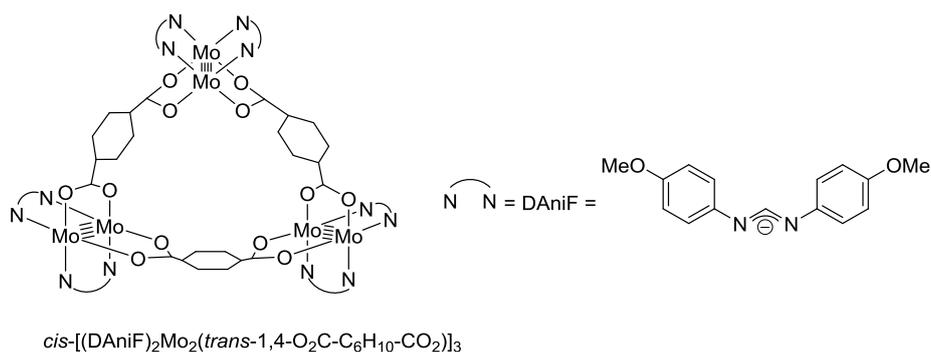


Figure 12. Molecular structure of the compound *cis*- $[(\text{DAniF})_2\text{Mo}_2(\text{trans-1,4-O}_2\text{C-C}_6\text{H}_{10}\text{-CO}_2)]_3$.³⁶

1.6.4 Molecular Dimolybdenum(II) Squares

Molecular squares of the general type $([\text{Mo}_2]\text{L})_4$ represent another possible molecular structure, which can be formed by the reaction of four Mo_2^{4+} units with the same amount of suitable dicarboxylic linker molecules. One literature known example is the complex *cis*- $[(\text{DAniF})_2\text{Mo}_2(\text{O}_2\text{C}-\text{CHCH}-\text{CO}_2)]_4$,⁴⁰ which was isolated in the group of *Cotton* using the tetrabutylammonium salt of the 180° linker fumaric acid and *cis*- $[(\text{DAniF})_2\text{Mo}_2(\text{NCCH}_3)_4][\text{BF}_4]_2$ as starting materials. Figure 13 illustrates the general structure of a molecular square and gives examples of applied linkers.^{1,38,39}

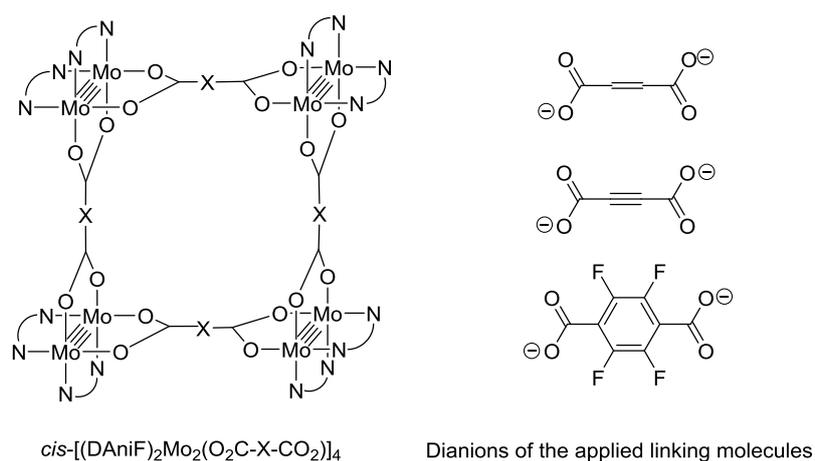


Figure 13. General structure of a molecular square and examples of applied linkers.⁴⁰

1.7 Bisphosphine Substitution of Dimolybdenum(II) based Systems

In the past, a variety of multiply bonded dimetal complexes starting from Mo_2^{4+} based precursors and bidentate bisphosphine ligands has been isolated and fully characterized, which proves that bisphosphines are in general suitable ligands to coordinate to the Mo_2^{4+} moiety. Furthermore, it is shown that several structural motifs, such as bisphosphine and carboxylate substitution, may occur in one dimolybdenum(II) complex at the same time.¹

Compounds of the general formula $\text{Mo}_2\text{X}_4(\text{LL})_2$ (LL = bisphosphine ligand) have to be mentioned in this context.⁴¹⁻⁴⁸ The complex $\text{Mo}_2\text{Br}_4(\text{dmpm})_2$ ⁴³ (**V**) (dmpm = bis(dimethylphosphino)methane) (Figure 14) therefore serves as an example. The blue compound was synthesized by adding a *n*-hexane solution of dmpm to a tetrahydrofuran solution of the dinuclear paddle-wheel precursor $[\text{Mo}_2(\text{O}_2\text{CCF}_3)_4]$ followed by an addition of Me_3SiBr . Characterization was done by UV-Vis spectroscopy in dichloromethane and NMR spectroscopy (^1H , $^{31}\text{P}\{^1\text{H}\}$). Suitable crystals for single crystal X-ray diffraction were obtained by diffusion of a benzene/*n*-hexane mixture into a tetrahydrofuran solution of $\text{Mo}_2\text{Br}_4(\text{dmpm})_2$.

By introducing carboxylic functionalities as substituents, dimolybdenum(II) complexes of the general type $[\text{Mo}_2(\text{O}_2\text{CR})_2\text{X}_2(\text{LL})_2]$,⁴⁸⁻⁵⁰ $[\text{Mo}_2(\text{O}_2\text{CR})_2(\text{LL})_2][\text{BF}_4]_2$ ^{24,25,51,52} or similar axially coordinated compounds^{53,54} could be isolated. The reaction of $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_4]$, dppma (= bis(diphenylphosphino)methylamine) and Me_3SiCl in tetrahydrofuran at room temperature afforded the pink product $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_2(\text{dppma})_2]$ ⁴⁹ (**VI**) shown in Figure 14. It was, amongst others, characterized by single crystal X-ray diffraction of crystals obtained by layering an acetonitrile solution of the complex with *n*-hexane and diethyl ether. The compound $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{dppe})_2][\text{BF}_4]_2$ ²⁴ (**VII**) (dppe = 1,2-bis(diphenylphosphino)ethane) illustrated in Figure 14 was synthesized starting from $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_4]$, dppe and $[\text{Mo}_2(\text{NCCH}_3)_{10}][\text{BF}_4]_4$ as a BF_4 -anion source in tetrahydrofuran and acetonitrile. It represents an example of a dimolybdenum(II) complex coordinated by both bisphosphines and carboxylates as well as BF_4 counterions.

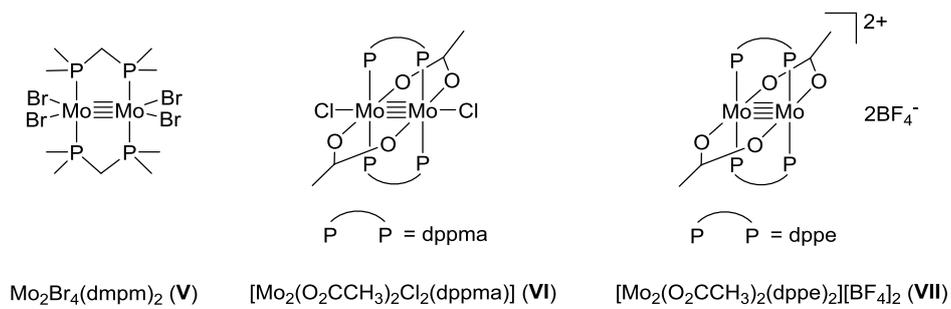


Figure 14. Examples of dimolybdenum(II) complexes featuring bisphosphine substitution (V) and both bisphosphine and carboxylate substitution without (VI) and with BF_4^- counterions (VII).^{24,43,49}

1.8 Metal-organic Frameworks and Selected Applications

Since the overall aim of this work is the synthesis and characterization of potential building blocks for metal-organic frameworks (MOFs), the following chapter gives an insight into selected applications.

In general, MOFs can be regarded as crystalline hybrid materials, which consist of inorganic parts (metal ions or fragments of metal complexes) called secondary building units (SBUs) and which are connected by organic linkers leading to the formation of multidimensional frameworks. Due to the high porosity, the vast internal surface areas and the possibility to modify the inorganic and organic elements almost infinitely qualifies MOFs for a plethora of applications.^{2,55-65}

1.8.1 Gas Separations in Metal-organic Frameworks based on Adsorption

Adsorptive separations of gas mixtures are based on a difference in adsorption/desorption properties of components in a mixture, whereat the adsorption capacity and selectivity of the adsorbent plays a predominant role. The adsorption capacity is influenced by properties of the adsorbate, the nature and size of the pores in the adsorbent and external factors, such as temperature and pressure. The selectivity depends as well on the natures of the adsorbent and adsorbate and is also controlled by the working parameters. Desirable qualities of a good adsorbent are, besides good capacities and selectivities, preferred desorption kinetics and an easy regeneration, which is often induced by changing the conditions temperature or pressure. Several mechanisms^{66,67} exist to explain gas adsorptive separation by porous materials, whereby the following three are briefly described. (1) Certain components of a gas mixture cannot enter the pores of the adsorbent due to their size or shape, while others are immediately adsorbed when entering the adsorbent (molecular sieving effect). (2) Certain components of the mixture are preferably adsorbed by the adsorbent due to a different adsorbate/surface interaction (thermodynamic equilibrium effect). (3) Different diffusion rates favor certain elements of the mixture, i.e. the fastest one is adsorbed first (kinetic effect).^{68,69}

Due to energetic and environmental reasons, the separation of light molecules, such as H₂, O₂, N₂, CO₂ and CH₄, has become a challenge of recent research, which might be solved to some extent by the application of MOFs. Thereby, it has been proved that the tuning of the pore sizes and structures of the MOFs have an impact on the selectivity of adsorption.⁶⁸

Since the reduction of the greenhouse gas CO₂ is nowadays a highly relevant topic, one literature known example of a MOF bearing a selective adsorption of CO₂ towards other gases is discussed. The MOF Zn₂(tcom)(bipy)⁷⁰ (tcom = tetrakis[4-(carboxyphenyl)oxamethyl]methane, bipy = bipyridine), which was obtained by the self-assembly of tetrakis[4-(carboxyphenyl)oxamethyl]methane, zinc nitrate hexahydrate and bipyridine in dimethyl formamide, shows a high selective adsorption of CO₂ over H₂ and N₂. The reason for the selective sorption of CO₂ over N₂ is thereby explained by the small size of the framework pores and the selective binding of CO₂ on the walls of the framework. Almost no N₂ is absorbed, which is also true for similar experiments performed with H₂. Thus, the separation of the gas mixture is based on the size/shape differences of the respective components of the mixture and might find an application in CO₂ separation from synthesis gas. Though a lot of promising results have been obtained in the field of CO₂ separation over other gases by the help of MOFs, some problematic aspects, such as omnipresent water as a component of the mixture decomposing the MOF, should not be neglected.^{68,71}

1.8.2 Hydrogen Storage in Metal-organic Frameworks

MOFs have obtained attention as potential adsorbents for the storage of hydrogen as a result of their variable pore sizes and frameworks, which might help to reduce the dependency on fossil fuels. In general, hydrogen is the element with the highest occurrence on earth, whereat less than 1% exists as molecular hydrogen and a large proportion is bound, for example in water. As a result of its low molecular weight and a high molar combustion heat, the energy value of hydrogen is remarkable on a unit mass basis and water is generated as a byproduct when burnt with oxygen. Nevertheless, drawbacks, such as a low heating value per volume deduced from a low density in the gaseous and liquid phase (high pressure and very low temperature), have to be considered. Furthermore, the very low boiling point of hydrogen implies additional difficulties. Currently, hydrogen storage includes cooled high-pressure tanks based on chemisorption or physisorption. A pure tank-based storage of hydrogen is problematic regarding both safety and economic reasons.⁷²⁻⁷⁴

One possibility to maximize the interaction of hydrogen and the MOF is to optimize the pore size of the pores of the framework. Both theoretical and experimental studies prove that the best pore size is around 6 Å, which is around two times the effective kinetic diameter of molecular hydrogen.^{72,75}

The interaction of MOFs with a polyhedral cage structure and aligned unsaturated metal centers and hydrogen is high. In general, it can be stated that the interaction of hydrogen and MOFs with unsaturated metal centers is higher than with those having saturated metal centers. The MOFs PCN-12 and PCN-12' (PCN = porous coordination network)⁷⁶ can serve as examples proving the importance of alignment of the unsaturated metal centers. PCN-12 was synthesized by reacting $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ with the linker $\text{H}_4(\text{mdip})$ (mdip = 5,5'-methylene-diisophthalate) under solvothermal conditions at 85 °C and dimethylacetamide as solvent and PCN-12' starting from $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ with the linker $\text{H}_4(\text{mdip})$ at 120 °C and dimethylsulfoxide as solvent. In these two MOFs, polymorphism can be observed due to the two possible extreme conformations of the organic ligand mdip (Figure 15). The unsaturated metal sites of the PW based MOFs, which were obtained by removing coordinated solvent molecules, are aligned in PCN-12 and misaligned in PCN-12'. This structural difference causes a distinction in hydrogen uptake, which is 3.05 wt% for PCN-12 and 2.40 wt% for PCN-12' at 77 K and 1 atm and can be explained by a direct interaction of the metal centers with hydrogen.⁷²

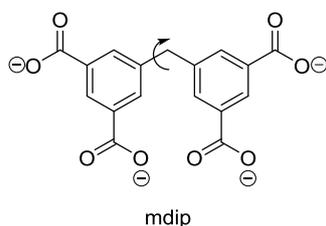


Figure 15. Structure of the organic linker mdip.⁷⁶

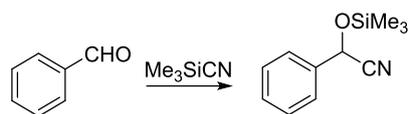
In addition to the structure of the pores of the MOF and the coordination properties of the metal, the nature of the metal ions influences the binding energy of the metal and hydrogen.⁷⁷ An isostructural MOF series of the type $\text{M}_2(\text{dhtp})$ ⁷⁸ (dhtp = 2,5-dihydroxyterephthalate, M = Mg, Mn, Co, Ni, Zn) has been studied in order to determine the dependency of the metal on the binding energy of hydrogen. The trend $\text{Zn}^{2+} < \text{Mn}^{2+} < \text{Mg}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+}$ was observed and explained by differences in coordination preferences.⁷²

1.8.3 Catalytic Activity of Metal-organic Frameworks

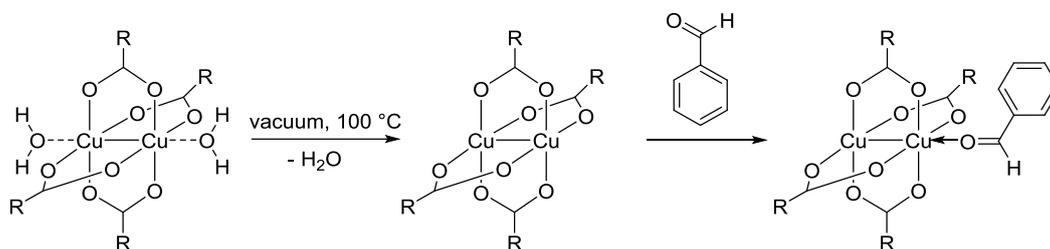
There are several ways, how metal-organic frameworks can obtain catalytic activity.⁷⁹⁻⁸³ In order to generate a catalytically active MOF encapsulation of the active species into the pores of the porous material is possible. Moreover, the MOF can be the host for metal clusters being responsible for the catalytic performance. A third way of catalytic functionalization of MOFs can be described by using suitable linking molecules with catalytic sites. Finally, the organic parts of the framework can be post-synthetically modified with metal species, which are responsible for the catalytic activity.⁸⁴

The compound Cu@MOF-5, which consists of copper particles of the size 3-4 nm in the pores of a cubic framework arranged by Zn₄O building blocks and terephthalic anions as linkers (MOF-5), serves as an example, in which the MOF serves as a host for catalytically active metal clusters. In that case, the generation of methanol from synthesis gas is catalyzed by the copper particles in the pores of MOF-5.⁸⁵

The coordination polymer [Cu₃(TMA)₂(H₂O)₃] \cdot xH₂O⁸⁶ (TMA = benzene-1,3,5-tricarboxylic acid, trimesic acid) synthesized by *Chui* et al. represents an example, in which the metal nodes of the frameworks can serve as catalytically active centers. An improved synthesis of that compound,⁸⁷ which does not lead to impurities of Cu₂O influencing catalytic tests, starts from the educts Cu(NO₃)₂ \cdot 3H₂O dissolved in de-ionized water and trimesic acid in ethanol followed by heating of the mixture at 393 K for 12 h in an autoclave. In contrast to other MOFs, [Cu₃(TMA)₂(H₂O)₃] \cdot xH₂O has the advantage of accessible Cu sites, since these *Lewis* acid coordination sites are situated on the inside of the pore wall. The framework is arranged by weakly bound Cu₂ clusters coordinated by four carboxylates leading to a PW structure. Weakly bound water molecules coordinate to the remaining axial coordination sites. These primary building units are linked by the organic linker trimesic acid to form a 3D cubic network featuring open pores, which are filled with 12 water molecules, respectively. Removing of the water molecules is possible by heating the material (100 °C) in vacuum and indicated by a colour change from blue-turquoise to dark-violet leading to catalytically active Cu sites, which can for example be used for the cyanosilylation of benzaldehyde (Scheme 1 and 2). Though some positive conclusions can be made for this reaction, drawbacks, such as a low yield of 57% and a limited thermal stability in the presence of aldehydes, have to be considered and underline the need of improvements.^{81,87}

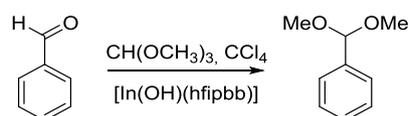


Scheme 1. Cyanosilylation of benzaldehyde.⁸⁷



Scheme 2. Activation of $[\text{Cu}_3(\text{TMA})_2(\text{H}_2\text{O})_3] \cdot x\text{H}_2\text{O}$ and subsequent adsorption of benzaldehyde.⁸⁷

The In(III) containing MOF $[\text{In}(\text{OH})(\text{hfipbb})]^{88}$ synthesized by the reaction of $\text{In}(\text{OAc})_3$ and the bent linker 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (= H_2hfipbb) using the solvents water and ethanol in an autoclave for 72 h at 170 °C represents another *Lewis* acid catalyst. The structure of this MOF can be described as thick layers featuring square-shaped channels and it turned out to be a good heterogeneous catalyst for aldehyde acetalization. It was possible to achieve 100 % conversion in 15 min for the acetalization of benzaldehyde with $[\text{In}(\text{OH})(\text{hfipbb})]$ (Scheme 3). This catalyst is stable in organic solvents as well as in water. Furthermore, it can be recovered by the help of filtration and reutilized for at least 4 subsequent cycles without any loss in either selectivity or yield. The fact that there is a significant difference in catalytic activity between $[\text{In}(\text{OH})(\text{hfipbb})]$ and $[\text{In}(\text{OH})(\text{hfipbb})] \cdot x\text{Py}$ (Py = pyridine), the same MOF with pyridine inside the pores, can be regarded as a prove that catalysis is performed in the pores of the framework.⁷²



Scheme 3. Acetalization of benzaldehyde using $[\text{In}(\text{OH})(\text{hfipbb})]$ as catalyst.⁸⁸

2. Objective

One objective of this work is the reaction of the dinuclear complex $[\text{Mo}_2(\text{NCCH}_3)_{10}][\text{BF}_4]_4$ (**1**) with dicarboxylic acids in order to isolate large Mo_2^{4+} unit containing coordination compounds and investigate the influence of the structure of the linking molecule on the final molecular structures of the obtained products. In addition, the optimization of reaction parameters regarding the yield of the synthesized compounds, such as solvent, temperature and molar ratio of the starting materials, is another aim of this work.

Since all isolated products starting from **1** and dicarboxylic linkers exhibit a defined structure and additional coordination sites, i.e. weakly bound and therefore easily replaceable nitrile ligands, further reactions with these compounds and bidentate ligands, such as bisphosphines, have to be carried out. Thus, the applicability of the nitrile substituted complexes as precursors for further substitution reactions, which might enable even larger building blocks serving as potential building blocks for MOFs, can be determined.

In order to fully characterize the obtained coordination compounds, NMR- (^1H , ^{11}B , ^{13}C , ^{19}F and ^{31}P), IR- and UV-Vis spectroscopy as well as elemental analysis and TG-MS measurements have to be applied. With respect to the molecular structure of the complexes, single crystal X-ray diffraction is inevitable, which implies that suitable methods for crystal growth have to be developed.

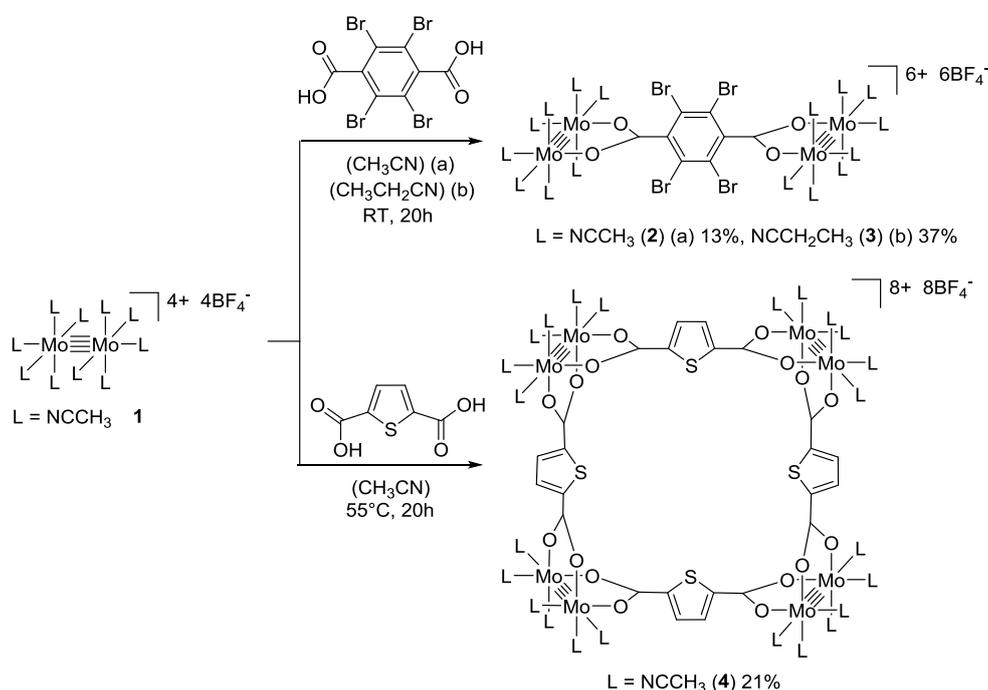
3. Results – Summaries of Publications

This chapter contains summaries of the publications, which have been prepared during the course of this dissertation. The appendix of this thesis contains the full manuscripts.

3.1 Synthesis and Characterization of Dimeric and Square-shaped Dicarboxylate-bridged Dimolybdenum(II) Coordination Compounds

Dominik Höhne, Eberhardt Herdtweck, Alexander Pöthig and Fritz E. Kühn,
Inorganica Chimica Acta, 2015, **424**, 210-215

During this work, the reactions of the dinuclear precursor $[\text{Mo}_2(\text{NCCH}_3)_{10}][\text{BF}_4]_4$ (**1**) with the dicarboxylic linkers tetrabromoterephthalic acid and 2,5-thiophenedicarboxylic acid in different nitrile solvents are examined (Scheme 4). The resulting dimeric coordination compounds $[(\text{CH}_3\text{CN})_8\text{Mo}_2(\text{O}_2\text{C}-\text{C}_6\text{Br}_4-\text{CO}_2)\text{Mo}_2(\text{NCCH}_3)_8][\text{BF}_6]_6$ (**2**), $[(\text{CH}_3\text{CH}_2\text{CN})_8\text{Mo}_2(\text{O}_2\text{C}-\text{C}_6\text{Br}_4-\text{CO}_2)\text{Mo}_2(\text{NCCH}_2\text{CH}_3)_8][\text{BF}_6]_6$ (**3**) and the molecular square $[(\text{CH}_3\text{CN})_6\text{Mo}_2(\text{O}_2\text{C}-\text{C}_4\text{H}_2\text{S}-\text{CO}_2)]_4[\text{BF}_4]_8$ (**4**) prove that the structure of the products cannot always be derived from the structure of the used linkers, but other effects, such as steric demands, have to be taken into account. Regarding complexes **2** and **3**, the respective yields can be increased almost threefold by changing the solvent from acetonitrile to propionitrile.



Scheme 4. Syntheses of compounds **2-4** starting from **1**.

Complexes **2-4** are fully characterized by NMR spectroscopy (^1H , ^{11}B , $^{13}\text{C}\{^1\text{H}\}$, ^{19}F), IR spectroscopy, elemental analysis, TG-MS measurements and UV-Vis spectroscopy, compounds **2** and **4** additionally by single crystal X-ray diffraction. The structures of **2** and **4** are presented in Figure 16. The dimeric structures of **2** and **3** (even at a ratio of **1**:linker = 1:1) are surprising, since the reaction of **1** with tetrafluoroterephthalic acid in acetonitrile leads to a square-shaped compound²⁷ underlining the influence of the structure of the linking molecule on the molecular composition of the products. Complex **4** is square-shaped, though the structure of the linker 2,5-thiophenedicarboxylic acid militates for the formation of triangular products, as it is found for the 120° linker 5-hydroxyisophthalic acid.²⁷ In contrast to the molecular square formed starting from **1** and the linker tetrafluoroterephthalic acid in acetonitrile,²⁷ only the Mo_2^{4+} entities on opposite side of the distorted square-shaped compound **4** are positioned parallel to each other, which is a result of the molecular structure of the applied linker. Due to the easily replaceable remaining nitrile ligands, the macromolecular compounds **2-4** serve as examples of potential building units for MOFs.

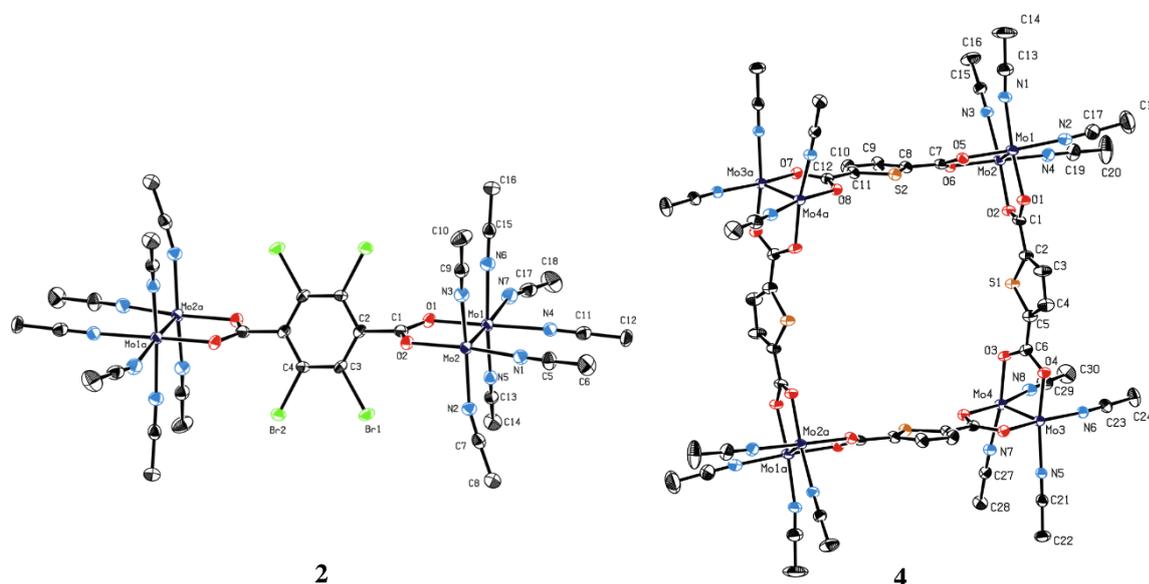
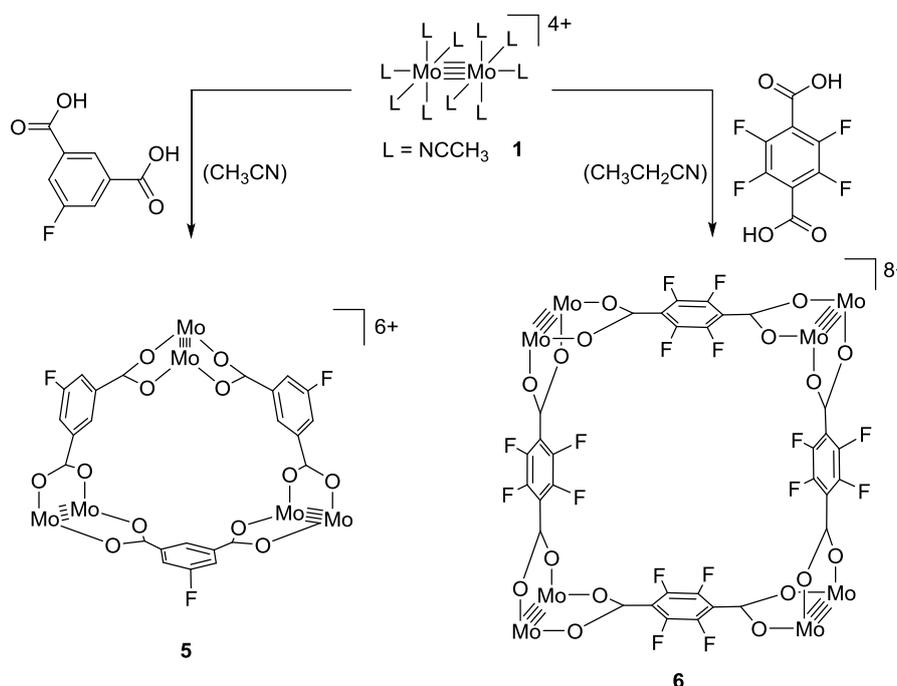


Figure 16. ORTEP style plot of the cationic parts of compounds **2** and **4** in the solid state (thermal ellipsoids are drawn at a 50% and 30% probability level, respectively). Selected bond lengths (\AA): **2** Mo1–Mo2 2.1656(5), Mo1–O1 2.091(2), Mo2–O2 2.096(2), Mo1–N4 2.145(3). **4** Mo1–Mo2 2.1522(7), Mo3–Mo4 2.1567(7), Mo1–O1 2.083(4), Mo2–O2 2.085(4), Mo1–N1 2.153(7), Mo2–N3 2.146(5).

3.2 Synthesis and Characterization of Dimolybdenum(II) Complexes Connected by Carboxylate Linkers

Xu-Min Cai, Dominik Höhne, Mathias Köberl, Mirza Cokoja, Alexander Pöthig, Eberhardt Herdtweck, Stefan Haslinger, Wolfgang A. Herrmann and Fritz E. Kühn,
Organometallics, 2013, **32**, 6004-6011

The reactions of the dinuclear compound $[\text{Mo}_2(\text{NCCH}_3)_{10}][\text{BF}_4]_4$ (**1**) with organometallic carboxylates, namely ferrocenemonocarboxylic acid and ferrocenedicarboxylic acid, lead to the products *cis*- $[(\text{CH}_3\text{CN})_6\text{Mo}_2(\text{O}_2\text{C-Fc})_2][\text{BF}_4]_2$ and $[(\text{CH}_3\text{CN})_4\text{Mo}_2(\text{O}_2\text{C-Fc-CO}_2)]_4[\text{BF}_4]_8$, respectively. The emphasis of my contribution to this work, based on previous work in the group,⁸⁹ is put on the reactions of the organic linkers 5-fluoroisophthalic acid and tetrafluoroterephthalic acid with **1** in nitrile solvents, whereat the trimeric compound $[(\text{CH}_3\text{CN})_6\text{Mo}_2(m\text{-bdc-F})]_3[\text{BF}_4]_6$ (**5**) and the molecular square $[(\text{CH}_3\text{CH}_2\text{CN})_4\text{Mo}_2(\text{O}_2\text{C-C}_6\text{F}_4\text{-CO}_2)]_4[\text{BF}_4]_8$ (**6**) can be isolated (Scheme 5).



Scheme 5. Syntheses of compounds **5** and **6** starting from **1**. Nitrile ligands and BF_4 counterions are omitted for clarity.

As expected, the reaction of **1** with the 120° linker 5-fluoroisophthalic acid in acetonitrile results in the formation of the triangular-shaped compound **5**, which was also found for the reaction of the 120° linker 5-hydroxyisophthalic acid with **1** in acetonitrile.²⁷ Changing of the solvent of

the reaction of **1** and tetrafluoroterephthalic acid from acetonitrile to propionitrile has no influence on the obtained molecular structure of the products. In both cases molecular squares are isolated. However, the yield is halved, when propionitrile is used instead of acetonitrile as solvent.²⁷

Regarding compound **5** in the solid state, the formation of hexagonal shaped 2D layers of triangles can be observed, which can be explained by bridging C-H \cdots F interactions between axially coordinated BF₄ counterions and equatorially bound acetonitrile ligands.

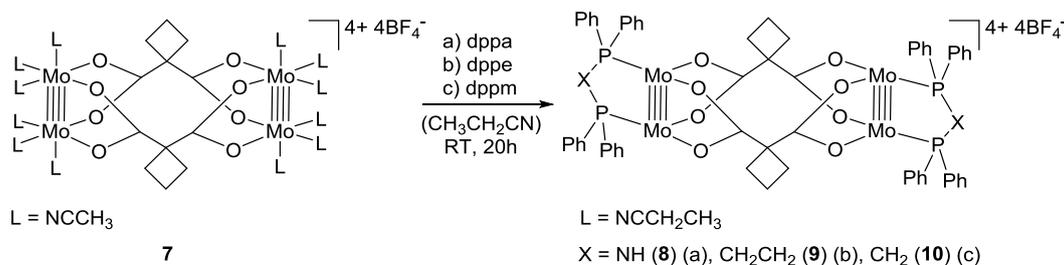
Complexes **5** and **6** serve as additional examples of potential building blocks for MOFs. It is obvious that the remaining weakly coordinated nitrile ligands of these compounds are accessible for further substitution reactions, which might lead to a controlled synthesis of larger 3D coordination compounds with defined pore sizes depending on the structure of the applied linking molecule.

3.3 Loop shaped Dicarboxylate-bridged Dimolybdenum(II) Bisphosphine Compounds – A Rational Synthesis

Dominik Höhne, Eberhardt Herdtweck, Alexander Pöthig and Fritz E. Kühn,

Dalton Transactions, 2014, **43**, 15367-15374

In this work, three examples of bisphosphine-substituted dicarboxylate-bridged dimolybdenum(II) complexes are presented. One equiv. of the molecular loop $[(\text{CH}_3\text{CN})_6\text{Mo}_2(\text{O}_2\text{C}-\text{C}_4\text{H}_6-\text{CO}_2)]_2[\text{BF}_4]_4$ (**7**) reacts with two equiv. of bis(diphenylphosphino)amine (dppa), 1,2-bis(diphenylphosphino)ethane (dppe) or bis(diphenylphosphino)methane (dppm) in propionitrile, which leads to the still loop-shaped complexes **8-10** (Scheme 6). Thereby, it is proven that compound **7** features reactive coordination sites, which can be used for building up larger coordination compounds by the reaction with suitable linking molecules, such as bis(bisphosphines). Hence, the assumption of a potential application of **7** and the isolated products **8-10** as building blocks for metal-organic frameworks (MOFs) is justified.



Scheme 6. Syntheses of compounds **8-10** starting from **7**. Propionitrile ligands at the Mo centers of the products **8-10** are omitted for clarity.

Complexes **8-10**, which can be isolated in moderate yields and exhibit a fair air- and moisture stability, are, amongst others, characterized by NMR spectroscopy. It turns out that the substitution of **7** with bisphosphines results in a splitting of the signals of the cyclobutane rings in the respective ^1H NMR spectra, which can be explained by the fixed conformation of the cyclobutane rings due to the coordination of the bulky bisphosphine ligands and which is proved by 2D NMR experiments. The proton signals of the coordinating bisphosphine ligands are, compared to those of the free ones, low field shifted and split in the case of dppe and dppm.

Crystals of compounds **8** and **9** obtained by layering a saturated propionitrile solution of the respective complex with *n*-pentane are used for the determination of the molecular structures by means of single crystal X-ray diffraction (Figure 17). All Mo centers show an octahedral

coordination sphere and the two parallel orientated Mo_2^{4+} moieties, which are substituted by one bisphosphine ligand, respectively, are connected by two linking molecules of 1,1-cyclobutanedicarboxylic acid.

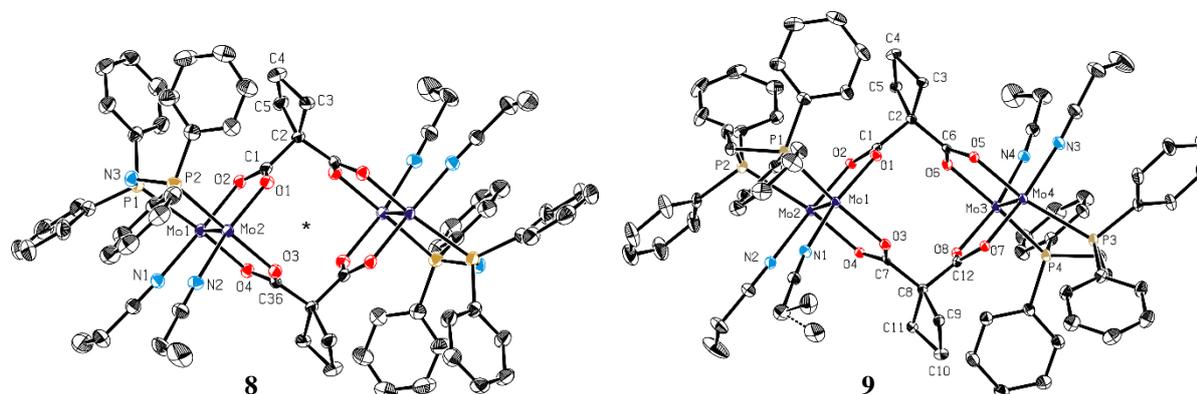


Figure 17. ORTEP style plot of the cationic parts of compounds **8** and **9** in the solid states (thermal ellipsoids are drawn at a 50% and 30% probability level, respectively). Selected bond lengths (Å): **8** Mo1–Mo2 2.1477(6), Mo1–O2 2.086(2), Mo1–O4 2.111(2), Mo1–N1 2.143(3), Mo2–N2 2.146(3), Mo1–P1 2.553(1). **9** Mo1–Mo2 2.1453(5), Mo1–O1 2.082(3), Mo2–O2 2.092(3), Mo1–N1 2.135(4), Mo2–N2 2.138(4), Mo1–P1 2.560(1), Mo2–P2 2.604(1), Mo3–Mo4 2.1470(5).

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4. Bibliographic Data of Published Articles

In order to provide the reader of this dissertation with details concerning the publications summed up in Chapter 3, the respective bibliographic data are listed in this chapter.

4.1 Synthesis and Characterization of Dimeric and Square-shaped Dicarboxylate-bridged Dimolybdenum(II) Coordination Compounds

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DOI: 10.1016/j.ica.2014.08.043

Hyperlink: <http://www.sciencedirect.com/science/article/pii/S002016931400543X>

4.2 Synthesis and Characterization of Dimolybdenum(II) Complexes Connected by Carboxylate Linkers

Xu-Min Cai,[†] Dominik Höhne,[†] Mathias Köberl, Mirza Cokoja, Alexander Pöthig, Eberhardt Herdtweck, Stefan Haslinger, Wolfgang A. Herrmann* and Fritz E. Kühn*

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Published in: *Organometallics*, 2013, **32**, 6004-6011.

DOI: 10.1021/om400518f

Hyperlink: <http://pubs.acs.org/doi/abs/10.1021/om400518f>

4.3 Loop shaped Dicarboxylate-bridged Dimolybdenum(II) Bisphosphine Compounds – A Rational Synthesis

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Published in: *Dalton Transactions*, 2014, **43**, 15367-15374.

DOI: 10.1039/C4DT01560F

Hyperlink: <http://pubs.rsc.org/en/content/articlelanding/2014/dt/c4dt01560f#!divAbstract>

5. Summary and Outlook

In order to synthesize Mo_2^{4+} based coordination compounds with the potential application as building units for MOFs, compound **1**, which was isolated starting from $\text{Mo}(\text{CO})_6$, or more specifically from $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_4]$ (see Introduction), was reacted with organic dicarboxylic linkers. Thereby, different structural types, such as the molecular dimers $[(\text{CH}_3\text{CN})_8\text{Mo}_2(\text{O}_2\text{C}-\text{C}_6\text{Br}_4-\text{CO}_2)\text{Mo}_2(\text{NCCH}_3)_8][\text{BF}_4]_6$ (**2**) and $[(\text{CH}_3\text{CH}_2\text{CN})_8\text{Mo}_2(\text{O}_2\text{C}-\text{C}_6\text{Br}_4-\text{CO}_2)\text{Mo}_2(\text{NCCH}_2\text{CH}_3)_8][\text{BF}_4]_6$ (**3**), the molecular triangle $[(\text{CH}_3\text{CN})_6\text{Mo}_2(m\text{-bdc-F})][\text{BF}_4]_6$ (**5**) and the square-shaped complexes $[(\text{CH}_3\text{CN})_6\text{Mo}_2(\text{O}_2\text{C}-\text{C}_4\text{H}_2\text{S}-\text{CO}_2)_4][\text{BF}_4]_8$ (**4**) and $[(\text{CH}_3\text{CH}_2\text{CN})_4\text{Mo}_2(\text{O}_2\text{C}-\text{C}_6\text{F}_4-\text{CO}_2)_4][\text{BF}_4]_8$ (**6**) could be synthesized and characterized. It turned out that a prediction of the obtained molecular structure of the products cannot necessarily be derived from the structure of the applied linker. For the reactions of **1** with the 180° linker tetrabromoterephthalic acid in both acetonitrile and propionitrile, molecular dimers were synthesized no matter which ratio of the starting materials was chosen (1:0.5 or 1:1). The reaction of **1** with 2,5-thiophenedicarboxylic acid lead to the formation of the molecular square **4**, though a molecular triangle was expected due to the angle of the carboxylic functionalities of the linker. Thus, it can be concluded, that other effects, such as steric properties concerning linkers and thermodynamic effects, might have an influence on the formed molecular structures of the products. Figure 18 summarizes the main idea of synthesizing larger molecules starting from the mononuclear compound $\text{Mo}(\text{CO})_6$.

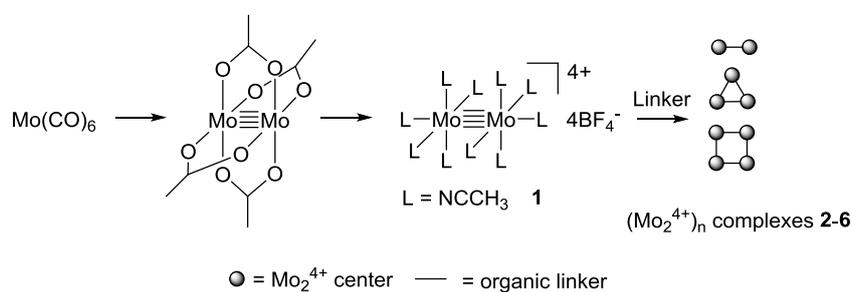


Figure 18. General illustration of the syntheses of the Mo_2^{4+} based coordination compounds **2-6** starting from **1** and organic linkers and starting materials for the isolation of **1**.

In order to prove the reactivity of nitrile coordinated carboxylate-bridged Mo_2^{4+} based complexes with regard to the potential synthesis of macromolecular 3D compounds, the molecular loop $[(\text{CH}_3\text{CN})_6\text{Mo}_2(\text{O}_2\text{C}-\text{C}_4\text{H}_6-\text{CO}_2)]_2[\text{BF}_4]_4$ (**7**) was reacted with bisphosphines. Treating the molecular loop **7** with two equiv. of the bisphosphines dppa, dppe and dppm in propionitrile afforded the products $[(\text{CH}_3\text{CH}_2\text{CN})_4(\text{X})\text{Mo}_2(\text{O}_2\text{C}-\text{C}_4\text{H}_6-\text{CO}_2)]_2[\text{BF}_4]_4$ ($\text{X} = \text{dppa}$

(**8**), dppe (**9**), dppm (**10**)), respectively, whereat the loop-shaped structure of **7** is maintained and each dimolybdenum unit is substituted by one bisphosphine ligand. Thus, it can be concluded, that complex **7** is a suitable precursor for the synthesis of large coordination compounds due to remaining reactive coordination sites. Hence, the carboxylate-bridged dimolybdenum(II) loop **7** was furthermore reacted with the bis(bisphosphine) linker $(\text{Ph}_2\text{P})_2\text{NCH}_2\text{CH}_2\text{N}(\text{PPh}_2)_2$ ⁹⁰ in a molar ratio of 2:1, whereat the isolation of a dimer of two bis(bisphosphine) connected loops was expected (Figure 19). Indeed, a reaction of compound **7** and the linker in propionitrile could be observed and proved by means of ¹H- and ³¹P NMR spectroscopy. The ³¹P NMR spectrum of the isolated pink product in CD₃CN shows one signal at 109.62 ppm, which underlines that all P atoms are equivalent and a selective reaction took place (no signals of the free linker $(\text{Ph}_2\text{P})_2\text{NCH}_2\text{CH}_2\text{N}(\text{PPh}_2)_2$ were found in the ³¹P NMR spectrum due to an insufficient solubility in CD₃CN). Unfortunately, several attempts to isolate crystals of the product failed. Neither changing the solvent from propionitrile to acetonitrile or benzonitrile, nor the change of the crystallization method from layering saturated solutions with *n*-pentane, respectively, to diffusion of diethyl ether into a saturated solution of the product lead to suitable crystals. Thus, the final molecular structure could not be determined by means of single crystal X-ray diffraction.

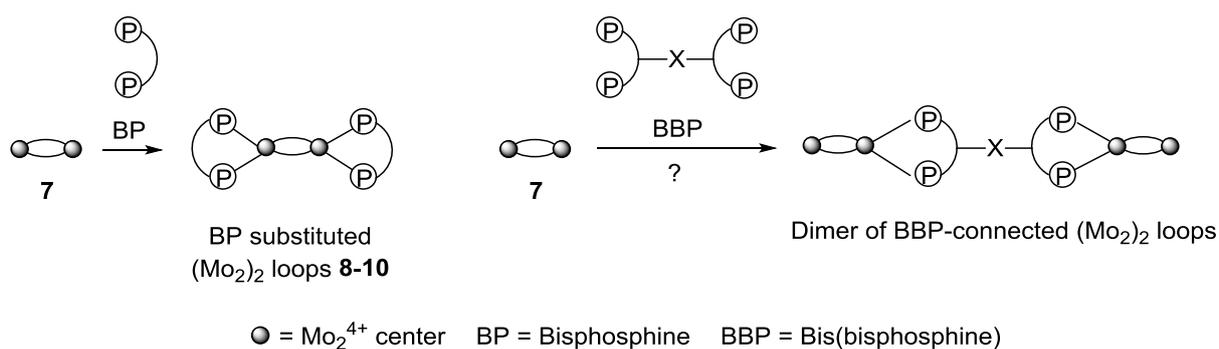


Figure 19. Syntheses of compounds **8-10** starting from **7** and the idea of synthesizing dimers of $(\text{Mo}_2)_2$ loops by the reaction of **7** with bis(bisphosphines).

Since the bis(bisphosphine) linker $(\text{Ph}_2\text{P})_2\text{NCH}_2\text{CH}_2\text{N}(\text{PPh}_2)_2$ was proved to be reactive towards carboxylate-substituted dimolybdenum(II) compounds, further reactions with the complexes $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ ²⁵ and $[(\text{CH}_3\text{CH}_2\text{CN})_8\text{Mo}_2(\text{O}_2\text{C}-\text{C}_6\text{Br}_4-\text{CO}_2)\text{Mo}_2-(\text{NCCH}_2\text{CH}_3)_8][\text{BF}_4]_6$ (**3**) were carried out. In both cases, reactions could be observed and verified by color changes of the initial reaction solutions. The reaction of $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ and the bis(bisphosphine) linker in acetonitrile resulted in a plurality of products, which can be derived from several peaks in the range 105-117 ppm (with

a main peak at 108.79 ppm) in the ^{31}P NMR spectrum of the isolated purple solid in CD_3CN . Again, no crystals could be obtained for both reactions, which excludes the structure determination by means of single crystal X-ray diffraction.

In order to obtain tubular arrays, complexes **7-10** could be reacted with axial linkers in future experiments. Suitable linkers might be 4,4'-bipyridine, 1,4-dicyanobenzene or pyrazine.

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7. List of Publications and Curriculum Vitae

7.1 List of Publications

- 1) ”*Synthesis and Characterization of Dimolybdenum(II) Complexes Connected by Carboxylate Linkers*”, Xu-Min Cai, **Dominik Höhne**, Mathias Köberl, Mirza Cokoja, Alexander Pöthig, Eberhardt Herdtweck, Stefan Haslinger, Wolfgang A. Herrmann and Fritz E. Kühn, *Organometallics*, 2013, **32**, 6004-6011.
- 2) ”*Loop shaped Dicarboxylate-bridged Dimolybdenum(II) Bisphosphine Compounds – A Rational Synthesis*”, **Dominik Höhne**, Eberhardt Herdtweck, Alexander Pöthig and Fritz E. Kühn, *Dalton Transactions*, 2014, **43**, 15367-15374.
- 3) ”*Synthesis and Characterization of Dimeric and Square-shaped Dicarboxylate-bridged Dimolybdenum(II) Coordination Compounds*”, **Dominik Höhne**, Eberhardt Herdtweck, Alexander Pöthig and Fritz E. Kühn, *Inorganica Chimica Acta*, 2015, **424**, 210-215.

7.2 Presentation

08/2015 250th ACS National Meeting and Exposition
Boston, United States of America
Presentation: “*Dicarboxylate-connected and Bisphosphine-substituted Dimolybdenum(II) Coordination Compounds*”

7.3 Curriculum Vitae

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Education

- 10/2012-09/2015 **PhD Candidate**
 Technical University Munich, Chair of Inorganic Chemistry
 Dissertation:
„Synthesis and Characterization of Dicarboxylate-bridged and Bisphosphine-substituted Dimolybdenum(II) Complexes as Potential Building Blocks for Supramolecular Coordination Compounds “
 Tasks: Synthesis of organic ligands and metal-organic coordination compounds and their characterization (ESI-MS, TGA, XRD, NMR-, UV-Vis and IR spectroscopy and CV)
- 10/2010-07/2012 **Master of Science in Chemistry**
 Technical University Munich, Munich
 Major subject: Inorganic and metal-organic chemistry
 Minor subject: Organic chemistry
 Topic of the Master’s Thesis:
„Mononuclear and dinuclear acetonitrile complexes for the systematic synthesis of 1D-polymers as potential building units for MOFs“,
 Final grade: 1.3
- 08/2011-12/2011 **Exchange Semester**
 Uppsala University, Uppsala, Sweden
 Course: Inorganic Analytical Chemistry (ICP-MS, AAS, AES, XRF, ESCA, SEM, EDS)

10/2007-08/2010	<p>Bachelor of Science in Chemistry Technical University Munich, Munich Topic of the Bachelor's Thesis: <i>„Polymerisation behavior and synthesis of C2-symmetric ansa-Hafnocenes“</i>, Final grade: 2.2 Tasks: Polymerisation of propene (Characterization via DSC)</p>
09/2006-05/2007	<p>Civilian Service Kinderhilfe Fürstenfeldbruck, Fürstenfeldbruck</p>
09/1997-06/2006	<p>Abitur Graf-Rasso Gymnasium, Fürstenfeldbruck, Final Grade: 2.2</p>

Work Experience and Internships

03/2015-04/2015	<p>Practical Course Assistant Singapore Singapore Polytechnic, TUM Asia, Singapore Tasks: Supervision of students in the course “Advanced Inorganic Chemistry and Analytical Chemistry“</p>
10/2011-12/2011	<p>Research Internship Uppsala University, Uppsala, Sweden Institute for Materials Chemistry Tasks: Diamond coating of silicon wafers via chemical vapor deposition (Characterization via XRD, Raman, SEM)</p>
08/2008-03/2009	<p>Employee European Patent Office European Patent Office, Munich Tasks: Classification of Li-ion batteries</p>

Additional Information

Foreign languages	English (business fluent), French (advanced)
Publications	3 publications in chemical journals
Soft-Skill course	Communication in International Teams and Difficult Situations
Computer literacy	Microsoft Office (very good), Mestre Nova (very good), Sci Finder (advanced), Reaxys (very good), ChemDraw (very good)
Hobbies	Sport (active member in a soccer team since 1991, tennis, diving), Long distance journeys (New Zealand, South Africa, USA, Thailand)