Helmut Werner

H. Werner has recently published his ***10th article*** *since 2000 in Angewandte Chemie:*
"Carbene-Transition Metal Complexes Formed by Double C–H Bond Activation": H. Werner, *Angew. Chem.* **2010**, *122*, 4822–4837; *Angew. Chem. Int. Ed.* **2010**, *49*, 4714–4728.

Helmut Werner

Date of birth:	April 19, 1934
Position:	Professor Emeritus of Inorganic Chemistry, University of Würzburg (Germany)
Education:	1958 Diploma thesis and first PhD thesis (unfinished, because of my escape from East Germany) with Franz Hein, University of Jena (Germany) 1961 PhD with Ernst Otto Fischer, Technische Hochschule München (Germany) 1962–1963 Postdoc with John H. Richards, Caltech Pasadena (USA) 1963–1966 Habilitation, Technische Hochschule München 1967–1968 Lecturer, Technische Hochschule München 1968–1975 Assistant Professor and Professor at the University of Zurich (Switzerland) 1975–2002 Professor and Chair of Inorganic Chemistry, University of Würzburg (Germany)
Awards:	**1987** Fellow of the Royal Society of Chemistry; **1988** Alfred-Stock-Prize of the German Chemical Society; **1988** Member of the German Academy of Sciences "Leopoldina"; **1994** Centenary Medal and Lectureship of the Royal Society of Chemistry; **1994** Max Planck Award; **1995** J. C. Mutis/Alexander von Humboldt Award; **1995** Paolo Chini Memorial Lectureship; **2001** Honorary Doctor from the University of Zaragoza (Spain); **2004** Gordon-Stone Lectureship; **2006** Honorary Doctor from the University of Jena
Current research interests:	Synthesis, structure, and reactivity of organometallic compounds of the electron-rich transition metals; more recently: historical developments in inorganic and organometallic chemistry
Hobbies:	Classical music (especially W. A. mozart and, as a previous member of a Bach choir for boys, J. S. Bach); history of the 19th and 20th century; soccer (for 62 years, when we won the regional championship of the youth class C teams)

My favorite subject at school was … mathematics.

My first experiment … which I did together with a friend at the age of 11 was an oxyhydrogen gas explosion.

I chose chemistry as a career because … I wanted to do experiments and my chemistry teacher told me cagily that as a mathematician I would mostly sit on a chair or stand at the blackboard.

When I wake up I … enjoy a cup of good Indian tea and have a pleasant breakfast with my wife, which can last up to an hour since I became Professor Emeritus.

The best advice I have ever been given (by E. O. Fischer) was … "not to stand on one leg", which means not to rely on only analytical or only spectroscopic data of a new compound, but to use the entire spectrum of scientific techniques for a well-founded proposal.

If I could have dinner with three famous scientists from history, they would be … Friedrich Wöhler (who proved that inorganic and organic chemistry are two sides of the same coin), Edward Frankland (who by searching for stable radicals founded organometallic chemistry), and Alfred Werner (who revolutionized the chemistry of coordination compounds).

The most significant scientific advance of the last 100 years has been … the elucidation of the structure of DNA.

The biggest problem that scientists face is … not to follow what is fashionable in a certain field but to adhere faithfully to their chosen goals.

I am waiting for the day when someone will discover … a method to mimic photosynthesis in the lab with the same efficiency as in nature.

One of my favorite books is … the autobiography of Carl Zuckmayer "Als wär's ein Stück von mir".

My favorite food is … a spicy Thuringian sausage, fried over pine cones and quenched with Thuringian beer.

How is chemistry research different now than at the beginning of your career?

52 years ago, when I came to Munich and began the work on my PhD thesis in the Fischer group, I did almost everything by myself. After having prepared a new metal complex, I carried out the elemental analysis and determined the molecular weight. When I used a tertiary phosphine other than triphenylphosphine, such as tributyl- or tricyclohexylphosphine, I had prepared it myself. The only spectrometer was an IR instrument; a 60-MHz NMR spectrometer wasn't available until 1961. As a consequence, my PhD thesis contained only 73 pages and the outstanding dissertation of Walter Hafner, disclosing the spectacular synthesis of bis(benzene)chromium and the preparation of the first chromium and vanadium cyclopentadienyls, contained even less (exactly 41 pages). My PhD students, who finished during the last two decades, and all of whom were very committed but didn't work any harder than we did 50 years ago, needed 250 to 300 pages to present their results; about one fourth of the content was used to summarize the spectroscopic data. The instrumental techniques have indeed made a tremendous leap forward and have made structural proposals much more substantiated.

Has your approach to chemistry research changed since the start of your career?

Not really. In my Habilitation thesis, as the first in Germany to the best of my knowledge, I carried out kinetic studies on substitution reactions of organometallic compounds, with the aim to elucidate the mechanism of those reactions. At the beginning I had to think about an appropriate methodology and had to study the work of pioneers in the field, in particular that of Ingold, Basolo, and Pearson. Thirty years later, 10 years before I retired, we started to investigate the catalytic activity of a series of rhodium and iridium complexes prepared in our laboratory, again without any experience in this matter. Once more, we had to establish the necessary technique and carefully study the work of predecessors such as Halpern, Wilkinson, and Brunner. However, what has definitely changed is that nowadays every graduate student or postdoc has access to the IR, UV, and NMR instruments and that the determination of the crystal structure of a new compound can be done almost instantaneously. Another difference compared to the early days is that during the last two decades most of my PhD students spent several months up to one year in the group of a foreign colleague with whom we collaborated, particularly in Spain, France, Great Britain, and the USA.

Has your approach to publishing your results changed since the start of your career?

Yes, mainly for two reasons. The first is due to my move from Zurich to Würzburg. In Würzburg, I started from zero and had to rebuild a new research group. Moreover, as the chairman of the institute, I had much more teaching and administrative duties than in Zurich. The consequence was that owing to my lack of time for the group we published nearly as many communications as full papers between 1977 and 1980. Later on, it became a rule that after my co-workers had presented their new results, we discussed in detail whether it was worth writing a communication or to complete the work and publish a full paper. Thus, since the mid 1980s the ratio between communications and full papers decreased from about 1:1 to 1:4. At the same time, and this is the second reason, we gradually changed from German to English as the preferred language of our manuscripts. While until the mid 1980s about 2/3 of our papers were published in German and 1/3 in English, during the next decade the ratio reversed and since the mid 1990s English became almost the sole language. Sometimes it broke my heart not to use my mother tongue, but since not only the Anglo-Saxons but also the great majority of foreign scientists published their work in English, the change was essential. In view of this situation, it is really a gift still to read the most interesting part of the *Angewandte* in German!

What do you think the future holds for your field of research?

A lot, I am convinced. Although several "hot topics" that use the prefixes "nano", "supra", or "bio" are dominating at present, synthetic organo-transition-metal chemistry remains irreplaceable, in particular for new achievements in homogeneous catalysis. I have no doubt that a renaissance in this field of research is coming, and I would be extremely happy to witness this progress.

What has been you biggest influence/motivation?

First of all my scientific supervisors, Franz Hein and Ernst Otto Fischer. I learned from Hein that above all it is crucial to maintain your convictions and in difficult moments not to stand aside. Fischer taught me that success is the result of hard work, and that it is rewarding not to take the line of least resistance. Later in my career, I learned in particular that it is not only possible to motivate students, but that you yourself can be motivated by creative co-workers to explore new scientific routes.

What is the secret to publishing so many high-quality papers?

It is simply and solely the collaboration with talented, open-minded, and effective co-workers. Without them, progress and success in science is impossible.

My 5 top papers:

1. “Tricarbonylhexamethylborazolechromium”: R. Prinz, H. Werner, *Angew. Chem.* **1967**, *79*, 63; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 91 – 92.
   Benzene C_6H_6 and borazine $B_3N_3H_6$ are isoelectronic and isosteric molecules. This motivated Egon Wiberg in the 1930s to call borazine “inorganic benzene”. In association with kinetic studies to generate $[(C_6Me_6)Cr(CO)_3]$ from $[Cr(CO)_6]$ and after it had been shown between 1955 and 1960, mainly by the group of Fischer, that benzene and its derivatives were able to form not only sandwich complexes $[M(C_6R_6)_2]$ but also half-sandwich type compounds $[(C_6R_6)M(CO)_3]$, we became interested in trying to prepare an analogous compound with $B_3N_3Me_6$ instead of C_6Me_6 as the ligand. Luckily, we didn’t know that several other groups had already attempted to achieve this goal but had failed. With $[(CH_3CN)_3Cr(CO)_3]$ as the starting material, Richard Prinz (my first PhD student) prepared $[(B_3N_3Me_6)Cr(CO)_3]$ in 90% yield, which excited the borazine community and half a year later led to my position at Zurich.
2. “The Synthesis of the First Double Sandwich Complex: The Dinickeltricyclopentadienyl Cation”: H. Werner, A. Salzer, *Synth. React. Inorg. Metal-Org. Chem.* **1972**, *2*, 239 – 248.
   Fischer had already had the idea to cover a sandwich (“burger”) with another structural level and to form a double sandwich (“double burger”) in the 1950s, and later it was strongly supported by the observation of the cations $[Ni_2(C_5H_5)_3]^+$ and the Fe_2 counterpart by mass spectrometry. In 1971, Albrecht Salzer succeeded at the synthesis of the nickel complex. In his PhD studies, he had investigated the reactivity of nickelocene towards nucleophilic and electrophilic reagents and, upon treatment of $[Ni(C_5H_5)_2]$ with trityl chloride, had obtained $C_5H_5CPh_3$. Next, by using $[CPh_3]BF_4$ instead of $[CPh_3]Cl$ he isolated, besides $C_5H_5CPh_3$, the BF_4 salt of the double sandwich (subsequently called triple decker) $[Ni_2(C_5H_5)_3]^+$ in nearly quantitative yield. One year later, the structure of the compound appeared on the cover of the abstract of papers of the VI. International Conference on Organometallic Chemistry and soon was included in the text books.
3. “Electron-Rich Half-Sandwich Complexes—Metal Bases *par excellence*”: H. Werner, *Angew. Chem.* **1983**, *95*, 932 – 954; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 927 – 949.
   Based on the work of Hieber in the 1930s, it was well known that metal carbonylates such as $[Co(CO)_4]^-$ or $[Fe(CO)_4]^{2-}$ readily react with electrophiles. The Vaska compounds *trans*-$[IrCl(CO)(PR_3)_2]$, prepared in the 1960s, with a 16-electron configuration and a free pair of electrons at the metal, also proved to be Lewis bases. Before 1970, however, there were only a few hints that coordinatively saturated uncharged complexes with an 18-electron configuration can behave similarly. In our work, carried out between 1974 and 1983, we showed that half-sandwich type complexes $[(C_nR_n)M(L)(PR_3)]$ with $n = 5$ (M = Co, Rh) and $n = 6$ (M = Ru, Os), and L = CO, C_2H_4, C_2R_2, $P(OR)_3$ etc., possess a Lewis basicity comparable to the Vaska compounds and react with electrophiles by attack at the metal center and not at one of the ligands. Complexes such as $[(C_5R_5)M(PMe_3)_2]$ (R = H, Me; M = Co, Rh) are basic to the extent that they react with the weak acid NH_4^+ even at − 78 °C by protonation at the metal. The review gave an up-to-date summary about the progress in this field.
4. “Closing the Gap between MC_3 and MC_5 Metallacumulenes: The Chemistry of the First Structurally Characterized Transition-Metal Complex with $M{=}C{=}C{=}C{=}CR_2$ as the Molecular Unit”: K. Ilg, H. Werner, *Chem. Eur. J.* **2002**, *8*, 2812 – 2820.
   After having prepared metallacumulenes of the type *trans*-$[MCl(L)(P\mathit{i}Pr_3)_2]$ with M = Rh, Ir, and $L = C{=}CR_2$, $C{=}C{=}CR_2$, and $C{=}C{=}C{=}C{=}CR_2$, which undergo C−C, C−O, C−N, and C−P coupling reactions under mild conditions, it became a real challenge to prepare the missing link in the chain with $L = C{=}C{=}C{=}CR_2$. An additional stimulus was that at that time no single complex with such a C_4R_2 ligand, which is extremely labile in the free state, had been structurally characterized. Kerstin Ilg developed an ingenious, in hindsight simple, method to generate the cumulated C_4 chain at the iridium atom, and she confirmed by X-ray crystal-structure analysis that the MC_4 unit is almost perfectly linear. Unexpectedly, reactions of *trans*-$[IrX(C_4Ph_2)(P\mathit{i}Pr_3)_2]$ ($X = CH_3$, N_3) with CO did not lead to an insertion of CO but to an insertion of the C_4Ph_2 cumulene into the $Ir{-}CH_3$ or $Ir{-}N_3$ bond.
5. “The Truly Symmetrical Doubly-Bridging Mode of Trimethylphosphine in a Dinuclear Rhodium Complex”: T. Pechmann, C. D. Brandt, H. Werner, *Chem. Commun.* **2003**, 1136 – 1137.
   In textbooks of inorganic and coordination chemistry it was frequently stated that, in contrast to CO and isocyanides, tertiary phosphines, which belong to the most well known ligands for low-valent transition-metal complexes, can coordinate to metal atoms only in a terminal but not in a bridging way. Based on previous results by Peter Schwab, Thomas Pechmann (my last PhD student) showed in the first part of his thesis (see *Angew. Chem.* **2000**, *112*, 4069–4072; *Angew. Chem. Int. Ed.* **2000**, *39*, 3909–3911) that in the dinuclear complex $[Rh_2(\mu\text{-}CPh_2)_2(PMe_3)(acac)_2]$ the phosphine ligand occupies a bridging position. It was somewhat unsatisfactory, however, that in this compound the two bond lengths Rh−P differed by approximately 0.3 Å, which left some doubt whether the behavior of PMe_3 as a ligand is exactly comparable with that of CO and CNR. In a rather elegant approach, Thomas succeeded in displacing the chelating acetylacetonato ligands by chloride ions and to isolate the complex $[Rh_2Cl_2(\mu\text{-}CPh_2)_2(\mu\text{-}PMe_3)]$, in which the Rh–P distances are equal and thus the phosphine is linked in a truly symmetrical doubly bridging mode to the rhodium atoms.

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