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## **Reflections of Wolfgang Beck on the research of his research and that of his coworkers in Coordination Chemistry, Organometallic Chemistry and Bioinorganic Chemistry**

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### **Abstract**

Wolfgang Beck reports some reflections on his research and that of his coworkers in Coordination Chemistry, Organometallic Chemistry and Bioinorganic Chemistry. The chapter includes IR Spectroscopy, Historical Aspects, Ligands of Complexes which have been studied, Results in Organometallic Chemistry and with Complexes of biologically important Ligands. Especially the high merit of his coworkers is emphasized.

**Keywords :** Reflections of Wolfgang Beck in chemistry

Dedicated to my highly esteemed colleague Dr. Dr. h. c. Hubert Schmidbaur on the occasion of his 90th birthday

First of all, I would like to state that I consider it as great privilege to have been called in 1968 to the Ludwig-Maximilians-Universität München, to the place of my most famous predecessors Justus von Liebig, Adolf von Baeyer, Richard Willstätter, Heinrich Wieland, Rolf Huisgen and Egon Wiberg and I am always very thankful for this gracious fate.

Various fields of coordination and organometallic chemistry have found my interest:

## 1. IR Spectroscopy

F. A. Cotton [1] has introduced IR spectroscopy as novel method into organometallic chemistry. For my PhD thesis with my highly esteemed Professor Walter Hieber I was introduced by Erwin Weiss [2], Otto Vohler [3] and Adolf Jahn [4] into dipole moment measurement [2] and IR spectroscopy including group theory [3,4]. For my habilitation I studied with my first PhD student and friend Karlheinz Lottes the change of NO IR wavenumbers of nitrosyl complexes in different solvents and NO absorptions of various NO complexes [5]. With Robert Nitzschmann we were among the first to study the IR intensity of CO absorptions in metal carbonyls [6], and a high increase of the intensity of CO absorption was observed in anionic metal carbonyls, due to a polar [7] C-O bond, caused by metal to CO back bonding [6].•

With Alex Melnikoff application of IR intensity was reported for the determination of angles between C-O bonds in metal carbonyls, whose CO vibrations have different symmetry [8] and for a correlation between IR intensity and atomic polarisation in „symmetric" (dipole moment free) metal carbonyls [9]. Intensities of CO and NO absorptions were used with R. Schlodder and S. Vogler for a scale of donor ability of anionic ligands [10].

Many most important and remarkable communications on the intensity of CO absorptions in metal carbonyls were reported by Orgel [7], Anderson and Brown, Kettle and Paul [11], Bor [12], El-Sayed and Kaesz, Kaesz and Bau, Bigorgne, Abel and Butler, Wing and Crocker, Lewis, Manning and Miller (the latter been cited by Bor [12]) and particularly by Darensbourg [13].

At the beginning of our research on fulminate complexes I studied the IR spectrum of the fulminate ion  $\text{CNO}^-$  [14].

## 2. Historical Aspects

Our studies on fulminate complexes, on fulminic acid and on indigo complexes should remind on the classic work of Liebig, von Baeyer and Wieland.

Liebig studied metal fulminates and fulminic acid in his first research work [15] and this chemistry found the interest of Heinrich Wieland [16, 17].

Heinrich Wieland [17] and the couple Winnewisser [18] have to be praised for their great research on fulminic acid.

Greatfully I remember the highly motivated and even courageous collaboration with Erich Schuierer, Klaus Feldl and Peter Swoboda [19,20]. We could characterize and stabilize fulminate complexes - by using large coligands or large cations which dilute the energy rich parts and lead to non explosive compounds [20]. The structures of fulminate complexes could be determined and have been calculated by Thomas Klapötke and the  $^{14}\text{N}$ -NMR spectra of fulminate complexes were reported by Werner Becker [21]. The classical mercury fulminate (Knallquecksiber) could be recognized as molecular species  $\text{ONC-Hg-CNO}$  by X-ray crystallography [22].

With Klaus Feldl the H-CNO structure of fulminic acid could be established by its IR spectrum [23], which was ascertained by Manfred and Brenda Winnewisser [18], who recognized H-CNO as novel „quasi linear" molecule.

The synthesis and determination of the constitution of indigo was a highlight and master piece in Baeyer's research and a most difficult proof at that time [24]. The existence of metal complexes of indigo has been demonstrated by Kunz, Kuhn and Machemer [25]. My excellent PhD student Christoph Schmidt [26] succeeded - after a very long time without success - with untiring experimental strength to crystallize new chelate complexes of the indigo anion. The chemistry of metal complexes of indigo and related dyes has been further developed by Christoph Schmidt [26] and by the fine work of Andreas Lenz [27] and has been reviewed [26]. After 20 years since our report again interest for indigo metal complexes arose [26].

We could introduce a great variety of ligands into metal complexes:

### **3. The pseudo halides fulminate $\text{CNO}^-$ , the azide $\text{N}_3^-$ , tricyanomethanide $\text{C}(\text{CN})_3^-$ , quadrate $\text{C}_4\text{O}_4^{2-}$ , tetrathioquadrate $\text{C}_4\text{S}_4^{2-}$ , hyponitrite $\text{N}_2\text{O}_2^{2-}$ , curcumine anion, stable organic radicals.**

The fulminate ligand could be shown to build up a strong ligand field, similarly as cyanide [28]. With our studies on fulminate complexes I would like to praise Karl Schorpp and Wolfgang Weigand for the safe synthesis of  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CNO})_2$  via the oxidative addition of nitromethane to  $\text{Pt}(\text{PPh}_3)_4$ . [21, 28]. Isomerization of fulminate  $\text{CNO}^-$  to isocyanate  $\text{NCO}^-$  has been calculated by Florian Holsboer [29] and experimentally proved for the isomerization of  $(\text{Ph}_3)_2\text{Pt}(\text{CNO})_2$  to  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{NCO})_2$  in the presence of organic carbonyl compounds [30] and for  $(\text{OC})_5\text{W-CNO}^-$  to  $[(\text{OC})_5\text{W-NCO}]^-$  [30]. The latter isocyanate complex is also formed by

addition of the azide anion to  $W(CO)_6$  [31]. The reactions of Cr, Mo, W hexacarbonyls with the azide anion was studied with my highly motivated coworker Halvor Stang Smedal [31,32] and could be cleared by the support of Dr. W. Pfab (BASF Ludwigshafen) [32] and was followed by kinetic studies of Helmut Werner and Horst Engelmann and were reviewed [32]

As very remarkable result appears the formed NH analogue of fulminate  $[(OC)_5W\cdot CNNH]^-$  which was proved as 1,3-dipole in (3+2)-cycloaddition reactions [33].

With the azide ligand many novel metal complexes could be obtained, again stabilized by large cations and could be structurally characterized [34]. My creative colleague and friend Wolfpeter Fehlhammer has given a comprehensive overview of these azido complexes [35] and their novel reactivity [36]:

Coordinated azide was shown

- to react with CO to yield the isocyanate  $NCO^-$  ligand [32, 37], which independently was found by Colmann et al. [37] and which alternatively is also formed by reaction of metal carbonyls with the azide anion [31, 32].
- to undergo - with the famous Huisgen [3,2]-dipolar cycloaddition in mind [38] - [3+2] cycloaddition with nitriles, isonitriles, alkynes and carbon disulfide to afford five membered heterocyclic ligands [35].

Recently, Sadler and coworker [39] reported reactions of azido Pt(IV) complexes with alkynes and emphasized that cycloaddition proceeds without copper catalysts. The cycloaddition reactions at the coordinated azide ligand normally proceed without a catalyst [36]. The first example of a reaction of an azido complex of Pd(II) was found in my group [40].

In collaboration with H. Köhler (University Halle) [41] we studied (during GDR time) the coordinative behaviour of tricyanomethanide  $C(CN)_3^-$  [42]. Unfortunately, my esteemed colleague H. Köhler could not continue his interesting research in the free unified Germany, due to his early death.

Franz Götzfried and Janina Altman studied Pt complexes of quadratic acid [43] and Franz Götzfried and Reinhard Grenz presented in my group novel complexes of tetrathioquadratate as bridging bis(chelate) forming ligand [44].

Frank Kühlwein [45] was very successful to synthesize a series of various chelate complexes of the curcumin anion, obviously a new class in coordination chemistry. We were very

delighted, when Frank Edelmann and coworkers [46] praised our work in his impressive review on curcumin complexes as pioneering and even stated what can be learnt from our publication. At present curcumin complexes find attention for possible therapies of various diseases [47]. Complexes of other dyes were also studied by Franz Kühlwein [45].

In the course of our study on nitrosyl complexes Engelmann and Smedal [48] synthesized compounds of trans-hyponitrite  $\text{Ph}_3\text{PM-ON-NO-MPPh}_3$  (M=Sn, Pb). The structure of the tin compound was determined by X-ray crystallography [49] and used by Daniel Beck and Peter Klüfers for the preparation of hydrogenhyponitrite ruthenium complexes [50]. Ruthenium complexes are of interest for the reductive dimerization of NO which was described by Böttcher and coworkers [51] to form a trans- $\text{N}_2\text{O}_2$ -bridged diruthenium complex.

My interest was always devoted to radicals. Thus, with Karlheinz Schmidtner the coordination of the stable di-tert.-butylnitroxide to cobaltdichloride was investigated [52].

Later, a series of metal complexes with functionalized nitroxides as ligands could be obtained and structurally characterized [53, 54].

I would like to remember gratefully my first PhD students Karlheinz Lottes, Robert E. Nitzschmann, Erich Schuierer, Halvor Stang Smedal, Klaus Feldl, Karl-Heinz Stetter, Karlheinz Schmidtner, Horst Engelmann, Wolf Peter Fehlhammer, Peter Pöllmann, ShawkyTadros, Manfred Bauder, Henning Bock, Peter Swoboda for the successful and harmonic collaboration in the years 1963-1970.

#### 4. Organometallic Chemistry

An elegant method for the synthesis of a large series of hydrocarbon bridged metal complexes has been developed by addition of anionic organometallic compounds, mainly carbonylmetallates, as nucleophiles to  $\pi$ -coordinated hydrocarbons [55]. I would like to emphasize the many impressive contributions to this topic with unusual novel hydrocarbon bridges by Bernhard Olgemöller und Klaus Raab [56], Hans-Joachim Müller [57], Josef Breimair [58], Bernhard Niemer [59], Michael Wieser [60], Stephan Hüffer [61] and Jasna Milke [61]. Only some examples of their fine PhD results are given. Thus, the addition of  $[\text{CpMo}(\text{CO})_3]^-$  (M = Mo, W), of  $(\text{CO})_5\text{Re}^-$  or of  $\text{Os}(\text{CO})_4^{2-}$  to the cation  $[(\text{CO})_5\text{Re}(\text{C}_2\text{H}_4)]^+$  has led to the ethylene bridged compounds  $[(\text{CO})_5\text{Re-CH}_2\text{CH}_2\text{-Re}(\text{CO})_5]$  and  $[(\text{OC})_3\text{CpM-CH}_2\text{CH}_2\text{-M}(\text{CO})_3\text{Cp}]$ ,  $(\text{OC})_5\text{ReCH}_2\text{CH}_2\text{Os}(\text{CO})_4\text{CH}_2\text{CH}_2\text{Re}(\text{CO})_5$  complexes [56,59].

Even complexes with a single carbon atom as bridge between two metal atoms could be obtained by Knauer in his PhD thesis [62].

Another topics in organometallic chemistry which we followed were complexes with weakly bonded coordinated anions, mainly hexafluorophosphate and tetrafluoroborate, which proved to act as strong organometallic Lewis Acids [63]. Here, Klaus Schloter [64], Karlheinz Sünkel [63], Klaus Raab [65], Elisabeth Lippmann und Roland Krämer,[66], Philipp Rosendorfer [67], Peter Fritz [68] and Elke Fritsch [69] and many coworkers in my group [63] have great merits. Important examples for the precursors of Lewis Acids were  $\text{Cp}(\text{OC})_3\text{MX}$  ( $\text{M} = \text{Mo}, \text{W}$ ) and  $(\text{OC})_5\text{ReX}$  ( $\text{X} = \text{FBF}_3, \text{FPF}_5$ ) and  $(\text{OC})_4\text{Re}(\text{OC}_2\text{H}_5)\text{FBF}_3$ ,  $(\text{OC})_2(\text{Ph}_3\text{P})_2\text{Mo}(\text{O}_3\text{SCF}_3)_2$  (precursors for two and three coordination sites).

Remarkable results are the isolation of the dichloromethane complex  $[\text{Cp}(\text{CO})_3\text{Mo}(\text{CH}_2\text{Cl}_2)]\text{PF}_6$  [64] and the NMR detection of the dynamic behaviour of the coordinated  $\text{BF}_4^-$  ligand by Klaus Schloter and Mathilde Appel [64].

The use of  $\text{Re}(\text{CO})_5\text{FBF}_3$  has led Klaus Raab, Peter Fritz and Wolfgang Sacher [68] to a series of complexes with simple and complex anions also as bridging ligands. Elke Fritsch and Jürgen Heidrich [68] presented evidence for the high reactivity of  $\text{Re}(\text{CO})_5\text{FBF}_3$ .

As highlights in this field the reactions of  $[\text{Re}(\text{CO})_5]^-$  and  $[\text{ReCO}_5]^+$  have been emphasized [69]. Of high interest appears the tris – by  $\text{Re}(\text{CO})_5^+$  - metalated carbonate and sulfide  $[(\text{CO})_5\text{Re}]_3\text{X}$  ( $\text{X}=\text{CO}_3, \text{S}$ ) by Josef Breimeir and Klaus Raab [69]. With Mathilde Appel, Torsten Weidmann and Shahram Mihan we consider the series  $(\text{OC})_5\text{Re}-\text{C}\equiv\text{C}-\text{Re}(\text{CO})_5$ , [70],  $(\text{OC})_5\text{Re}-\text{CH}=\text{CH}-\text{Re}(\text{CO})_5$  [70],  $(\text{OC})_5\text{Re}-\text{CH}_2-\text{CH}_2-\text{Re}(\text{CO})_5$  [56] as attractive. Shahram Mihan, Peter Fritz and Peter Steil found that,  $(\text{OC})_5\text{Re}-\text{C}\equiv\text{C}-\text{Re}(\text{CO})_5$ ,  $(\text{OC})_5\text{Re}-\text{C}\equiv\text{CR}$  and  $(\text{OC})_5\text{Re}-\text{CH}=\text{CH}_2$  can function as ligands [70, 71]. As another highlight may be considered the first with Elisabeth Lippmann, Thomas Kerscher, Bernd Aechter, Christian Robl and particularly with Peter Hofmann at Heidelberg observed isomerization of a cis-bis(alkyne) complex to a cyclobutadiene Re complex [71].

Interesting reactions of metal carbonyls with three membered heterocycles (aziridine, episulfide, epoxide, diaziridine) have been studied by Wolfgang Danzer and Roland Höfer [73,74], which proceed by ring opening. Aziridine-carboxylate complexes were studied by Thomas Hauck [74].

The reactions of the classical HNC (isohydrocyanic) complexes of Fe, Au and Pt with epoxides, which interestingly have been already studied by Baeyer and Villiger in 1901 [75], led Wolfgang Weigand and Matthias Schaal to carbene complexes [76].

A short excursion has been made with metal complexes of polymeric ligands [77].

## **5. Bioinorganic and bioorganometallic chemistry - Metal complexes with biologically important ligands [78]**

In one of the early publications in bioorganometallic chemistry Bernhard Purucker [79] synthesized complexes of nucleobases and nucleosides from metal carbonyls and Pd and Pt compounds. Further complexes with nucleobases and nucleotides as ligands were contributed by Mano Mohan Singh [80], Yorgos Rosopolos [80] and Gerhard Bauer [81] and Roland Krämer [82].

A series of early complexes with sugar derivatives as ligands could be prepared and characterized by Peter Lednor and Gerhard Thiel [83], Yvonn Nagel [84], Jingtang Chen and Thomas Pill and my esteemed colleague Hildebert Wagner [85], Yuanlin Zhou [86], Stefan Krawielitzki [87], Eva-Maria Ehrenstorfer-Schäfers [88]. The chemistry of sugars as ligands has been developed by Peter Klüfers and coworkers [89] in a pioneering and comprehensive way.

In my group Roland Hubel [90], Christopher Missling [91] and Martin Schweiger [92] were successful with organometallic complexes with alkaloids as versatile ligands. Complexes with other biologically interesting ligands include those with drugs by Stefan Krawielitzky [93], Oliver Woisetschläger [e.g. with barbituric acid, 94] and Roland Hubel [95], Thomas Pill, Hildebert Wagner and his coworkers [96] and those with hormones as ligands by Eva-Maria Ehrenstorfer-Schäfers [96] and Janina Altman [97] and by Bernhard Miller and my dear colleagues Wolfgang Steglich and Harabalos Zorbas on cis-dichloroplatinum complexes with N-alkyl-ethylenediamine and isoquinoline ligands and their antitumor activity [98].

In the last years of my active career we concentrated our interest on the coordination and organometallic chemistry of metal complexes with amino acids and peptides [99]. In the following some main reports to this theme are shown together with relevant reviews:

One of the main topics was the summary of several aspects in the chemistry of complexes of amino acids and peptides (synthesis, reactions, catalysis, pharmacological activity) which were covered by Kay Severin and Ralf Bergs [99].

Other topics were “Metal Ions and Metal Complexes as Protective Groups of Amino Acids and Peptides - Reactions at Coordinated Amino Acids” [99] and „Synthesis and Reactivity of Platinum and Palladium Complexes of Amino Acids and Peptides“ [99].

Here, important contributions were accomplished by Bernhard Purucker [100] and Norbert Steiner and Ehrenstorfer-Schäfers [101]. As very attractive topic appears “Formation of Peptides in the Coordination Sphere of Metal Ions and of Classical and Organometallic Complexes and some Aspects of Prebiotic Chemistry” [102]. Here, particularly, the most important contributions by Bernhard Purucker [103], Herbert Bissinger, Michael Girnth – Weller with platinum complexes [104], Roland Krämer and Michael Maurus [105], Winfried Hoffmüller and Jan Schapp with catalytic peptide formation [106] and Katharina Haas [107] with organometallic half-sandwich complexes have to be emphasized. Katharina Haas has developed a facile synthesis of cyclotetrapeptides [108] from which Markus Lang could synthesize cyclams [108]. Interestingly, tetracyclopeptides of Ni(II) and Pd(II) with functional side chain could be obtained by Jan Schapp and Katharina Haas [109]. A selective hydroxylation of glycine in a nickel(II)-cyclotetrapeptide complex is certainly noteworthy [110].

Many further contributions to bioinorganic chemistry have been accomplished via the introduction of organometallic substituents as labels into amino acids or peptides with high motivation by the fine work of Doris Freiesleben [111], Bernd Kayser [112], Werner Bauer [113], Ingo Zahn, Reinhold Urban and Theo Ederer [114] including the very remarkable 2-cyclopentadienyl glycine by Harald Dialer [115, 116] and by my dear faithful friend Wolfgang Steglich [115] and including propargylglycine [117] and C=C and alkyne bridged amino acid [117], which may be of use for labelling of amino acids.

A large series of organometallic half-sandwich complexes with amino acids or peptides has been synthesized e.g. by the highly motivated coworkers Roland Krämer [105], Harald Dialer [116], Walter Ponikvar [117, 122], Ralph Bergs [118], Kay Severin [119], Winfried Hoffmüller [106, 123], Katharina Haas [107, 120], Daniela Koch [121] and Stefan Krawielitzki [88].



We also studied derivatives of amino acids - many Schiff-bases - as ligands and here the remarkable and important work by Eberhard Ambach [124], Andreas Böhm [125], Norbert Steiner [126], Armin Fehn [127], Bernhard Schreiner [128], Oliver Briel [129] Oliver E. Woisetschläger [130], Reinhold Urban [131], Theo Ederer [132] has to be marked.

In the same way the fine contributions by Peter W. Lednor, Hans Georg Fick and Herbert Trampisch, [133], Michael Girnth-Weller [134], Ingo Zahn, Elfriede Schuhmann [135], Daniela Koch [121] and Markus A. Lang and Markus Prem [136] have to be emphasized. N-diphenylphosphino-amino acids [133], N-dithiocarboxy-amino acids [134] and thioglycinate and thioalaninate [135] and 2-thienylglycine [135] and oxocarbonyl N-protected amino acids and isocyanoacetyl-peptide esters [136] have been introduced as ligands.

From our platinum compounds with amino acids the interest arose for their possible application as antitumor agents – the most active cis-platinum kind – and in collaboration with Prof. Helmut Schönenberger and his coworkers at the University Regensburg a series of in vivo and in vitro anti cancer studies on  $\text{Cl}_2\text{Pt}(\text{aminoacid ester})_2$  and  $\text{cis-Cl}_2\text{Pt}(\text{peptide ester})_2$  compounds have been performed [136] and various encouraging results have been observed [137].

In conclusion of my short summary of our research I would like to recall some chiral complexes from my excellent coworkers, since amino acids and peptides are strongly associated with chirality. Gottfried Huttner, Wolfgang Danzer found a complete asymmetric synthesis of a Mo-aminoacyl chelate complex [138]. Wolfgang Petri and Joachim Meder synthesized histinato complexes of Mo and W [139]. Wolfgang Petri and colleagues obtained chiral dicarbonyl(cyclopentadienyl) complexes of Mo and W with amino acid anions [139], Hans Georg Fick chiral Mo and W complexes with diphenylphosphinoamino acid esters [138] and Roland Krämer et al. a series of chiral half-sandwich complexes of Rh, Ir, Ru with amino acid and their derivatives [140]. The structures of the chiral complexes  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{acetone})$  and of  $\text{Cp}^*(\text{Me}_2\text{SO})(\text{Cl})(\text{thyminato})$  Iridium could be determined [141].

Karlheinz Sünkel and Winfried Hoffmüller observed, that the trimerization of a  $\text{Cp}^*\text{Ir}(\text{prolinate})$  complex occurs with chiral self recognition [142]. By use of an optically active Pd complex the enantiomeric ratio of chiral amino acids can be determined, interesting work by Andreas Böhm and colleagues [143]. With Andreas Böhm and Henri Brunner chiral half-sandwich complexes of Rh and Ir with Schiffbases from salicylaldehyde and amino acid esters could be obtained, partly with high diastereoselectivity [142].

Recently, I had the pleasure with an old love in chemistry, with nitrosyl complexes. The very sensitive trinitrosyl iron complexes  $\text{Fe}(\text{NO})_3\text{X}$  ( $\text{X}=\text{Br}, \text{I}$ ) which readily lose  $\text{NO}$ , from my diploma work with Professor Walter Hieber, could be ascertained by X-ray crystallography [145] and the structure of the classical complex  $\text{Pd}(\text{NO})\text{Cl}$ , first described by Reinhard Jira in 1988, could be solved [146]. Another nitrosyl complex which we studied was  $\text{V}(\text{NO})_3\text{Cl}_2$  [147]. Eberhard Ambach and Michael Maurus were successful to synthesize some nitrosyl complexes with amino acid carboxylate ligands  $[(\text{ON})\text{Pt}(\text{NH}_2\text{CHR}\text{CO}_2)_2]^+$  and chiral  $\text{Cp}(\text{ON})(\text{I})\text{Mo}(\text{NH}_2\text{CHR}\text{CO}_2)$  [148].

## **6. In the following section I would like to add some further examples from the research in our group with appreciation of the coworkers.**

Karl Heinz Stetter: Homogeneous pentafluorophenylmercapto-metal complexes [149].

Manfred Bauder: Reactions of hydrido-platinum(II) complexes with organic acids: amido complexes [150]

Manfred Bauder: G. La Monica, Sergio Cenini, Renato Ugo: Interaction of triphenylphosphine platinum (0) complexes with organic azides [151]

Ernst-Jürgen Schier, Wolfgang Sacher: Metal carbonyls with anions of cyclic imides [152]

Johann Christian Weis: Linkage isomers of benzazole-carbonyl complexes of Cr, Mo, W [153]

Couple P. and B. Kreutzer: Reactions of azido complexes  $(\text{Ph}_3\text{P})_2\text{M}(\text{N}_3)_2$  ( $\text{M}=\text{Pd}, \text{Pt}$ ) with sulfanes [154]

Couple Bernhard und Luitgart Olgemöller: Synthesis and reactions of cationic chloro(phosphine)platinum complexes [155]

Henning Bock and Rainer Schlodder: Cyanamide complexes of transition metals [156]

Wolfram Rieber: Synthesis of transition metal complexes of pentafluorophenyl hydrazine [157]

Reinhard Grenz, Franz Götzfried, Elmar Vilsmaier:  $(\text{ON})_2\text{Fe}(\text{SH})_2\text{Fe}(\text{NO})_2$ . The acid of Roussin salt [158]

Rudolf Schierl: A simple route to dithiocarbimidato-platinum (II) complexes [159]

Matthias Schaal, Wolfgang Weigand: Reactions of cyano complexes of Fe(II), Ru (II), Os (II) and Pt(II) with  $\alpha, \beta$  -unsaturated carbonyl compounds: Oxoisocyanide complexes [160]

Wolfgang Weigand: Oxoisocyanide complexes of Fe(II), Ru(II), Pd(II),Pt(II) [161]

Erich Leidl: Platinum (II) complexes with 4-isonitroso-oxazolone [162]

Martin J. Schweiger, Gerhard Müller: Metalated cyclobutenediones [163]

Peter M. Fritz: Rheniooxy(organyl)carbene complexes of Cr, Mo, W [164]

Herbert Wanjek: Pd(II) Complexes with dehydro- $\alpha$ -iminoacid esters as ligands [165]

Martin J. Schweiger, Elisabeth Lippmann, Christian Robl, Heinz Berke, Herbert D. Kaesz: Diacyl bridged complexes of Re, Mo, Ru, Cu [166]

Peter Steil: Pentacarbonyl(phosphine)rhenium complexes [167]

Elke Fritsch, Thomas Kerscher: Cationic pentacarbonyl-carbene complexes of Mn and Re [168]

Kay Severin, Gunter Trojandt, Wolfgang Steglich: Macrocyclic titanium (IV) complexes with C<sub>3</sub> symmetric synthetic peptides [169]

Josef Breimaier, Torsten Weidmann: Addition of anionic Fischer-Carbene-Complexes to coordinated unsaturated hydrocarbons with C-C coupling [170]

Hans-Jörg Bentele, Stefan Hüffer: Addition of hydrofulleride C<sub>60</sub>H<sup>-</sup> to coordinated unsaturated hydrocarbons [171]

Elfriede Schuhmann, Janina Altmann, Konstantin Karighiosoff: Bis(platinum(II)) und Bis(palladium(II)) complexes with amides of  $\alpha$ ,  $\omega$ -dicarboxylic acids [172]

Volker Weinrich: Reactions of carbonylmetalates with fumaric acid dichlorides: 2,4-Bis(pentacarbonylmangan and rhenium)but-2-enolide [173]

Andreas Geisbauer, Salam Mihan: Oxidation of Fischer-Carbene-Complexes to dimeric hydrocarbon bridged complexes [174]

Markus Prem: Complexes of Pd(II), Pt(II), Au(I) with the anion [N(CO<sub>2</sub>R)<sub>2</sub>]<sup>-</sup> (R = t-butyl) [175]

Rostislav Lampeka, Shahram Mihan: Isoxazole and isoxazoline carboxylates as ligands in metal complexes [177]

Rostislav Lampeka, Ralf Bergs, Rocio Fernandes de Bobadilla, Shahram Mihan: Halfsandwich complexes with amides of 2-hydroxyimino carboxylic acids [178]

Hans Joachim Meder, Wolfgang Petri and Kay Severin, Ralf Bergs, Michael Maurus, Shahram Mihan and Roland Krämer, Herbert Wanjek: Metal complexes with 2-iminocarboxylate ligands [179-181]

Barbara Wagner, Ute Taubald: Stabilization of 1-pyrroline at palladium (II) [182]

Bernd Kaiser, Christopher Missling, Jörg Krizek, Heinrich Nöth:  $\alpha$ -metallated amino acids [183]

Markus Prem, Werner Bauer; Metal complexes of oxazolones and oxazolinones [184]

Andy Hor: Nucleophilic attack of pentacarbonyl rhenate (-I) on sulfur [185]

Harald Brix: Reactions of carbonylcyclopentadienylhydrides with  $\alpha$ -aminoacetylenes [186]

Claus Herdeis: Platinum (II) complexes of vinylogous amino isocyanides [187]

Many results in 700 publications have been presented in series (with accompanying reviews):

11 Publications on „Metal complexes with three membered cyclic heterocycles"

12 Publications on „Metal complexes of dyes". Review [26]

21 Publications on „Spectroscopic investigations on metal complexes"

52 Publications on „Hydrocarbon bridged metal complexes" Review [55]

64 Publications on „Pseudohalide metal complexes" (W. Beck, W. P. Fehlhammer, MTP Int. Review of Science, Inorg.Chem.1, Vol.2, 1972, 283), including fulminate [15,17, 28] and azide complexes [32,36]

77 Publications on „Organometallic Lewis Acids. Review [63,70]

176 Publications on „Metal complexes with biologically important ligands" Reviews [89, 99,102]

11 Publications on studies for antitumor activity of platinum amino acid and peptide complexes [137]

10 Publications on complexes with organic radicals [53,54]

## 7. Concluding Remarks

I had the great privilege and luck that many excellent students joined my group and my sincere thank is devoted to them for the many attractive contributions and for the always

harmonic cooperation. I want to thank my loyal most helpful and kind companions in our research for many years - Wolfpeter Fehlhammer, Karlheinz Sünkel and Wolfgang Weigand.

My deep thank is due to the coworkers who solved the structures of our new metal complexes so competently which often was very important to ascertain our chemistry besides the information on bonding: Heinrich Nöth (my esteemed colleague in many years), Peter Mayer, Ulrich Nagel, Kurt Polborn, Walter Ponikwar, Karlheinz Sünkel, Martin Steimann, Barbara Wagner.

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I had in mind to write a book on the history of chemistry at LMU in continuations of the very interesting and comprehensive book by Wilhelm Prandtl „Geschichte des chemischen Laboratoriums der bayerischen Akademie der Wissenschaften in München" in order to thank

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