Journal of Organometallic Chemistry, [illegible]
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE WAY TO NOVEL SANDWICH-TYPE COMPLEXES

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I. Introduction

It was during my postdoctoral year at Caltech in Pasadena, [illegible] spring of 1962, that I read for the first time through the textbook by Basolo and Pearson, "Mechanisms of Inorganic Reactions" [illegible]. There were two short paragraphs entitled "The oxo reaction" and "[illegible] polymerization" both comprising [illegible] pages which had something to do with the importance of organometallics in reaction mechanisms, in all of the other 334 pages nothing was said about how reactions of organometallic compounds might occur. It seemed to me that this topic was a more or less unexplored area in organometallic chemistry, a field which had been overlooked during the period of expansion between 1952 and 1962 when almost every month new types of compounds possessing a metal-to-carbon bond were described.

Having recognised this, I had already decided before I came back to Munich to begin my own researches ("Habilitationsarbeit") with kinetic and mechanistic studies in the field of organometallics. In spite of my enthusiasm, this work proved to be very difficult. During all my years as an undergraduate and graduate student I had never had an opportunity to attend a number of lectures or a practical course in reaction kinetics, and my small amount of knowledge came only from my attendance at some seminars held by Professor Rolf Huisgen in Munich and Professor George Hammond in Pasadena. This handicap, however, was at least partly compensated by the substantial (and idealistic) support from my former supervisor Ernst Otto Fischer, who frankly confessed that questions of kinetics and mechanisms had played no determining role in his research activities up to that time.

II. The beginnings

The first question was, however, how to start the research? On looking into Basolo and Pearson's textbook, I saw that by far the most detailed chapter was that concerned with substitution reactions of octahedral metal complexes. Those complexes possessing O_h symmetry, e.g. of composition $M(CO)_6$, were

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of course, well known in organometallic chemistry, and because these metal hexacarbonyls as well as their substituted derivatives also seemed appropriate for very obvious reasons (solubility in organic solvents, stability in air etc.), I decided to study first their ligand displacement reactions, as shown in eq. 1—3.

$$M(CO)_6 \xrightarrow[-CO]{L} M(CO)_5L \xrightarrow[-CO]{L} M(CO)_4L_2 \quad (1)$$

$$M(CO)_6 + C_6R_6 \rightarrow C_6R_6M(CO)_3 + 3\ CO \quad (2)$$

$$M(CO)_4L_2 + C_6R_6 \rightarrow C_6R_6M(CO)_3 + CO + 2\ L \quad (3)$$

Fortunately, I did not know that at about the same time Bob Angelici at Iowa State and David Brown at Dublin had become interested in the same problems. When learnt about this (through the first publications of these groups [1,2]), we were already out of the woods [3]. The rapid and really impressive progress made in the field of the kinetics of substitution reactions of carbonylmetal complexes in the short period between 1963 and 1968 had been well documented in four independent reviews [4], as well as in an additional chapter (of nearly 100 pages) included in the second edition of Basolo and Pearson's textbook which was published in 1967 [5].

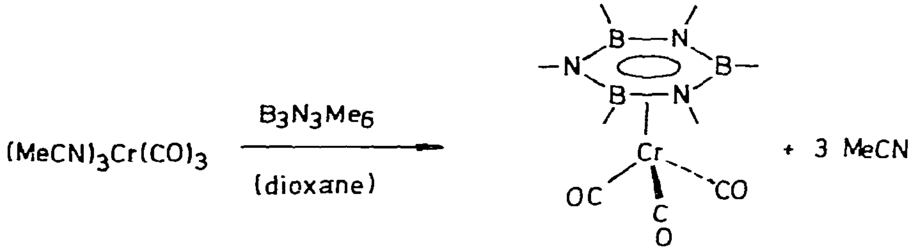
III. The first borazinemetal complexes

The experience which we gained during our studies on the kinetics and mechanisms of the ligand replacement reactions mentioned above prompted us to use, besides arenes and triolefins, some related ligands, particularly those for which the corresponding metal carbonyl complexes were unknown. My first Ph.D. student, Richard Prinz, had started as an undergraduate at the University of Munich where Professor Egon Wiberg held the chair of Inorganic Chemistry, and he had already learned in his second and third year about the relations between carbon—carbon and boron—nitrogen compounds. Professor Wiberg had worked very actively in the thirties with borazine and its derivatives, and it was he who suggested in 1940 for obvious reasons the phrase "inorganic benzene" for the parent heterocycle $B_3N_3H_6$. Thus, Richard Prinz knew about the analogy between C_6H_6 and $B_3N_3H_6$, and although the reactivities of the two ring systems towards Lewis-acids are remarkably different, we tried to use borazines instead of benzenes as ligands in our substitution reactions. We thought that if borazines could form any sandwich or half-sandwich type complexes analogous to the benzene derivatives, coordination to a $M(CO)_3$ moiety (where M is Cr, Mo or W) might offer the best prospect.

It was actually the first run (started with 9 mg $Mo(CO)_6$ and 50 mg $B_3N_3Me_6$ in 100 ml of a 7 : 3 mixture of decane and cyclohexane [6]) which gave strong support to the idea that the expected complex $B_3N_3Me_6Mo(CO)_3$ was intermediarily formed. By using UV spectroscopic measurements, we first observed a decrease in intensity of the $Mo(CO)_6$ band at 289 nm and a simultaneous increase in intensity in that region (at about 325 nm) where the UV maximum of arenemolybdenum tricarbonyls appears. After some time (at 112°C after 30 minutes) the intensity of the new band decreased and the concurrent darkening of the solution indicated that decomposition of the primary reaction product occurred [6]. We were also unable, upon heating the same reaction on a preparative scale, to isolate even traces of the desired complex $B_3N_3Me_6Mo(CO)_3$.

Since we nevertheless believed in the significance of our spectroscopic results we looked for alternative synthetic routes to borazinemetal tricarbonyls. At exactly the same time, Karl Öfele (who worked next to our bench) discovered a new synthesis of arenechromium tricarbonyls $ArCr(CO)_3$ starting with $Cr(CO)_3py_3/Ar$ and $BF_3 \cdot OEt_2$ [7]. Although this method worked well even with thiophene and selenophene, it did not open the door to the borazine complexes.

The key to success was the choice of $Cr(CO)_3(MeCN)_3$ as a starting material. Using dioxane as the solvent, Richard Prinz in his first experiment with the tris(acetonitrile) complex obtained a 90% yield of $B_3N_3Me_6Cr(CO)_4$ [8], and was able to carry out with the material from this single run all the spectroscopic measurements described in his thesis [6].



(4)

The ease of formation and the stability of $B_3N_3Me_6Cr(CO)_3$ made us euphoric, and after the isolation and characterisation of some other half-sandwich type complexes of general composition $R_3B_3N_3R'_3Cr(CO)_3$ [9] containing hexaalkylborazines as ligands, we started a series of experiments directed towards the synthesis of the "full" sandwich, e.g. $Cr(B_3N_3Me_6)_2$. Since we had learnt in the meantime, particularly from the results of the X-ray analysis of $B_3N_3Et_6Cr(CO)_3$ [10], that the bonding between benzene and the $Cr(CO)_3$ fragment was comparable to that between borazine and this fragment [11], we concluded that the synthetic pathways known for bis(benzene)chromium might also be applicable for the bis(hexamethylborazine) analogue.

It soon became apparent that this was an obvious misjudgement. My coworker Karl Deckelmann performed probably more than one hundred experiments all directed towards the synthesis of $Cr(R_3B_3N_3R'_3)_2$ (R, R' = Me, Et) or the corresponding cation, but had no real success [12]. Since we had at least some vague indications that hexaalkylborazines might form a sandwich complex (see, e.g. the results of the ring ligand exchange reactions between the compound "$3[Cr(C_6H_6)_2]AlCl_4 \cdot 4\ AlCl_3$" and $Et_3B_3N_3Me_3$ [12]) and since we knew about Ruch's prediction [13] that $Cr(B_3N_3H_6)_2$ should compare in stability with $Cr(C_6H_6)_2$, we did not, in spite of all our disappointments, discard the project, but looked for alternative routes which had not been tried for $Cr(C_6H_6)_2$. The principal idea was to use either a preformed (and labile) sandwich-type molecule or something like a "naked" metal atom and react this with the borazine ligand. We failed again (as did Peter Timms who some years later tried to synthesize $Cr(B_3N_3Me_6)_2$ by using the metal atom technique [14]), but during this time we gained some knowledge about the reactivities of sandwich complexes in general, and we tried to use this for other purposes.

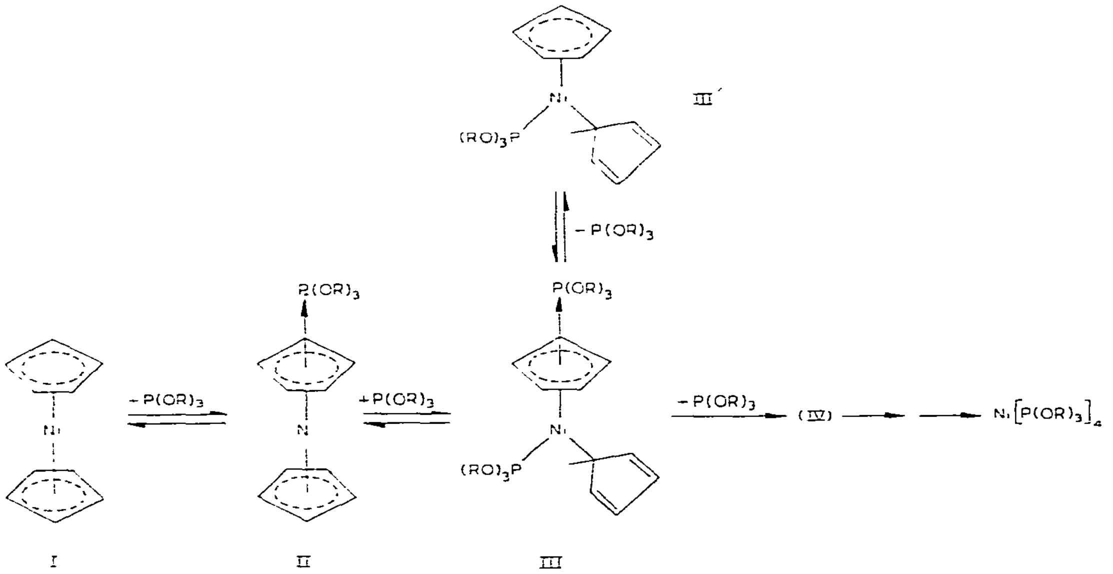
IV. The jump from the borazines to the triple-decker sandwiches

Upon looking over the numerous results on reactions of dicyclopentadienylmetal and dibenzenemetal compounds with Lewis-bases we felt that at least one of them seemed rather unusual. Whereas $Cr(C_6H_6)_2$, $C_6H_6MnC_5H_5$, $Fe(C_5H_5)_2$ and most of the other metallocenes $M(C_5H_5)_2$ (M = V, Cr, Ru, Os) are inert towards CO, CNPh or PPh_3 under normal conditions, $Ni(C_5H_5)_2$ reacts with these ligands even at 25°C or below to form the nickel(0) complexes NiL_4 [15].

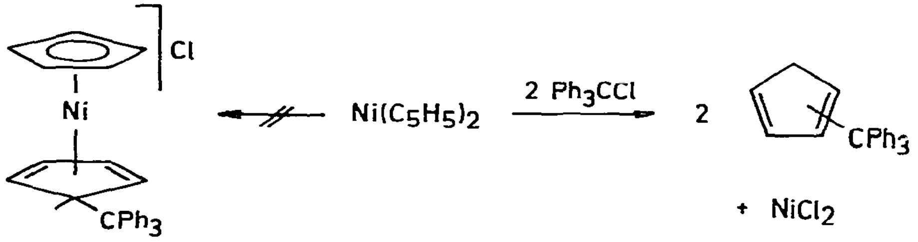
$$Ni(C_5H_5)_2 + 4\ L \rightarrow NiL_4 + C_{10}H_{10} \qquad (5)$$

We saw no obvious reason why this process (in which *two* metal-to-cyclopentadienyl bonds are broken) should have such a fairly low activation energy, and started to study the kinetics of this ring-ligand displacement reaction [16]. Using pseudo first-order conditions and $P(OEt)_3$ as the ligand L, we found a third-order rate law which was somewhat difficult to interpret [17]. As we thought (in accordance with some ideas of Ustynyuk and coworkers [18]) that a compound like III′ must be an intermediate in the reaction of $Ni(C_5H_5)_2$ with $P(OR)_3$, we proposed the following reaction scheme:

SCHEME 1 (from ref. 19)



One of our crucial assumptions (supported by UV spectroscopic measurements [20]) was that in the primary intermediate II one of the cyclopentadienyl rings behaves as a donor towards the phosphite and that this interaction facilitated the attack of the second $P(OR)_3$ molecule to form III. In those days we had trouble in obtaining acceptance of our idea that in the assumed 1 : 1 adduct nickelocene plays the role of a nucleophilic and the phosphite that of an electrophilic reagent. But there were some arguments from our own work which could be seen to support our proposal. Following the conclusions which I had drawn from the work done in J.H. Richard's group at Caltech [21], we postulated that $Ni(C_5H_5)_2$ should react with carbonium ions to produce a substituted cyclopentadienylnickel cyclopentadiene cation $[C_5H_5Ni(C_5H_5R)]^+$. However, when we used Ph_3CCl as a source of a stable carbonium ion R^+ we isolated, instead of the expected salt $[C_5H_5Ni(C_5H_5CPh_3)]Cl$, the hydrocarbon $C_{24}H_{20}$ (a mixture of 1- and 2-triphenylmethylcyclopentadiene) and $NiCl_2$ in quantitative yield [22].



(6)

Although at first sight this result seemed rather disappointing, the formation of the cyclopentadiene derivative indicated that the cation $[C_5H_5Ni(C_5H_5CPh_3)]^+$ possibly had been formed as an intermediate which had reacted with a second molecule of trityl chloride to yield the products.

Since chloride might not be a good anion to trap the dienyl-diene cation, we repeated the reaction of nickelocene with $[Ph_3C]PF_6$ instead of Ph_3CCl. The result was completely different, but again we did not isolate the expected complex $[C_5H_5Ni(C_5H_5CPh_3)]PF_6$. The dark microcrystalline product was actually the hexafluorophosphate of the first triple-decker sandwich, but although the material already obtained from the first run proved to be analytically pure, it took us quite a long time to recognize what a prize we had won. The stoicheiometry of the reaction is formulated in eq. 7 [23].

$$2\ Ni(C_5H_5)_2 + [Ph_3C]PF_6 \rightarrow [Ni_2(C_5H_5)_3]PF_6 + C_5H_5CPh_3 \qquad (7)$$

The idea that triple-decker sandwiches of general composition $[M_2(C_nH_n)_3]$ could exist and be stable enough to be isolated under ordinary conditions, was first put forward by Schumacher and Taubenest in 1964. These authors investigated the fragmentation behavior of dicyclopentadienylmetals in the mass spectrometer under various conditions and found that for M = Fe and Ni, binuclear species $M_2(C_5H_5)_3^+$ can be observed [24]. An ion—molecule reaction (shown in eq. 8) was assumed to be the final step in the formation of these binuclear cations.

$$M(C_5H_5)_2 \rightarrow M(C_5H_5)_2^+ \xrightarrow[-C_5H_5^{\bullet}]{} MC_5H_5^+ \xrightarrow{M(C_5H_5)_2} M_2(C_5H_5)_3^+ \qquad (8)$$

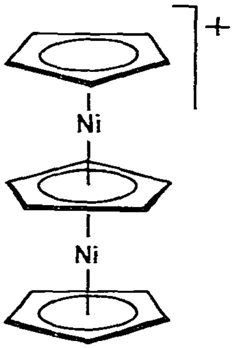
Confirmation that the compound which we had prepared according to eq. 7 was in fact the salt of a triple-decker sandwich was primarily based on the results of reactions of $[Ni_2(C_5H_5)_3]PF_6$ (and the corresponding tetrafluoroborate) with Lewis-bases. In nearly all cases we observed the quantitative formation of nickelocene and the mononuclear cation $[C_5H_5NiL_2]^+$ (L = PPh_3,

PBu_3, $P(OMe)_3$, $P(OPh)_3$, $AsPh_3$, etc.) [25].

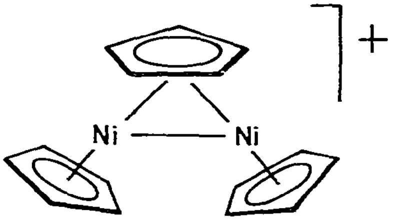
$$[Ni_2(C_5H_5)_3]X + 2\,L \rightarrow Ni(C_5H_5)_2 + [C_5H_5NiL_2]X \qquad (9)$$

With regard to the mechanism of this process, we assumed that the ligand L attacks one of the nickel atoms; this in turn leads to the removal of one "storey" of the triple-decker sandwich and finally (by addition of a second molecule of L to the fragment $C_5H_5NiL^+$) to the two products.

It was mainly the results of these cleavage reactions (and not those of the ^1H and ^{13}C NMR spectroscopic measurements) which favored our proposal of the triple-decker sandwich structure (A) and not the alternative (B), also mentioned in our first paper [23].

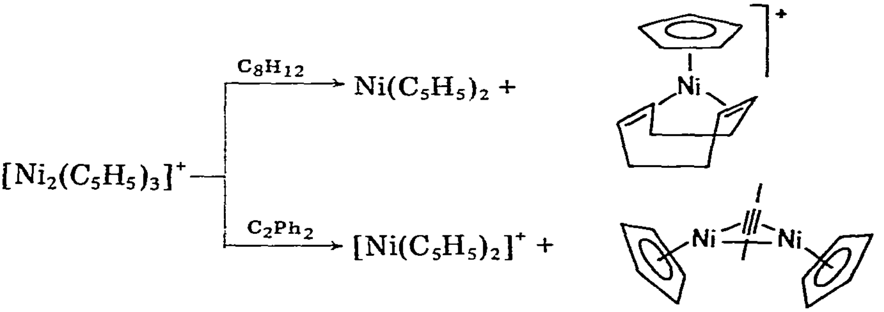


(A)



(B)

After the confirmation of structure (A) by X-ray analysis [26], we learned from further studies on the reactivity of $[Ni_2(C_5H_5)_3]BF_4$ towards π-donor ligands, that whereas diolefins such as norbornadiene or 1,5-cyclooctadiene react the usual way (i.e., analogous to 2,2′-bipyridine or diphos) to form the cations $[C_5H_5Ni(diene)]^+$ [27], acetylenes behave quite differently. The products with $C_2R_2 = C_2Ph_2$, PhC_2H and $C_2(COOMe)_2$ are not $Ni(C_5H_5)_2$, but rather the corresponding cation and the binuclear complexes $[C_5H_5Ni]_2$-(μ-C_2R_2) [28], which are structurally somewhat related to the compound (B) mentioned above.



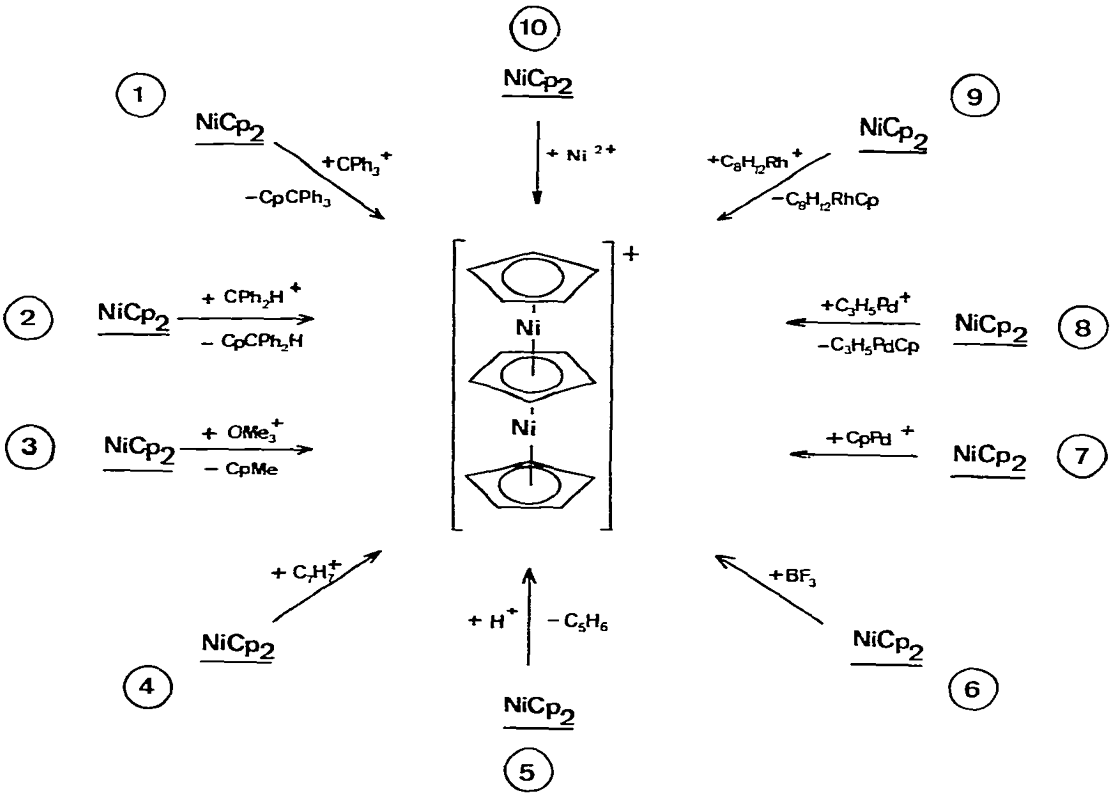
(10)

(11)

The reasons for the difference in reactivity between diolefins (and all the other "ordinary" ligands like PR_3, $P(OR)_3$, etc.) on the one hand and acetylenes on the other are not clear as yet, but may have to do with the great thermodynamic stability of the bis(cyclopentadienylnickel)alkyne complexes.

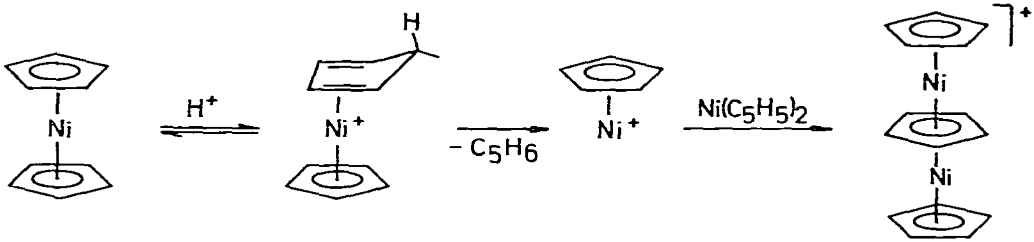
The novel structure, the ease of formation (according to eqn. 7), and the interesting reactivity of the cation $[Ni_2(C_5H_5)_3]^+$ prompted us, of course, to try the preparation of other triple-decker sandwiches. Since Schumacher and Taubenest [24] detected in the mass spectra not only the cation $[Ni_2(C_5H_5)_3]^+$ but also the corresponding species $[Fe_2(C_5H_5)_3]^+$ and $[FeNi(C_5H_5)_3]^+$, and since this fundamental result was supplemented later by the observation of analogous complexes, e.g. of composition $[Cr_2(C_5H_5)_3]^+$ and $[Cr_2(C_6H_6)_3]^+$ [29], we made every effort to synthesize these compounds on a preparative scale. Although we did not succeed, during the work we found several new synthetic routes to the dinickel complex. The results which were known at the end of 1973 and had been summarized at that time for a slide are shown in Scheme 2 [30]. The credit for this work is principally due to Albrecht Salzer, who discovered the triple-decker sandwiches only about six months after he started work on his dissertation in my group [31].

SCHEME 2



There was one question, however, which we always kept in our minds, and this was why is it so easy to form the dinickel cation $[Ni_2(C_5H_5)_3]^+$ (as well as the substituted analogues $[Ni_2(C_5H_4R)_3]^+$ [32]) whereas it is so difficult to isolate the other $[M_2(C_5H_5)_3]^+$ species which are observed under exactly the same conditions and with comparable intensities in the mass spectra? Is there anything wrong with the mechanistic concept which considers the ion—molecule reaction between $MC_5H_5^+$ and $M(C_5H_5)_2$ (see eq. 8) as the critical step in the formation of the dimetal cation?

The answer to the last question is probably in the negative. We were able to prove that in the reaction of nickelocene with acids HX, the cation $[C_5H_5NiC_5H_6]^+$ (with the added proton in the *exo*-position of the cyclopentadiene [33]) is initially formed, and that (under the influence of electrophilic reagents) it loses the diene to yield the "naked half-sandwich" $[C_5H_5Ni]^+$. Salts of this 14-electron species could be isolated with BF_4 and SbF_6 as anions [34]; they react, as expected, with $Ni(C_5H_5)_2$ to give a quantitative yield of the triple-decker sandwich. A mechanism of its formation using the proton as the electrophile was thus formulated as shown in eq. 12.



(12)

The disappointing feature of this piece of work was, of course, that the extremely reactive cation $[C_5H_5Ni]^+$ did not react with ferrocene to form the heterometallic dinuclear complex $[FeNi(C_5H_5)_3]^+$ which had previously been observed in the mass spectra *. The explanation, like many other explanations in the last ten years, came from Roald Hoffmann [35]. He and his coworkers calculated that triple-decker sandwiches $[M_2(C_5H_5)_3]$ as well as structurally similar complexes such as $[C_5H_5M(CO)_3MC_5H_5]$ or $[(CO)_3MC_5H_5M(CO)_3]$ should be stable if they have either 30 or 34 electrons in the valence shell. Whereas $[Ni_2(C_5H_5)_3]^+$ is a 34-electron complex, $[FeNi(C_5H_5)_3]^+$ is a 32-electron species and should behave as a diradical. This may explain why we failed to isolate it. $[Fe_2(C_5H_5)_3]^+$ on the other hand is a 30-electron complex and should be stable.The barrier to its synthesis is probably the exceptional stability of ferrocene, which readily reacts with electrophiles R^+, but, in contrast to nickelocene, does not give $[C_5H_5FeC_5H_5R]^+$ and (after elimination of the diene C_5H_5R) the cation $[C_5H_5Fe]^+$ but rather the substituted products $C_5H_5FeC_5H_4R$.

Although our last paper concerned with the chemistry of triple-decker sandwiches was sent to the editors of this Journal about four years ago, we still hope that we are not at the end of the project. We succeeded quite recently in isolating for the first time the two sandwiches $C_5H_5NiC_5Me_5$ and $Ni(C_5Me_5)_2$ [36], a result which may pave the way to corresponding palladium and platinum compounds, which are necessary as starting materials for triple-decker sandwiches such as $[M_2(C_5Me_5)_3]^+$, $[C_5Me_5MC_5H_5MC_5Me_5]^+$ (M = Pd, Pt), etc.

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* The reaction of $[C_5H_5Ni]BF_4$ with $Fe(C_5H_5)_2$ yields the ferricenium salt $[Fe(C_5H_5)_2]BF_4$ [34].

V. The most recent step: the bimetallic sandwiches

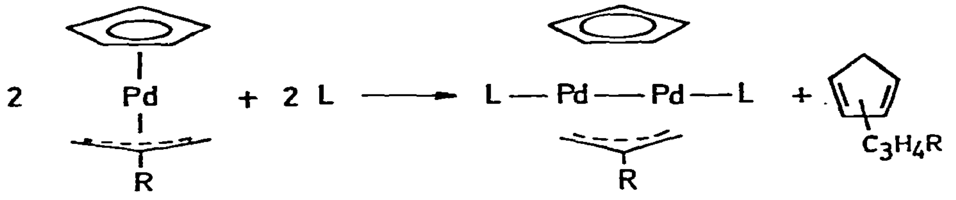
Whereas the first synthesis of the triple-decker sandwich $[Ni_2(C_5H_5)_3]^+$ was only loosely connected with our activities in the field of reaction mechanisms, the discovery of the novel binuclear (*Pd—Pd*) compounds (μ-C_5H_5)(μ-allyl)-Pd_2L_2, which are structurally related to the bimetallic sandwiches $(\mu\text{-}C_5H_5)_2$-Pd_2L_2, proved to be a direct consequence of our kinetic and mechanistic studies. As previously mentioned, we had had some difficulty in interpreting unequivocally the kinetic data which we had obtained for the reaction of $Ni(C_5H_5)_2$ and $P(OEt)_3$ [17]. As π-allyl-π-cyclopentadienylnickel has a structure similar to nickelocene (i.e., the planes of the ring and the carbon atoms of the allyl moiety are parallel to each other), we included this complex, which also reacts with various Lewis-bases L to yield NiL_4, in our studies. In contrast to $Ni(C_5H_5)_2$, the π-allyl complex $C_3H_5NiC_5H_5$ has the advantage of being diamagnetic, and therefore the course of its reactions with L can be followed by NMR spectroscopy.

Despite this advantage, the nickel compound $C_3H_5NiC_5H_5$ presents problems. As it only reacts at higher temperatures, e.g. with $P(OEt)_3$ in toluene, to form $Ni[P(OEt)_3]_4$, and as the primary steps seem to be the rate-determining ones [37], we failed to detect any definite intermediate and hence did not learn anything more about the separate steps of the ligand displacement process. The palladium complex $C_3H_5PdC_5H_5$ was a better prospect. It also reacts with Lewis-bases such as tertiary phosphites $P(OR)_3$ to yield $Pd[P(OR)_3]_4$, but under much milder conditions than the nickel analogue. When we learned about this, and afterwards combined the kinetic measurements with low-temperature NMR studies, the following mechanistic picture (which represents the course of the reactions of C_5H_5Pd(all), where all = C_3H_5, 2-MeC_3H_4, 2-t-BuC_3H_4, 1,1,2-$Me_3C_3H_2$) emerged [37,38]:

$$C_5H_5Pd(all) \xrightarrow{L} C_5H_5Pd(all)L \xrightarrow{L} C_5H_5Pd(all)L_2 \xrightarrow{L} \xrightarrow{L} PdL_4 \qquad (13)$$

According to this interpretation, the formation of the palladium(0) compounds PdL_4 is not initiated by the displacement of one of the organic groups but by addition of L to form a "1 : 1-adduct" as the primary intermediate. Most noteworthy, for all = 2-ClC_3H_4, the reaction stopped at the first stage, and we were able to isolate the complexes C_5H_5Pd(2-ClC_3H_4)L, which in some cases are stable at room temperature. They do not react with L to form C_5H_5Pd-(all)L_2 etc., but lose allene to yield C_5H_5Pd(L)Cl [39].

The stability of the primary intermediate C_5H_5Pd(all)L, however, is dependent not only on the type of the allylic ligand but also on the type of the ligand L. When we recognized this, we tried to isolate the corresponding compounds, e.g. with all = 2-MeC_3H_4 and L = $P(OPh)_3$ and PPh_3. During these experiments, we obtained a surprising result. The reaction of C_5H_5Pd(2-MeC_3H_4) with L in an exactly 1 : 1 stoicheiometric ratio primarily yields C_5H_5Pd-(2-MeC_3H_4)L, but these intermediates react further in solution to give stable binuclear complexes of the composition (C_5H_5)(2-MeC_3H_4)Pd_2L_2. The X-ray structural analysis proved that a sandwich-type species had been formed, in which the two organic ligands coordinate to both palladium atoms and enclose the Pd—Pd bond in sandwich fashion [40,41]. There is an almost linear P—Pd—Pd—P arrangement completely analogous to that found previously by Yamazaki et al. [42] in the complex $(C_3H_5)(I)Pd_2(PPh_3)_2$.



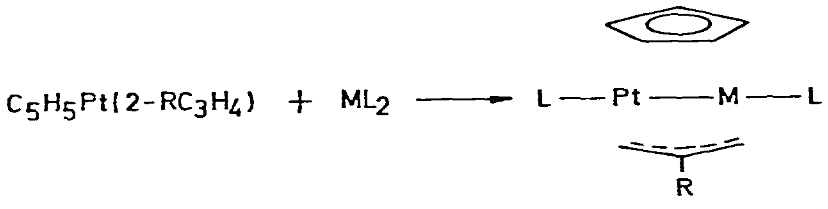
(14)

Our next goal was to elucidate the mechanism of formation of these unexpected products. As there was no doubt that the first steps in the reaction were those already depicted in eq. 13, we postulated that an intermediary compound PdL_2 is formed, either directly from $C_5H_5Pd(all)L$ and L or by elimination of the organic ligands from $C_5H_5Pd(all)L_2$, and then reacts with one molecule of the starting material $C_5H_5Pd(all)$ to yield the binuclear complex [30].

SCHEME 3

$$\begin{tikzcd}
\mathrm{C_5H_5Pd(all)} \arrow[r, harpoon, shift left, "L"] & \mathrm{C_5H_5Pd(all)L} \arrow[l, harpoon, shift left] \arrow[r, harpoon, shift left, "L"] \arrow[dr, "L", "-\mathrm{C_5H_5(all)}"'] & \mathrm{C_5H_5Pd(all)L_2} \arrow[l, harpoon, shift left] \arrow[d, "-\mathrm{C_5H_5(all)}"] \\
 & & \mathrm{PdL_2} \arrow[d, "+\mathrm{C_5H_5Pd(all)}"] \\
 & & \mathrm{(C_5H_5)(all)Pd_2L_2}
\end{tikzcd}$$

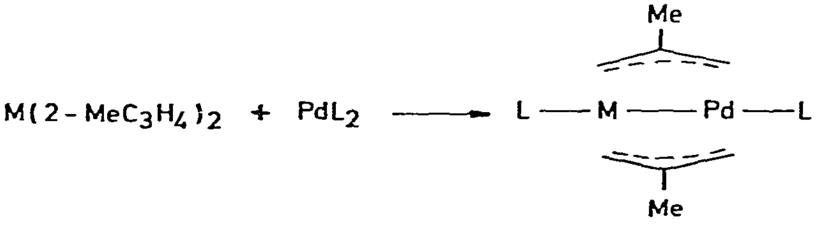
We had good luck because at about the time we first proposed the reaction sequence shown in Scheme 3 [43], both Musco [44] and Otsuka [45] described the preparation of the compounds PdL_2, where L is $P\text{-}i\text{-}Pr_3$, PCy_3, $P\text{-}t\text{-}Bu_3$, $PPh\text{-}t\text{-}Bu_2$, etc. These electron-deficient compounds are remarkably stable, a fact which is probably due to steric protection of the palladium atom by the bulky R groups. By using the PdL_2 complexes, we were able not only to confirm our assumption regarding the final step in the synthesis of $(C_5H_5)(all)Pd_2L_2$ (Scheme 3) but also to show that analogous binuclear complexes which contain two platinum atoms [46,47] or one platinum and one palladium atom [48] were accessible by the same route.



(15)

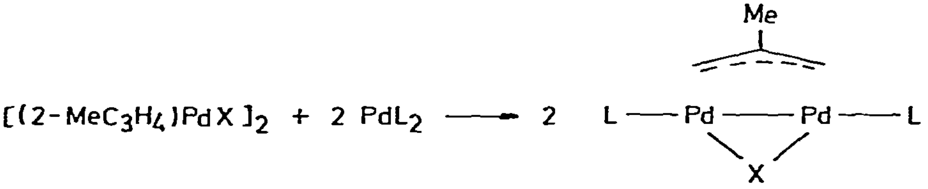
(M = Pd, Pt)

The key to success in the preparation of the interesting heterometallic complexes $(C_5H_5)(2\text{-}RC_3H_4)PdPtL_2$ was the use of the 14-electron palladium compounds PdL_2, which are much more reactive than the platinum analogues. These PdL_2 species also allowed the synthesis of other binuclear complexes containing either two allyl groups or one allyl group and one halogen or carboxylate in the bridging positions [46,49,50].



(16)

(M = Pd, Pt)



(17)

(X = Cl, I, RCOO)

The complexes $(2\text{-}MeC_3H_4)_2Pd_2L_2$ (L = P-i-Pr_3, PCy_3) and $(2\text{-}MeC_3H_4)_2PdPt(P\text{-}i\text{-}Pr_3)_2$ [48] were the first allyl-transition metal compounds in which not a single metal atom but a M_2 unit is coordinated sandwich-like by two π-bonded allylic ligands. The synthetic pathway shown in eq. 16 has most recently been supplemented by another, namely the thermal reaction of $(C_3H_5)_2PdL$ (in particular with L = PPh_3), which gives $(C_3H_5)_2Pd_2L_2$ and hexadiene [51].

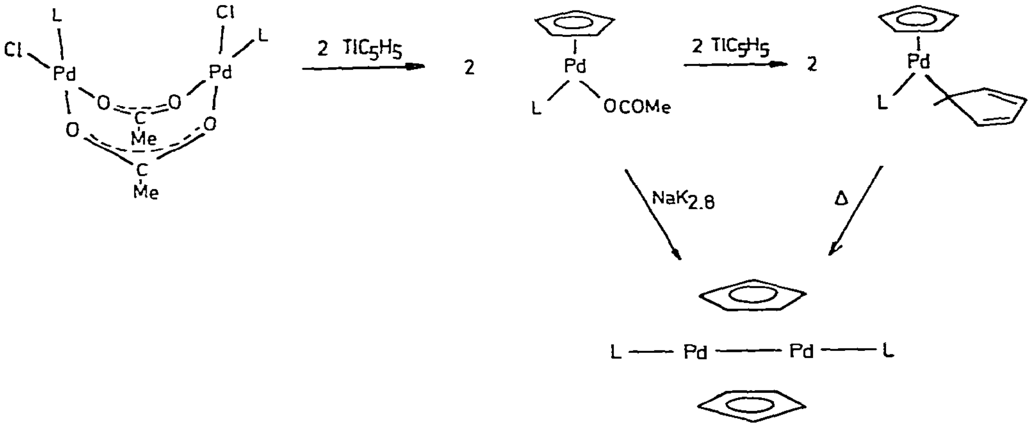
But even with the bis(μ-allyl)dipalladium complexes $(\mu\text{-all})_2Pd_2L_2$, we were still more than one step away from the true bimetallic sandwiches $(\mu\text{-}C_5H_5)_2Pd_2L_2$. The method of, as we call it, "1 : 1-addition" (i.e., the reaction of a substrate (X)Pd(Y) with PdL_2 to give $(\mu\text{-}X)(\mu\text{-}Y)Pd_2L_2$ without anything else),. which allowed the preparation of complexes with X = Y = all, X = C_5H_5 and Y = all, X = all and Y = halide or carboxylate, was not applicable to the synthesis of the bis(μ-cyclopentadienyl) compounds since the necessary starting material $Pd(C_5H_5)_2$ is unknown.

The route to success was found by following a trail described by Felkin and Turner [52]. During attempts to prepare palladium-containing Grignard compounds, these authors treated, for instance, $C_5H_5Pd(P\text{-}i\text{-}Pr_3)Br$ with Mg in THF but isolated, instead of the expected product $C_5H_5(P\text{-}i\text{-}Pr_3)PdMgBr(THF)_n$, the binuclear complex $(\mu\text{-}C_5H_5)(\mu\text{-}Br)Pd_2(P\text{-}i\text{-}Pr_3)_2$ in good yields. The corresponding bimetallic half-sandwiches $(C_5H_5)(X)Pd_2(PR_3)_2$ were also obtained by similar reactions of $C_5H_5Pd(PR_3)X$ (R = i-Pr, Ph, Cy; X = Cl, Br, I) with reducing agents such as $LiAlH_4$, $LiAlH(O\text{-}t\text{-}Bu)_3$, $NaBH_4$ or sodium amalgam [53].

When we learned of these results, we thought that for the synthesis of

$(C_5H_5)_2Pd_2L_2$ by a reductive route, it would be necessary to use a very strong halide-abstracting reagent, e.g. sodium sand or activated zinc. But even upon treating $C_5H_5Pd(PR_3)Cl$ or $C_5H_5Pd(PR_3)Br$ (R mainly i-Pr) with these reagents we failed. Just a small (seemingly unimportant) modification, namely the use of $C_5H_5Pd(P\text{-i-}Pr_3)OCOMe$ instead of the corresponding complex halide, brought success. As shown in Scheme 4, the cyclopentadienyl(phosphine)-palladium acetates react with sodium-potassium alloy $NaK_{2.8}$ to form the binuclear sandwiches in relatively good yields [54]. During further experiments, aimed at improving the preparation of the acetates $C_5H_5Pd(PR_3)OCOMe$, we observed that if instead of an exactly 1 : 2 ratio of $[Cl(L)Pd(\mu\text{-}OCOMe)]_2$ and TlC_5H_5 an excess of the thallium cyclopentadienyl is used, the desired sandwich complexes $(C_5H_5)_2Pd_2L_2$ are directly formed. This "one-pot synthesis" proceeds via $(\pi\text{-}C_5H_5)Pd(L)(\sigma\text{-}C_5H_5)$ as intermediates; they probably react by homolytic fission of the Pd—σ-C_5H_5 bond to yield the products.

SCHEME 4



When we also succeeded in isolating the mononuclear dicyclopentadienyl(phosphine)palladium complexes, we had killed two birds with one stone. First we now had a rather simple route to the bimetallic sandwiches, and second we had found (really not deliberately) novel types of fluxional molecules. As immediately became obvious from the NMR spectra at various temperatures, the compounds $(\pi\text{-}C_5H_5)Pd(L)(\sigma\text{-}C_5H_5)$ undergo two independent dynamic processes [55]: that with the higher activation energy (for which the coalescence temperature depends upon the size of the phosphine and decreases along the series $P\text{-i-}Pr_3 > PPh_3 > PMe_3$, is a π/σ-exchange of the two differently bound C_5H_5 ligands, while that with the lower activation energy, which for the three phosphines can be frozen out only below −80°C, is a metallotropic rearrangement (or, according to Cotton, a 1,2-shift).

The most recent result in this field is the synthesis of bimetallic sandwiches $(C_5H_5)(C_5Me_5)Pd_2L_2$ which contain one pentamethylcyclopentadienyl ring as a bridging ligand [56]. The next step must be, of course, the preparation of $(C_5Me_5)_2Pd_2L_2$, which we expect to be much more inert than the bis(cyclopentadienyl) compounds, and which may give a hint about how to isolate (or trap) the corresponding "ordinary" sandwich $Pd(C_5Me_5)_2$. Recalling all the unsuccessful attempts to prepare the compound $Pd(C_5H_5)_2$ [57], and considering the importance of the homologue $Ni(C_5H_5)_2$ as a starting material for the synthesis of hundreds of organometallics, the efforts seem to be worthwhile.

VI. Outlook

I have tried to summarize some of the results which we have obtained during the last 12—15 years and which may have some objective validity. It is possible of course, that the reader of the review could get the impression that the investigations carried out by my coworkers and myself developed straightforwardly without hindrance by high barriers and painful interruptions. This is the bright side of the picture. But there is another aspect and that is the real and great enthusiasm of the coworkers involved in that research; this always helped us to surmount the difficulties and to gain good results.

Although most of the work reported in this publication is concerned with the synthesis (and structure) of novel sandwich-type complexes, it must be emphasized that at various stages kinetic and mechanistic studies were the forerunners of success. In our hands the combination of kinetic and preparative work proved fairly often to be a good choice, and thus I feel that the final sentence of my first review written in 1968 [4] that "this combination ... will continue to be fruitful in the future" is still valid.

Acknowledgments

Finally I would like to thank all my co-workers and assistants in the laboratory without whose help in every sphere little could have been achieved. In a review of this kind it is possible to mention only some of them and to make reference to only a fraction of their publications. I am also indebted to the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie and Schweizerischen Nationalfonds for their support of my reseearch activities.

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