

Invited review

Success and serendipity during studies aimed at preparing carbenerhodium(I) complexes

Helmut Werner

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

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Abstract

The preparation of a series of new square-planar and half-sandwich type carbenerhodium(I) complexes will be described. The key to success is the use of the bis(stibane)rhodium compound *trans*-[RhCl(C₂H₄)(SbiPr₃)₂] as starting material from which in a stepwise manner the complexes *trans*-[RhCl(=CRR')(SbiPr₃)₂], *trans*-[RhCl(=CRR')L₂] (L = PiPr₃, AsiPr₃, SbEt₃) and [C₅H₅Rh(=CCR')L] (L = SbiPr₃, PiPr₃, PMe₃, CO, CN*t*Bu) have been obtained. Displacement of the carbene ligand in either *trans*-[RhCl(=CPh₂)L₂] (L = SbiPr₃, PiPr₃ or [C₅H₅Rh(=CPh₂)(PiPr₃)] by CO or CN*t*Bu leads to the formation of the corresponding carbonyl- or isocyanidrhodium compounds and the C–C coupling products Ph₂C=C=O and Ph₂C=C=N*t*Bu, respectively. The carbene ligand is also involved in the selective formation of the isomeric olefins CH₂=CHCPh₂H and Ph₂C=CHCH₃ on treatment of *trans*-[RhCl(=CPh₂)(SbiPr₃)₂] and *trans*-[RhCl(=CPh₂)(PiPr₃)₂] with ethene. The most spectacular reaction of the bis(triisopropylstibane) complexes, however, occurs on warming of *trans*-[RhCl(=CRR')(SbiPr₃)₂] in the absence of any substrate which yields the first representatives of dinuclear transition-metal compounds containing a tertiary stibane ligand in a bridging position. Some exploratory studies on the reactivity of the Rh₂(μ-SbiPr₃) complexes indicate that the triisopropylstibane can be replaced by SbMe₃, SbEt₃ or CN*t*Bu without destroying the dimetallic core of the molecule.

Keywords: Rhodium; Carbene complexes; Antimony; Stibanes

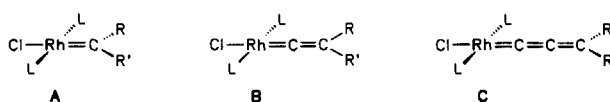
1. How it all began

It might not be considered by young chemists as encouraging if an older colleague starts a short review on some aspects of his recent work by saying that serendipity is one of the most important driving forces for a scientific career but the story reported in this article represents only one item of evidence that I have experienced in now almost exactly 35 years activity in research [1]. However, in 1988/1989 when I discussed with my coworkers the guidelines for a new research project we could not have dreamt of the final outcome of the work that we started at that time.

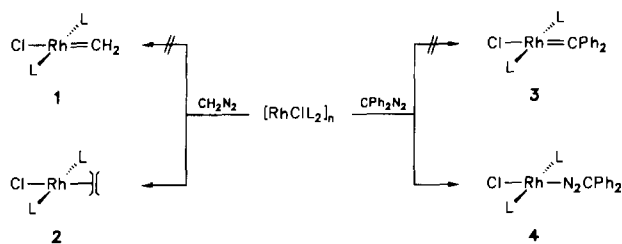
The original question arose as follows. After we had succeeded in preparing a variety of metallacumulenes of type **B** and **C** (Scheme 1) [2] and learnt that these underwent interesting addition and substitution as well as insertion reactions [3,4], we asked ourselves whether the missing link in this series, i.e. the corresponding carbenerhodium complexes of type **A**, could also be made.

We first tried to prepare the parent derivative **1** from [RhCl(PiPr₃)₂]_n [5] and CH₂N₂ but obtained **2**, and then attempted to prepare the diphenylsubstituted compound **3** from [RhCl(PiPr₃)₂]_n and CPh₂N₂ but isolated **4** (Scheme 2). Since even on heating, complex **4** does not eliminate N₂ but instead yielded *trans*-[RhCl(N₂)(PiPr₃)₂], the obvious conclusion was that diazomethane and its derivatives are not useful substrates for the synthesis of rhodium carbenes of type **A**.

Although the attempts to obtain the desired complexes **1** and **3** were unsuccessful they had an exciting outcome in the observation that both rhodium(I) compounds **2** and **4** could not only be interconverted into each other (Scheme 3) but in the presence of excess C₂H₄ and CPh₂N₂ were able to initiate a catalytic



Scheme 1. (L = PiPr₃).

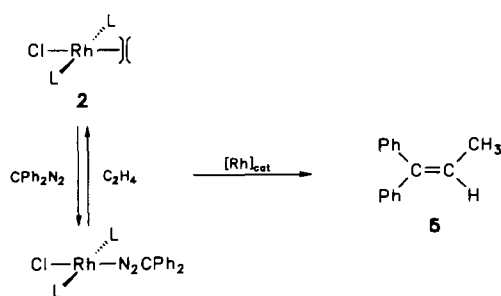
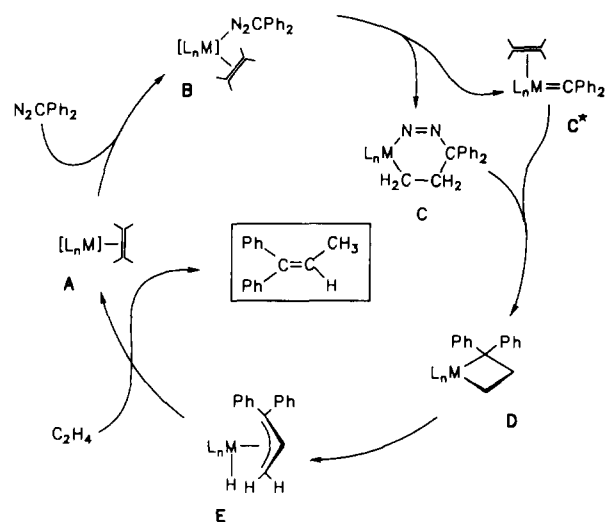
Scheme 2. (L = *PiPr*₃).

process leading exclusively to 1,1-diphenylpropene (**5**) as the organic product [6]. This novel C–C coupling reaction, in which formally two carbene fragments :CPh₂ and :CHCH₃ are joined, is noteworthy in so far as compounds of divalent rhodium such as [Rh₂(O₂C-CH₃)₄] are among the most efficient catalysts for the formation of disubstituted *cyclopropanes* from ethene and diazoalkane derivatives [7].

After we extended the scope of the catalytic reaction to find out whether functional groups in either the starting olefin (e.g. CH₂=CHCR₂OH) or the diazo compound (e.g. PhC(N₂)C(=O)Ph) were also tolerated [6,8], the crucial aspect was to establish the mechanism of the new olefin synthesis. We assumed that in the initial stage of the reaction both substrates, the olefin and the diazoalkane, are coordinated to the metal and subsequently either an MN₂C₃ six-membered ring **C** or a carbene(olefin)metal complex **C*** is formed (Scheme 4). From both species, a metallacyclobutane derivative **D** may be generated and lead via the η³-allyl(hydrido)-rhodium compound **E** to the olefinic product. Since **C*** is not only an intermediate in the postulated catalytic cycle but also possesses the structural features of the active species in the olefin metathesis reaction [9], a challenge remained to prepare square-planar carbene-rhodium(I) complexes and study their reactivity.

2. How we succeeded

The key to success for solving the above-mentioned problem was a variation of the formally innocent ligand L. When Peter Schwab, Justin Wolf and I discussed

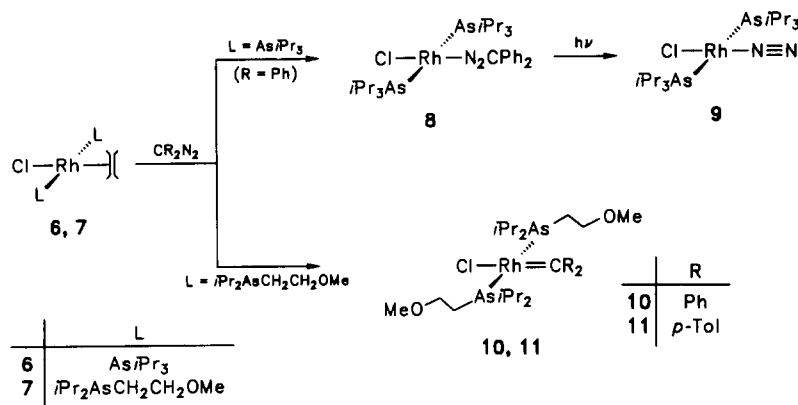
Scheme 3. (L = *PiPr*₃).

Scheme 4.

in late 1991 the research programme for Peter's Ph.D. thesis, we had the vague idea that instead of *PiPr*₃ a ligand of similar steric bulk but weaker donor strength might stabilize the Rh–N₂CR₂ bond in the assumed initial product, *trans*-[RhCl(N₂CR₂)L₂], and thus favor the formation of the corresponding carbene-rhodium(I) complex. We first used triisopropylarsane as the ligand L but found that the compound *trans*-[RhCl(N₂CPh₂)(*AsiPr*₃)₂] (**8**), formed on treatment of **6** with CPh₂N₂ (Scheme 5), reacted under UV irradiation to give **9** but not *trans*-[RhCl(=CPh₂)(*AsiPr*₃)₂] [10]. When we changed from L = *AsiPr*₃ to L = *iPr*₂AsCH₂CH₂OMe, quite unexpectedly we found the course of the reaction of *trans*-[RhCl(C₂H₄)L₂] (**7**) with CR₂N₂ (R = Ph, *p*-Tol) to be different. We observed the formation of an octahedral intermediate that probably contains the diazoalkane as a bidentate ligand and which loses N₂, either thermally or photochemically, to give the carbene complexes **10** and **11**, respectively [11].

Since the yields of compounds **10** and **11** were unsatisfactory, we went a step further and used *SbiPr*₃ instead of *PiPr*₃ or the arsanes. We were not really aware at the time that *trialkylstibane* complexes of the late transition metals are quite rare [12], possibly because the M–SbR₃ bond is weaker than the M–PR₃ and M–AsR₃ bonds. Even the first experiment was successful. Treatment of **12** with CPh₂N₂ in pentane at room temperature led to a rapid displacement of ethene by the diphenylcarbene ligand and gave compound **13** (Scheme 6) in 96% isolated yield [13]. The X-ray structural analysis of the olive-green crystals revealed that the rhodium has a somewhat distorted square-planar coordination sphere with an unexpected short Rh–C distance of 1.863(4) Å, indicative of a strong rhodium-to-carbene back bonding.

With other diazomethane derivatives, and even with C₄Cl₄CN₂, analogous carbene complexes **14**–**17** are



Scheme 5.

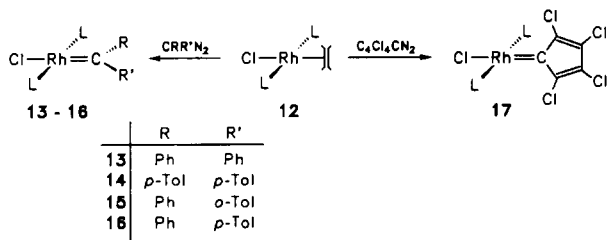
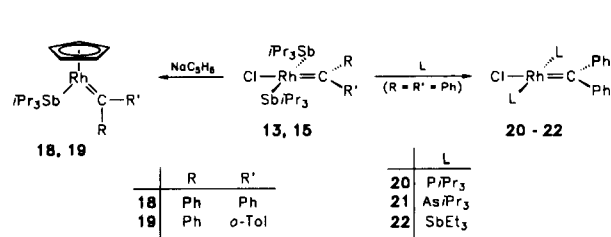
similarly obtained in quantitative yield [13,14]. All of these compounds are remarkably stable (they can be stored under argon at $-20\text{ }^{\circ}\text{C}$ for days) and have great potential as starting materials for the synthesis of other organorhodium derivatives. Scheme 7 illustrates that not only can half-sandwich type complexes such as **18** and **19** be prepared, but also, and much more interestingly, that the two stibane ligands, particularly in **13**, are readily displaced by $\text{P}i\text{Pr}_3$, $\text{As}i\text{Pr}_3$ or SbEt_3 , respectively [13,14]. The yield of **20** is 98%! Thus we had shown that a compound of type A (see Scheme 1), that was the original target of this work, could not be obtained by a direct route but could be obtained by an indirect route involving the use of $\text{Sb}i\text{Pr}_3$ to provide assistance.

A comparative study of the reactivity of the two structurally related diphenylcarbene complexes **13** and **20** revealed that they behave analogously sometimes but in one very exciting instance behave in a completely different way. The reactions of **13** and **20** with CO and $\text{CN}t\text{Bu}$ lead quantitatively to the carbonyl and the isocyanide compounds **23**, **24** and **25**, **26**, respectively. In both cases (see Scheme 8), the diphenylcarbene ligand is coupled to a CO or $\text{CN}t\text{Bu}$ molecule, and thus diphenylketene or the diphenylketenimine derivative $\text{Ph}_2\text{C}=\text{C}=\text{N}t\text{Bu}$ is formed as the byproduct. With ethene, however, the reactions of **13** and **20** take a different course. Whereas the bis(triisopropylphosphane) complex **20** affords 1.1-diphenyl-1-propene (**5**) (i.e. the olefin also obtained in the catalytic reaction),

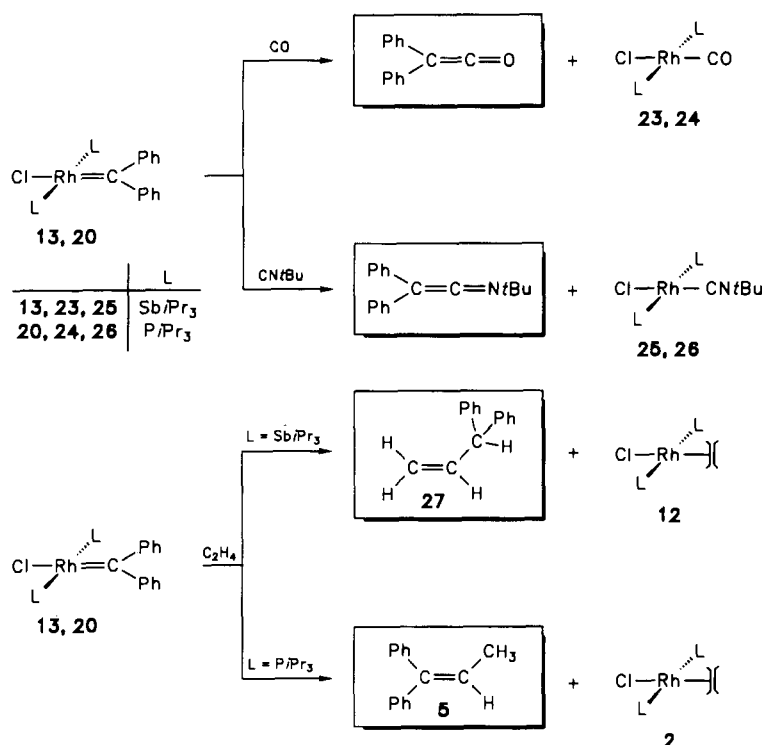
the analogous bis(triisopropylstibane) compound **13** reacts with C_2H_4 by insertion of the carbene ligand into one of the C–H bonds of the olefin to give the isomer **27**. In neither case was even a small quantity of the isomeric cyclic derivative 1.1-diphenylcyclopropane detected.

The reason why the two very similar starting materials **13** and **20** behave differently on treatment with ethene is not yet clear. It may be that the formation of the insertion product **27** proceeds via a hydrido(vinyl)-rhodium(III) intermediate which through migration of the hydride to the carbene ligand and subsequent coupling of the CHPh_2 and $\text{CH}=\text{CH}_2$ units yields the new olefin [14]. In this context, it is noteworthy that the non-carbene-containing rhodium(I) complexes $[\text{RhCl}(\text{P}i\text{Pr}_3)_2]_n$ and $[\text{Rh}(\eta^2\text{-O}_2\text{CCH}_3)(\text{P}i\text{Pr}_3)_2]$ also react differently with an excess of ethene and diphenyldiazomethane: whereas the chloro compound gives **5** (see Scheme 2), the acetato derivative gives exclusively **27** [15], a puzzling result that at present lacks a convincing explanation.

During a short period, which in retrospect could be considered as a time of relaxation, Peter Schwab also studied the reactivity of the cyclopentadienyl complexes **18** and **28** which are prepared from the square-planar precursors **13** or **20** and NaC_5H_5 [13,14]. In contrast to **13** and **20**, which both react with CO and $\text{CN}t\text{Bu}$ by cleavage of the carbene–rhodium bond (see Scheme 8), the reactions of the half-sandwiches **18** and **28** with these substrates take a different course. Whereas the stibane complex **18** on treatment with CO or $\text{CN}t\text{Bu}$

Scheme 6. (L = $\text{Sb}i\text{Pr}_3$).

Scheme 7.



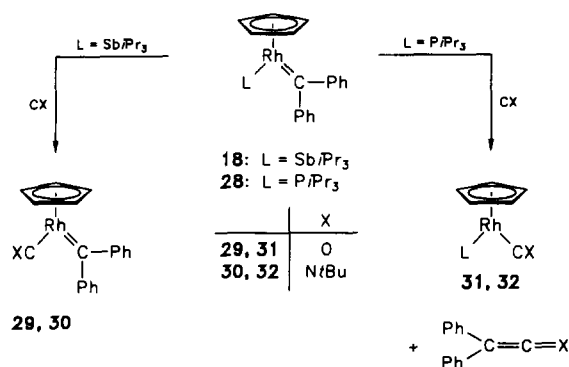
yields the mixed carbene(carbonyl) or carbene(isocyanid) compounds **29** or **30** (Scheme 9), the phosphane derivative **28** gives **31** or **32** together with diphenylketene and the corresponding ketenimine [14]. An X-ray structural analysis of **29** reveals [15] that the Rh–C(carbene) bond is significantly shorter than that in related CpRh complexes containing a Fischer-type carbene ligand, this is consistent with an increase in the bond strength upon replacing a :C(OMe)Ph by a :CPh₂ unit [16].

The results should also be mentioned of two further experiments undertaken to find out whether rhodium carbenes of general composition [C₅H₅Rh(=CR₂)(L)] behave like the corresponding rhodium vinylidenes [C₅H₅Rh(=C=CHR)(L)] [17]. They show (see Scheme

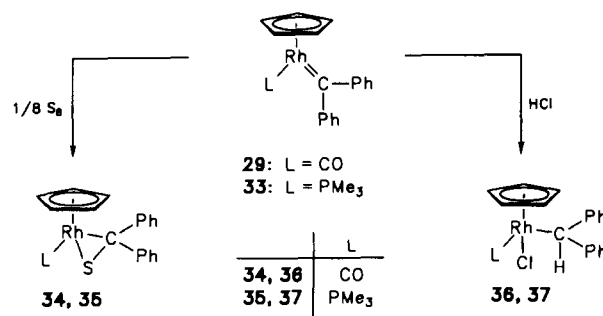
10) that the Rh=C bond not only in **33** (that was obtained by ligand displacement from **18** and PMe₃ [14]) but also in **29** is nucleophilic and that therefore both complexes, like many other CpML(L′)-type compounds, are metal bases [18].

3. Serendipity

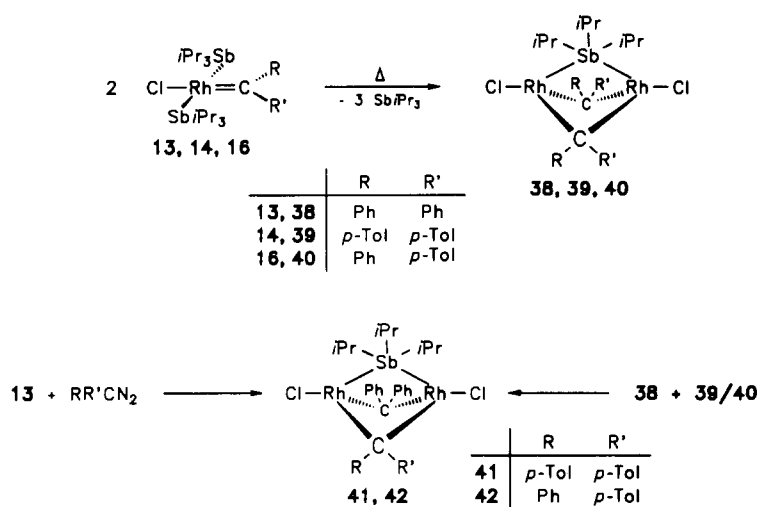
Peter Schwab had not only one golden hand but two. When he realized how labile the Rh–Sb*i*Pr₃ bonds in complex **13** and the related compounds **14**–**17** were, he attempted to study the reactivity of these species *in the absence* of any substrate. The original idea was that on heating, e.g. of **13**, one stibane ligand might be eliminated and the two 14-electron fragments [RhCl(=CPh₂)(Sb*i*Pr₃)] form a dimer with either Cl or CPh₂



Scheme 9.



Scheme 10.



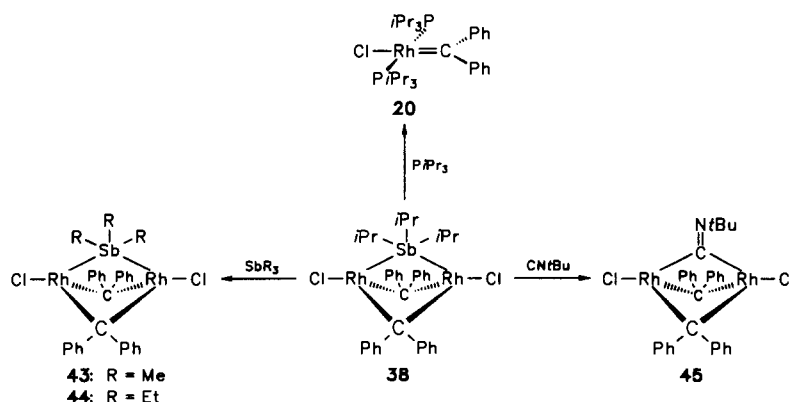
Scheme 11.

bridges. The outcome of the experiment, however, was completely unexpected. Peter isolated in ca. 80% yield a red crystalline solid that gave an elemental analysis corresponding to $\text{Rh}_2\text{Cl}_2(\text{CPh}_2)_2(\text{SbiPr}_3)$ (**38**) and an ^1H NMR spectrum indicating that the position of the stibane ligand in the dinuclear compound was different from that in the mononuclear precursor.

What could the unusual product be? Since it took us a while to grow suitable single crystals of **38** we speculated about the structure but, at least at the beginning, we were reluctant to believe that the stibane could be in a bridging position. Established knowledge, as found in textbooks [19], monographs [12] and review articles [20], seemed to be against such a possibility. However, the result of the X-ray structural analysis revealed [21] the hitherto unknown ability of tertiary stibanes to behave as bridging ligands, i.e. to form *two* Rh–Sb bonds. In addition to the relatively short Rh–Rh distance of 2.535 Å, which is indicative of a direct metal–metal interaction, the most noteworthy feature are the significantly longer Rh–Sb bond lengths in **38** than in **13** (the difference is ca. 0.1 Å) which is

consistent with the bridging mode of the SbiPr_3 ligand. It is also noteworthy that in addition to two very similar Rh_2 compounds **39** and **40** having two $\text{C}(p\text{-Tol})_2$ or two $\text{C}(\text{Ph})(p\text{-Tol})$ units in bridging positions (see Scheme 11), two unsymmetrical complexes **41** and **42**, which contain two different carbene ligands, were also prepared [14,21]. By both routes, the yield of the dinuclear product is excellent.

The final, and again unexpected, feature of this work was that the bridging SbiPr_3 ligand can be replaced by SbMe_3 or SbEt_3 without destroying the $\text{Cl}_2\text{Rh}_2(\mu\text{-CPh}_2)_2$ part of the molecule. Both compounds, **43** and **44** (see Scheme 12), are formed almost quantitatively [21]. A bridge exchange was also found to occur with the isocyanide CNtBu to give **45**, but attempts to prepare the dream complex containing a $\mu\text{-PiPr}_3$ instead of a $\mu\text{-SbiPr}_3$ ligand failed. Reaction of **38** with triisopropylphosphane leads, even in dilute solutions and under mild conditions, not only to the displacement of the stibane but also to cleavage of the CPh_2 bridges to yield the mononuclear compound **20**. Work with less bulky phosphanes and phosphites, with chloro- or fluo-



Scheme 12.

rophosphanes is in progress in the hope that one of these species, especially PF_3 [22], can also behave as a doubly-bridging ligand.

4. The lesson we learned

The scientific story described in this article could also have begun by asking: What can the ligand do for you? The answer now is: A lot! Of course, to modify the ligand sphere and to use, e.g. instead of an aqua complex a corresponding amine metal complex, or instead of a metal carbonyl an analogous metal phosphane compound, seems to be trivial, and certainly has been done since Alfred Werner pioneered the development of modern coordination chemistry. Nevertheless, it is still left to the intuition of the experimental chemist to decide what change of the type of ligand should be best, and could help in reaching the final goal of a particular research project. Today we know that in order to obtain a carbenerhodium(I) complex of type **A** (see Scheme 1) we need triisopropylstibane as the ligand **L**, but which of our readers would have predicted that this would be the key to success? The question of *why* SbiPr_3 is the best choice is still a matter of debate, and we hope that we will learn more about this when we are able to make comparisons with other groups of $\text{L}_n\text{M}(\text{PR}_3) - \text{L}_n\text{M}(\text{AsR}_3) - \text{L}_n\text{M}(\text{SbR}_3)$ complexes.

Where did serendipity play a role? In retrospect, the conclusion is that we have asked a reasonable question (Will a compound such as **13** react on thermolysis to give a chloro- or carbene-bridged dinuclear product?) and obtained the wrong answer. The wrong answer, however, proved absolutely exciting and opened the way into a new field of coordination chemistry that we are still eager to cultivate.

Acknowledgements

The hero of this work is undoubtedly Dr. Peter Schwab whom I would like to thank most sincerely for his enthusiasm and creativity. Dr. Justin Wolf also contributed significantly to its success because not only did he help Peter by discussing his work with him but also behaved as the advocatus diaboli whenever our proposals and explanations went beyond reality. I also thank Mrs. Ingrid Geiter for her skilful assistance in part of the experimental work and Mrs. Bettina Windmüller for typing and organizing the manuscript.

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