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ORGANOMETALLIC CHEMISTRY, COORDINATION CHEMISTRY, MAIN GROUP CHEMISTRY. WHERE ARE THE FRONTIERS AT PRESENT? *

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Summary

The traditional partitions of chemistry are not so clear-cut. Organometallic chemistry, by bridging organic and inorganic chemistry, has contributed largely to unifying the wider field of molecular chemistry over the entire Periodic Table. Its many interactions with analytical, physical and biological chemistry, material sciences, surface sciences, etc., are growing, as is its industrial impact. Where are the limits to organometallic chemistry today? Should it have a particular status? Frontiers have seldom been heuristic. The tremendous development of organometallic chemistry illustrates indeed that fertility results from approaches which integrate the knowledge, concepts and methods of research domains which were hitherto separate.

Results involving perfluorochemicals, transition metal-induced phosphorus chemistry and early transition metal organometallics are presented, which could just as well be claimed by organic chemistry as by inorganic chemistry, or fluorine chemistry, or coordination chemistry, or phosphorus chemistry, or...organometallic chemistry.

Introduction

Since I had never really thought of myself as an organometallic chemist, my participation in an International Symposium on Organometallic Chemistry raised some harrowing questions about what I should present. The first approach, in order to sort out which of the material among the team's results could pertain to organometallic chemistry, was to call on definitions. Several thorough essays (as in the prestigious series of Advances in Organometallic Chemistry [1]) which shed light on the historical development of the discipline, have been written on this, but I soon

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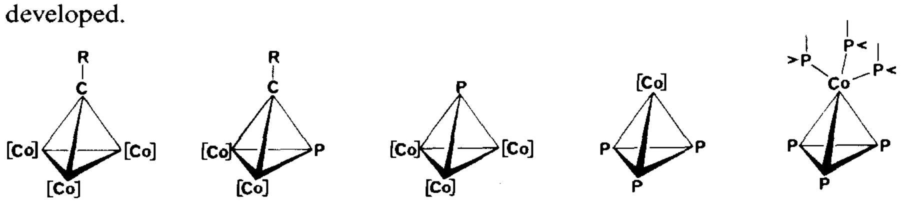
found out that the available definitions were often unable to convey the feeling for that specific but undefined "organometallic character" which is a prerequisite to publication in the pages of J. Organomet. Chem. [2].

I suspect that defining a field is easier at the time of its foundation than once it is well established. The exercise is all the more difficult as this field has proved more creative and successful. Starting as the chemistry of metal–carbon bonds, organometallic chemistry at maturity is now merging into a much broader corpus of knowledge in which it has become intimately interwoven with the organic, inorganic and coordination chemistry of metals and non-metals, with many extentions into biochemistry, pharmaceutical chemistry, surface chemistry, material and polymer sciences, engineering, biology, physics, etc...

This paper will not attempt to present any new, ultimate definition of organometallic chemistry. Under its somewhat provocative title it has no other pretention than to report some of the difficulties encountered by the author with boundaries and linesmen.

Ostracism and limelight

Defining frontiers implies inclusions and exclusions. The sorting of molecules into specific distinct categories is usually easy when they are considered individually, but often loses all its sense when series of structurally or electronically related compounds are considered, especially when they are derived one from the other by chemical reactions. This is all the more so as more unifying concepts and models are developed.



[Co] = Co[CO]$_3$

SCHEME 1. Which is in, which is out?

In the series of closely related species represented in Scheme 1, one observes the stepwise change from multi M–C bond-containing compounds to a compound which contains none, all metal–carbon bonds being progressively replaced by metal–phosphorus bonds [3]. These species are all structurally related; the Co(CO)$_3$ and RC groups and the phosphorus atoms play very similar roles, all three entities being electronically equivalent (in the sense that all three need three electrons to reach their optimal stable configuration) and isolobal. No one would want to discard one or another from the comparison on the pretext that it was not organometallic. In Scheme 2 are listed a few more of the very many sets of compounds in which the author has difficulty in discriminating the organometallic from the non-organometallic ones.

Also decisive in this respect are the author's background and interests, i.e. on which element, bond or property the spotlight will be directed. Thus my very first organometallic compound was made by a phosphorus chemist. Wanting to test the donor ability of phosphorus trioxide, P_4O_6, I used nickel carbonyl as a reagent (essentially because it was "on the shelf"). It turned out to be the perfect "choice"

$H_3Si{-}SiH_3$ $H_3Si{-}CH_3$ $H_3C{-}CH_3$

$F_3Si{-}SiF_3$ $F_3Si{-}CF_3$ $F_3C{-}CF_3$

$(H_3C)_2As{-}As(CH_3)_2$[a] $(H_3C)_2P{-}P(CH_3)_2$

$(H_3C)_2B{-}B(CH_3)_2$

$[Co(CO)_4]_2$ $Co(CO)_3(NO)$ $Co(NO)_3$

$Ni(CO)_4$ $Ni(PF_3)_4$ $Ni(CN)_4^{=}$

$NaCH_3$ Na_2CH_2 Na_3CH Na_4C[b]

[a] Described as the first organometallic compound (Cadet de Gassicourt, 1760).

[b] "Carbides will be excluded" [2]

SCHEME 2. To be or not to be organometallic? Further games.

for this purpose, since it readily afforded the tetrakis(tricarbonyl)nickel derivative $P_4O_6[Ni(CO)_3]_4$ (Fig. 1), an organometallic complex in which each phosphorus atom is bound to a tricarbonyl nickel fragment [4].

The ostracism of phosphorus as the central carbon-bound element, while carbon derivatives of its neighbours, silicon and arsenic, are well-accepted in the coterie of organometallic componds, is resented as particularly arbitrary by the chemist dealing with all three elements. Incoherence is apparent here; the fact that phosphonitriles, which contain no metal and no carbon atoms, and a fortiori no metal–carbon bonds, are found under the heading of "organometallic compounds" in Chem, Abstr. is an example.

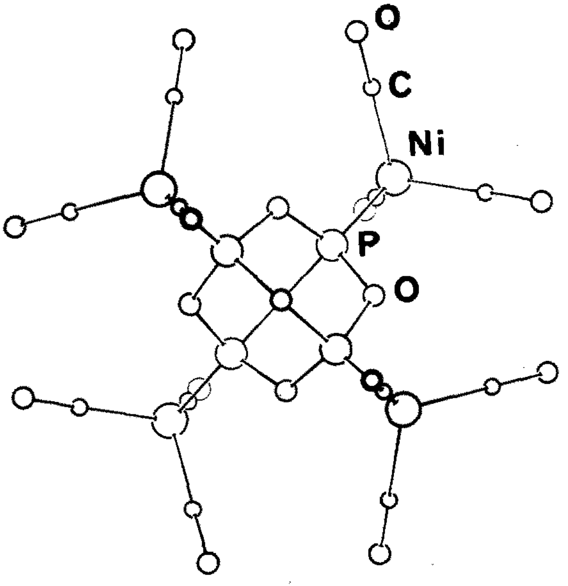
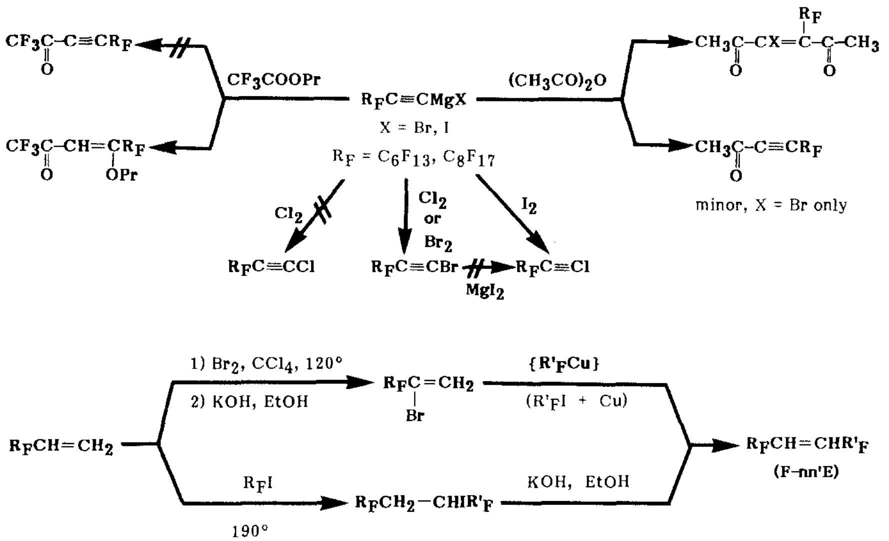


Fig. 1. Structure of $P_4O_6[Ni(CO)_3]_4$. Because of the symmetry the eye is focussed on the central P_4O_6 core.



SCHEME 3. Some perfluoroorganometallic chemistry relevant to blood substitutes.

Scheme 3 shows some *perfluoro*-organometallic chemistry [5]. It is meant to illustrate how different this chemistry can be from *hydro*-organometallic chemistry. The goal, here in the realm of fluoro-medical chemistry, is to obtain inert perfluorochemicals which are useful as oxygen carriers in blood substitutes; some of the most promising candidates for this belong to the series of bis(F-alkyl)ethenes [6]. These were first prepared by a reaction that is believed to involve a perfluoroorganocopper intermediate (note that it is the *gem*- and not the *vic*-diperfluoroalkylated compound that is obtained, whereas the contrary occurs in hydroalkyl chemistry). The spotlight here should obviously be focussed on fluorine, for it is fluorine that confers the desired properties (O_2-dissolving capacity and biocompatibility) and the distinctive chemistry to these materials. Whether they are prepared by the organocopper route or by the more classical thermal one is of little importance.

Organometallic chemistry without carbon–metal bonds?

Must the metal-bound carbon necessarily be carbon? An apparently impertinent question, but everybody senses that in many cases hydrogen, nitrogen, boron, phosphorus and other elements can replace carbon in the metal's coordination sphere without causing dramatic changes in a compound's behavior and without losing that distinct but indefinable organometallic character. Metal hydrides are officially accepted in the scope of the Journal of Organometallic Chemistry [2]. Nitrosyls have provided their crop of non-metal–carbon bond containing organometallics [7]. But what about phosphorus? Excluded as a central element, could it not in some cases play the role of carbon in the metal's coordination sphere? Very similar bonding models are indeed used to describe the metal carbonyl and metal-phosphane interactions, and the difference between the two ligands, in their effects on the metal, diminishes as the phosphane's π-accepting capacity increases.

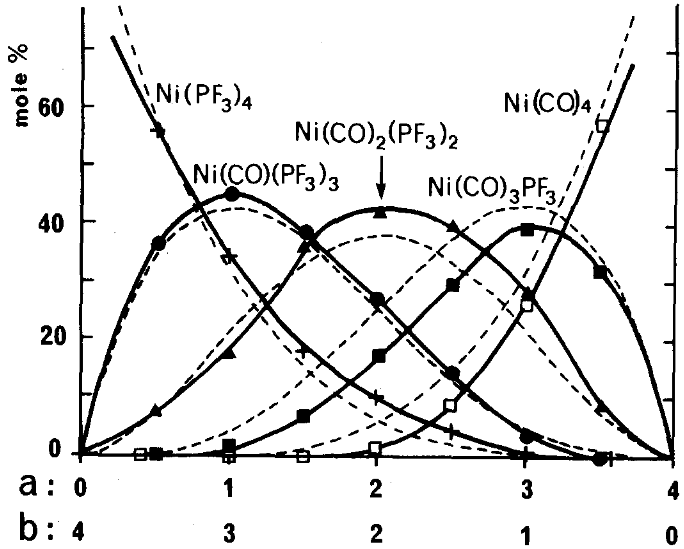


Fig. 2. Equilibrium distribution of the five adducts of the $Ni(CO)_{4n}(PF_3)_n$ series as a function of the $Ni(CO)_4/Ni(PF_3)_4$ ratio in the initial mixture (adapted from ref. 8a). The full lines join the experimental points; the dotted lines are calculated for a random distribution.

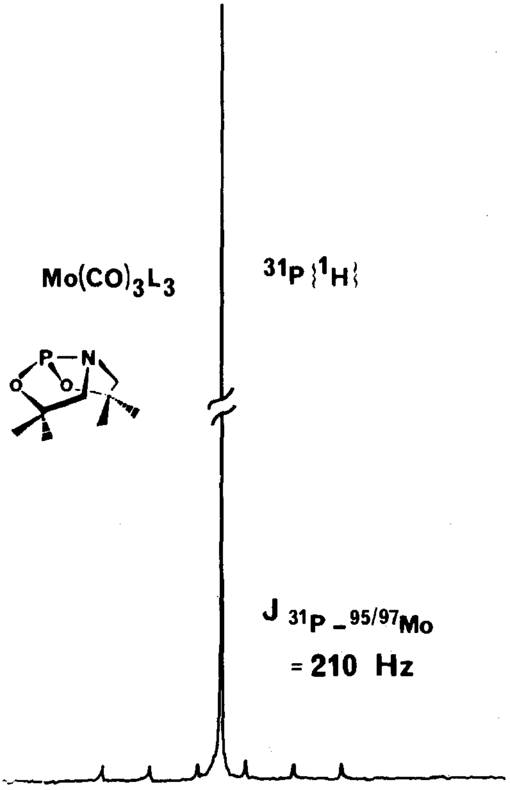


Fig. 3. The proton-decoupled ^{31}P NMR spectrum of a mixed carbonyl/phosphane molybdenum(0) adduct, showing satellites due to ^{31}P–$^{95/97}Mo$ coupling.

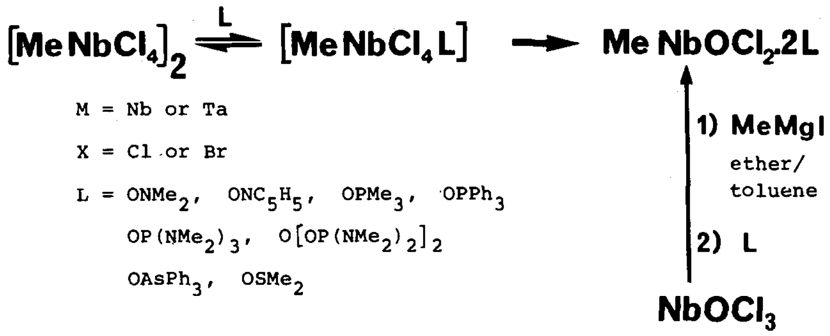
A pertinent illustration of this can be found in Clark's observation, made some years ago, that mixing nickel tetracarbonyl with tetrakis(phosphorus trifluoride)nickel gives a mixture of all the five possible symmetrical and mixed adducts, and, most remarkable, that their equilibrium distribution is very close to *random* (Fig. 2) [8]. This means that there is no notable thermodynamic preference for any of these species, hence that the two ligands indeed play very comparable roles.

Along the same lines, Fig. 3 presents a rather rare set of NMR data; it is the ^{31}P spectrum of a compound derived from $Mo(CO)_6$ by the replacement of three of the carbonyls by a bicyclic phosphorus ligand, which according to infrared data is strongly π-accepting, to give the *mer*-isomer. This spectrum shows the satellite peaks due to P-Mo coupling [9]. Since molybdenum has a strongly quadrupolar nucleus, with spin 5/2, such couplings are only observed if the electronic environment of the metal remains highly symmetrical, and in the usual phosphane-substituted molybdenum complexes they are not. The fact that sharp satellites are found here can be interpreted as meaning that the replacement of the carbonyls by this particular phosphane does not significantly perturb the electronic environment of the metal, hence that the two ligands play comparable roles in the metal's coordination sphere. Many other examples can be found of comparable behavior of phosphane and carbonyl ligands. Let us just mention that the only two fully characterized compounds known in which niobium displays an oxidation state of -1 are $[Nb(CO)_6]^-$ and $[Nb(PF_3)_6]^-$ [10].

The case of the passive metal-bound carbon

Some years ago we collected data on redistribution equilibria of various non-metals from Groups III to V, with the aim of discussing some of their thermodynamic and synthetic implications [11]. The ^1H NMR spectrum shown in Fig. 4 is of an equilibrated mixture of oligomers and polymers which is the result of the exchange of bridging oxygen with terminal fluorine atoms between the dimethylsilicon and the methylphosphonyl moieties of $[(CH_3)_2SiO]_3$ and $CH_3P(O)F_2$. This study revealed that the two non-metals are not randomly distributed, but tend to alternate regularly along the chain [11b]. When such experiments were performed on silicon, or on silicon and phosphorus, as described here, the results were at once accepted for publication in J. Organomet. Chem. [11c–e], but the parallel studies on phosphorus alone, although the two elements behave on this occasion in a very similar way (which was one of the principal conclusions of the work) were not even considered by that journal, and so was published partly in Tetrahedron and partly in Inorg. Chem. [11f,g]. Phosphorus were also accepted for J. Organomet. Chem. when associated with silicon, germanium, tin or arsenic [11h]. The irony is that the carbon–element bonds take no part whatever in any of the reactions being reported. The methyl groups remain passive, their role indeed being to limit the number of exchangeable sites on the central element and to serve as a probe in the NMR experiments.

It is nevertheless obvious that M–C bond-preserving reactions are in many cases directly relevant to organometallic chemistry, for example by providing information on the stability or inertness of this bond. Many critical examples of this can be found, especially in early transition metal chemistry. For a long time, complexes of these elements containing metal–carbon bonds were thought to be unstable electron-



SCHEME 4. Coordination chemistry round and about a preserved labile niobium–carbon bond.

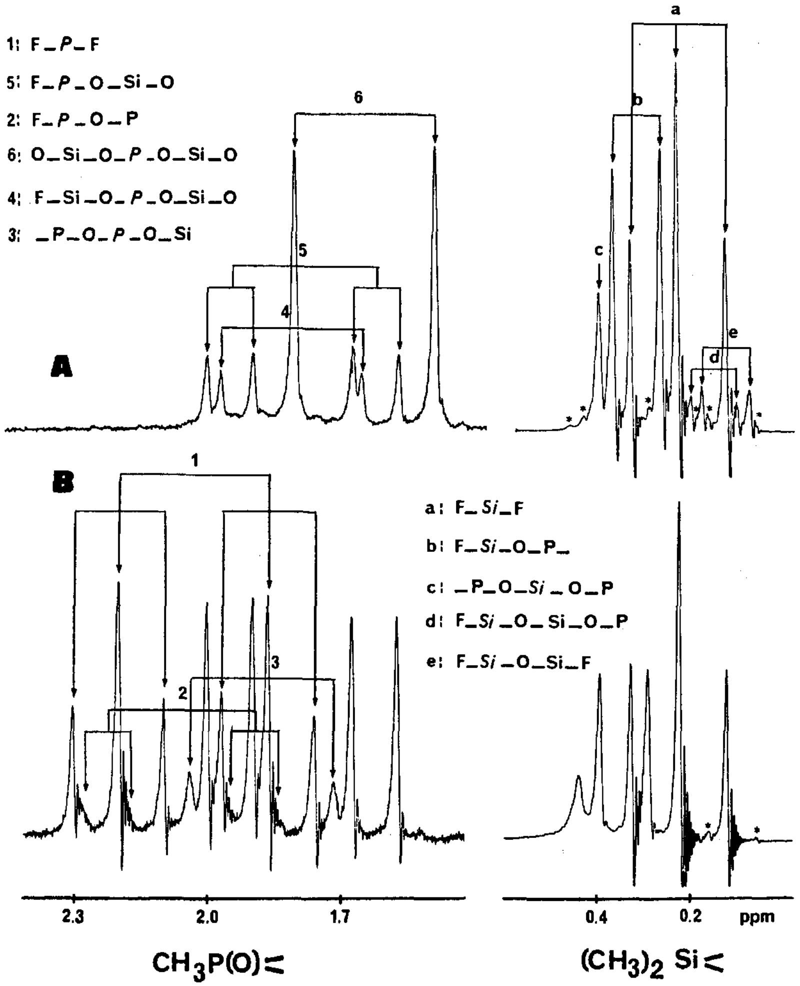
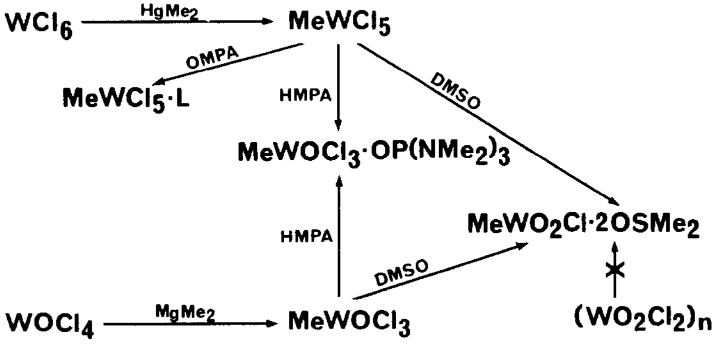
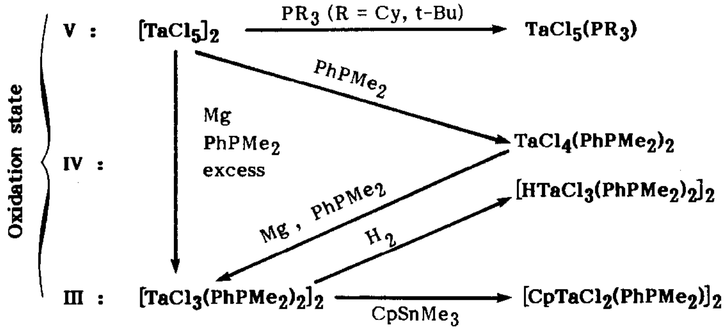


Fig. 4. Proton NMR spectra of the polymers produced by the exchange of terminal fluorine atoms vs. bridging oxygen atoms between a silicon atom and a phosphoryl group, the other sites being blocked by passive methyl groups (from ref. 11b).

ically on "theoretical" grounds, until the experimental chemists synthesized them and demonstrated that the problem was not one of bond stability but of lability, many low activation energy processes providing a plethora of decomposition pathways. We contributed to that field by showing that simple, not particularly sterically hindered, early transition metal methyl halides could be obtained in high yields when dimethylmercury or tetramethyltin were used as the alkylating agents under very strictly defined experimental conditions (Scheme 4). The next logical question was to explore how much chemistry could be done on such compounds *without* breaking the M–C bond. Scheme 4 shows, for example, that the chlorine-bridged $[MeNbCl_4]_2$ dimer, under the action of various oxo ligands, gives monomeric adducts of methylniobium oxychloride which can be isolated in close to quantitative yields [12]. These are reactions in which the environment of the metal is profoundly altered (the chlorine bridges disappear, two chlorine atoms are replaced by one double-bonded oxygen, two new coordination bonds are formed); the metal–carbon bond is the only one to remain unaffected in the whole coordination sphere. A similar set of reactions in which the M–C bond is preserved is shown in Scheme 5 for methyltungsten halides [13].



SCHEME 5. Turmoil in the methyltungsten's coordination sphere.

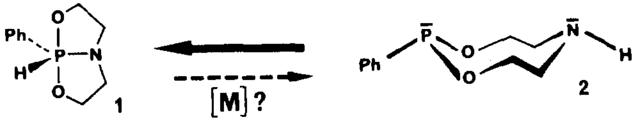


SCHEME 6. Access to Ta^{III} and Ta^{IV} complexes with an organometallic touch.

Closely related to this chemistry in many ways, among which are the need for strictly defined preparation and handling procedures (due to high sensitivity to oxygen and moisture, and to the ready occurrence of redox phenomena), is the chemistry of tantalum(IV) and tantalum(III) presented in Scheme 6 [14]. All of the compounds included somehow display similar "organometallic character", although only the cyclopentadienyl derivative (and the hydride) strictly belong to the field.

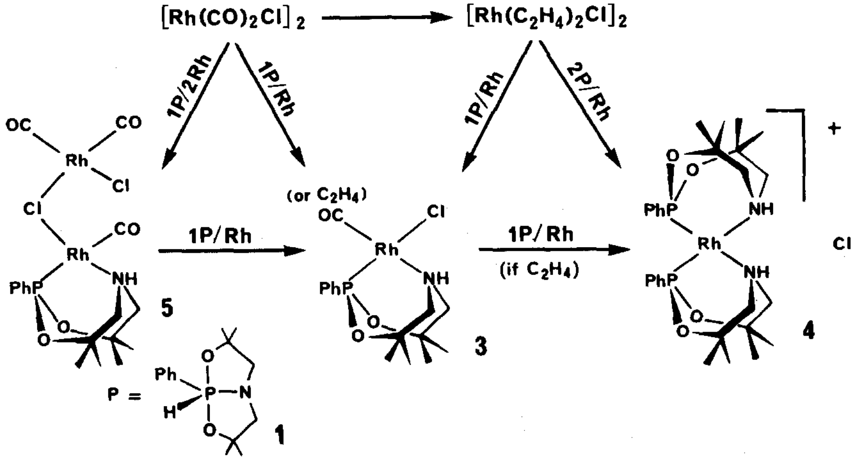
Blended chemistries

The following few schemes present a blend of phosphorus, organometallic and coordination chemistry. The initial question here was to find out whether the suspected tautomeric equilibrium (Scheme 7) between the bicyclic aminophosphorane **1** and its monocyclic amine/phosphane form **2** could be revealed and whether it is displaced by the action of Lewis acids. The phosphorane itself can hardly be expected to behave as a ligand as the pentacoordinated phosphorus atom has no electrons left for donation, and the phosphorus-bound nitrogen is expected to lose its donor capacity as its lone pair electrons are, according to the models currently used, drained into the *d*-orbitals of the phosphorus. In the open tautomer, on the other hand, it was anticipated that the two atoms would behave as independent 2-electron donor sites.



SCHEME 7. Using organometallics to unmask a hidden phosphorus/nitrogen ligand.

The complex $[Rh(CO)_2Cl]_2$ was chosen as a reagent to test this possibility (Scheme 8) because of the potential catalytic properties of the products: the metal would be located in a sort of cradle, **3**, in which it would be bound by two atoms of different character, more strongly by the soft π-acid phosphorus and in a more labile way to the nitrogen atom, which was thought to be propitious for catalysis; the hydrophilic NH group was expected to induce regioselectivity, and the cradle, by appropriate substitutions, could be made asymmetric and induce stereoselectivity. It

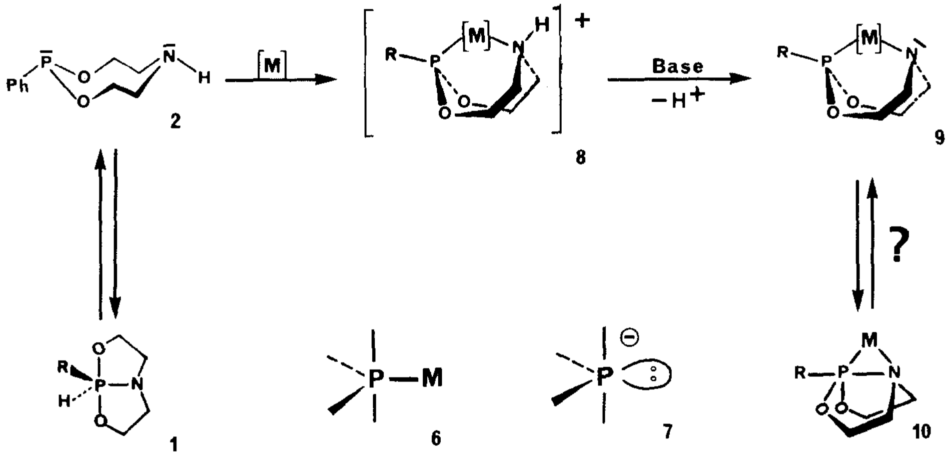


SCHEME 8. Dependence of the organometallic status on the stoichiometry of a reaction.

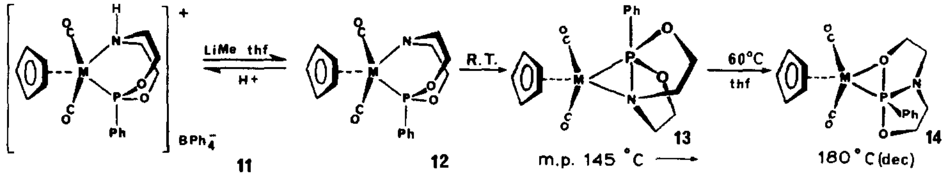
has also been shown that catalytic activity is in some cases enhanced by the presence of an amine, which here is built into the ligand [15].

The experimental data showed, indeed, that the bicyclic aminophosphorane reacts readily and quantitatively with $[Rh(CO)_2Cl]_2$ to yield complexes such as **3** of the open form tautomer of **1**. The grafting of a second amine/phosphane ligand onto the metal required the use of the more reactive organometallic complex $[Rh(C_2H_4)_2Cl]_2$; this gave the non-organometallic coordination compound **4**, which turned out to be the most active in catalysis [15]. A mere change in stoichiometry afforded the interesting new organometallic compound **5**, which is the first dinuclear rhodium compound with a single dissymmetric chlorine bridge [16].

Our approach to transition metal phosphoranides (i.e. complexes with the structural unit **6**, which contains a tetracoordinated anionic P(III) ligand **7**) also lies at the meeting point of several areas, consisting of transition-metal-activated phosphorus chemistry, using organometallic substrates and resulting in unexpected new organometallic chemistry. The strategy followed is outlined in Scheme 9. It is essentially based on the two tautomeric equilibria depicted in parallel on the left and right-hand sides of this Scheme [17]. The central cationic adduct **8** was thought to be a suitable candidate for proton abstraction, to yield (and this is where the questionmark lay) the amide complex **9** or the tautomeric phosphoranide **10**...or something else.



SCHEME 9. An approach to transition metal phosphoranides.



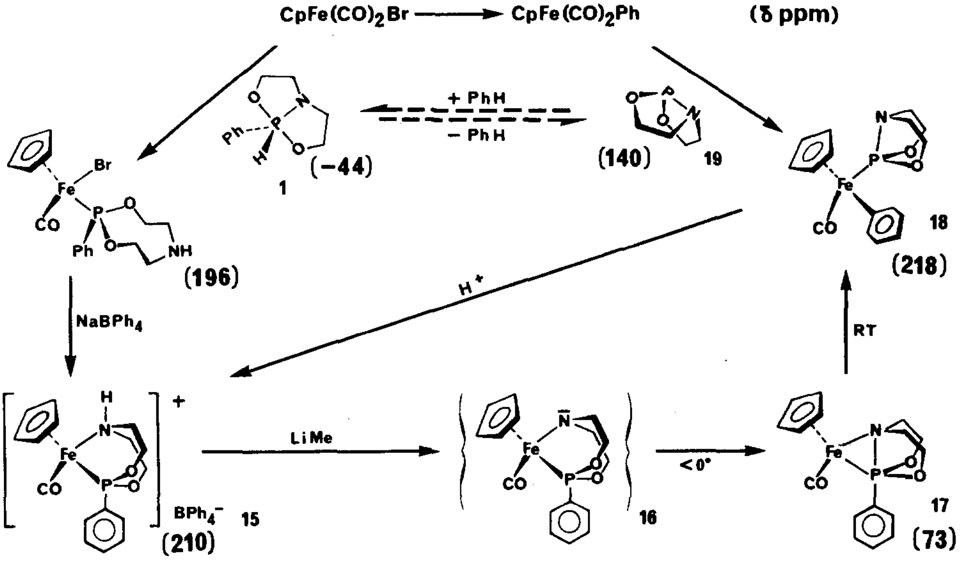
		11	12	13	14
$\delta\,^{31}P$	Mo	198	207	43.9	23.8
	W (J_{P-W})	169 (303)	181 (260)	6.4 (232)	15.5 (320)

SCHEME 10. Transition metal-driven phosphorus chemistry using organometallic substrates.

This approach worked out rather well in the case where [M] was $[(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2]$ (Scheme 10), and led to the first series of transition metal phosphoranides, although the first one we isolated was not the initially expected phosphorus- and nitrogen-coordinated compound **13**, but its more stable re-arranged isomer **14**, in which the oxygen atoms are back in their more favorable apical positions.

The only hint we had at first that the deep-red crystals isolated after cation **11** had been allowed to react with LiMe corresponded to a new species, was their unusual ^{31}P NMR signal at 23.8 ppm (while the phosphane site of the amide **9** should have given a signal around 200 ppm). An X-ray structure determination was necessary to establish definitely the nature of the compound with its unprecedented $\overset{\text{M}}{\text{P–O}}$ ring and very short (2.37 Å) P–Mo bond. The subsequent isolation of the unstable amide **12**, which forms first, then of the "kinetic" phosphoranide **13**, with its $\overset{\text{M}}{\text{P–N}}$ metallacycle, also unprecedented, completed the reaction sequence [18].

The same approach proved effective for the synthesis of molybdenum and tungsten cycloamphosphoranides [19]. However, while the molybdenum and tungsten phosphoranides **13** and **14** were stable compounds (with decomposition points at ca. 145 and 180°C, respectively), this was not the case with their iron analog, in which the phenyl group underwent a remarkable (and reversible) migration from phosphorus to iron [20]. Scheme 11 shows a whole cycle of reactions in which, again, organometallic chemistry, phosphorus chemistry, coordination chemistry, metal and nonmetal chemistry take part. The final product of the reaction of LiMe with **15** displayed a low-field ^{31}P singlet, and only the absence of $J(^{13}\text{C}^{31}\text{P})$ coupling with the phenyl carbon atoms convinced us that the compound we had isolated was not the amide **16**. The X-ray diffraction data showed that, while the P–N bond had indeed formed under the action of the base, the nitrogen atom was no longer bonded

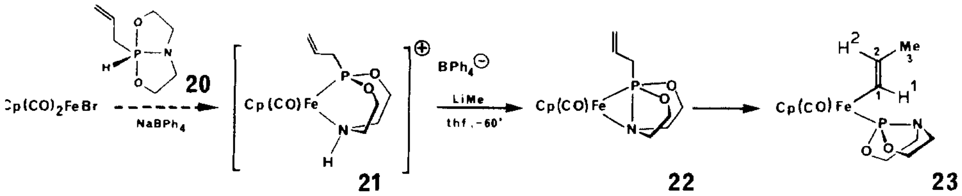


SCHEME 11. Unforseen organometallic chemistry resulting from interactions between phosphorus and transition metals.

to iron, and the phenyl group no longer to phosphorus. The same product, **18**, could also be obtained by first introducing the phenyl group onto the iron, and then substituting the bicyclic aminophosphane **19** for a carbonyl group. The subsequent action of a proton led to the same complex as that obtained by the reaction of (η^5-Cp)Fe(CO)$_2$Br with the phosphorane **1**, which is formally derived from the phosphane **19** by the oxidative addition of benzene.

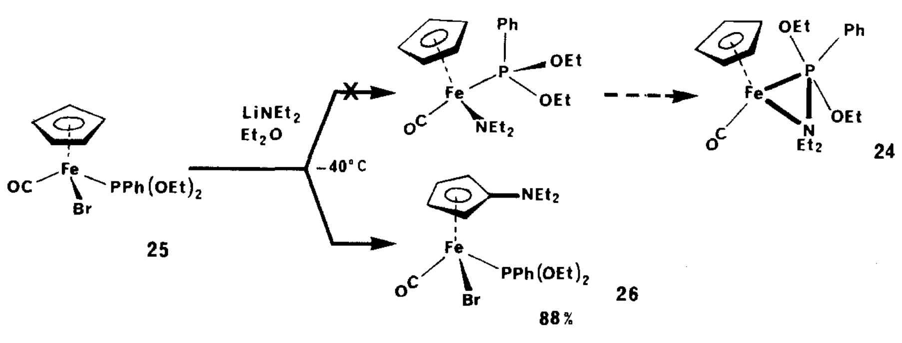
A closer investigation of the reaction showed that the iron phosphoranide **17** is an intermediate, and chemical labelling experiments showed that it is the same carbon atom which is alternately bonded to the metal and to the non-metal atoms [21], in contradistinction to the usual situation in orthometallation reactions.

The question naturally arose as to the extent of this reaction pattern, and whether advantage could be taken of it to form metal–carbon bonds. The behavior of bicyclic phosphoranes analogous to **1** but having substituents other than a phenyl group was therefore investigated, and this led, in the case of the allyl aminophosphorane **20**, to the observation of yet another reaction (Scheme 12). In its



SCHEME 12. From a phosphorus-bound allyl group to an iron-bound vinyl group.

reaction with LiMe, the cationic adduct **21** is first quantitatively converted into the phosphoranide **22** [22], but this is stable only below 0°C, and at room temperature it is converted into derivative **23**, in a reaction which involves the migration and rearrangement of the phosphorus-bound allyl group in **22** into an iron-bound vinyl group in **23**. The mechanism of this process most probably involves an insertion of iron into an allylic or a terminal vinylic C–H bond, followed by a 1,3-proton shift to the terminal olefinic or allylic carbon atom, respectively, with concomitant P–C bond cleavage. This unprecedented reaction pattern differs both from the phenyl group migration between phosphorus and iron discussed above which implies only the breaking of a P–C bond, and from an orthometallation reaction, which involves only the insertion of a metal into a C–H bond.



SCHEME 13. One-step amination of a coordinated cyclopentadienyl group. Further organometallic chemistry resulting from a mishap in coordination chemistry.

Another unexpected modification to a coordinated organic ligand was found when, with the aim of obtaining non-cyclic metal phosphoranides such as **24**, we treated the cyclopentadienyl iron complex **25** directly with a base (Scheme 13). Instead of the formation of amide or phosphoranide complexes, the adduct **26** was obtained in almost quantitative yield, providing a one-step amination reaction of the coordinated cyclopentadienyl ring [21].

Postscript

Only the obvious can be stated by way of a conclusion: organometallic chemistry now stands at the intersection of many disciplines and interests. Its definition(s) have probably lost most of their raison d'être (except for the organization of the body of established knowledge).

The constitution of a community of people who recognize themselves as organometallic chemists, however genial it is, may in large part be based on historical and cultural grounds. Frontiers, at a time when it has become possible to graft almost any organic fragment onto many metals (and conversely to introduce metal atoms into so many organic molecules) have become more elusive than ever, and this is not likely to improve as long as the field remains as creative as it is at present.

Acknowledgments

I wish to thank my (in)organophosphofluorometallic coordination chemist co-workers whose work has been presented here, the Indian and French Science Academies for travel funds, and Professor R.C. Mehrotra and his Staff for an outstanding reception in Jaipur.

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