Metal-Assisted P−H Bond Formation: A Step towards the Hydrogenation of White Phosphorus

Maurizio Peruzzini,*[a] Isaac de los Rios,[a] Antonio Romerosa,[b] and Francesco Vizza[a]

Dedicated to the memory of our unforgettable friend Professor José Antonio Ramírez (1957−2000)

Keywords: P−H bond formation / Phosphanes / Phosphorus / Transition metals

An overview of the chemistry of transition metal complexes containing P–H bonds is presented. Central to this microreview are those compounds in which the P–H bond is assembled by reactions entailing the transfer of one or more hydrogen atoms to white phosphorus or to P_x fragments resulting from P_4 activation and degradation within the coordination sphere of a transition metal complex. The relevance of these processes to the as yet unaccomplished hydrogenation of white phosphorus is briefly discussed.

Contents

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[a] ISSECC CNR,
Via Jacopo Nardi, 39, 50132 Firenze, Italy
Fax: (internat.) + 39-055/247-8366
E-mail: peruz@fi.cnr.it

[b] Área de Química Inorgánica, Facultad de Ciencias, Universidad de Almería,
04071 Almería, Spain

Maurizio Peruzzini (second from left) was born in Florence, Italy, in 1955. After his "Laurea" cum laude at the University of Florence in 1979 under the supervision of Luigi Sacconi and Piero Stoppioni, he joined the team led by Claudio Bianchini at ISSEC-CNR in 1986, where he is currently Senior Research Associate. He obtained the "Raffaele Nasini" gold medal prize awarded by the Inorganic Chemistry Division of the Societá Chimica Italiana in 1993 in recognition of his contribution to the chemistry of non-classical hydrides. His research interests are primarily in the field of organometallic chemistry and catalysis, as well as the activation and functionalization of pnicogen and chalcogen elements, mediated by transition metals. He has authored over 160 papers and patents and made more than 120 presentations at national and international meetings.

Isaac de los Rios (second from right) was born in Jerez de la Frontera, Spain, in 1970. He received his PhD from the University of Cadiz in 1997 under the guidance of M. Carmen Puerta. He is currently working on the activation and functionalization of white phosphorus in Florence at ISSECC-CNR in the group of Maurizio Peruzzini, with a Spanish Government grant. He has published about 15 papers in organometallic chemistry.

Antonio Romerosa (first from right) was born in Granada, Spain, in 1964. He graduated from the Universidad de Granada with a B.S. in Coordination Chemistry in 1987, and received his Ph.D. in organometallic borane chemistry from the Universidad Autónoma de Barcelona in January 1992. In the same year he undertook a postdoctoral research with Claudio Bianchini and Maurizio Peruzzini at ISSECC-CNR, Florence (Italy), before becoming Assistant Professor and then Associate Professor (1996) at the Universidad de Almería (Spain). He has performed postdoctoral research at ISSECC-CNR (Florence, Italy), Queen's University of Belfast (UK), the Instituto de Química (UNAM, México-DF), and Durham University (UK). His research interests cover fundamental aspects of both organometallic and bioinorganic chemistry. He has authored over 50 papers.

Francesco Vizza (first from left) was born in Cirò (KR), Italy, in 1957 and received his "laurea" in Biology from the University of Florence in 1982 under the supervision of Mario Ciampolini. He was then assistant researcher at the Department of Chemistry of the University of Florence, working in the field of macrocycle complexes. In 1986 he joined ISSECC-CNR, where he is presently Researcher and responsible for a catalysis laboratory. His current research interests are in the fields of homogeneous and heterogeneous catalysis (HDS, HDN, polymerization and copolymerization of olefins), chemistry of white phosphorus, transition metal complexes in therapy and diagnostics, and high-pressure NMR spectroscopy. He has authored about 85 papers and patents.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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1. Introduction

During the second part of the twentieth century there has been a spectacular renaissance of phosphorus chemistry, which has had a profound impact on a broad range of disciplines.[1] Few other branches of chemistry have had a greater influence on chemistry, biology, and material sciences, nor offer greater potential for addressing future needs and opportunities in far-reaching areas of science and engineering.

In keeping with the renowned interest of phosphorus chemistry, the coordination chemistry of elemental phosphorus, which was virtually unexplored until 1970, has now become a mature province of inorganic chemistry and has contributed important results to the resurgence of main group chemistry.[2] It begins from the reporting of $[(PPh_3)_2ClRh(\eta^2\text{-}P_4)]$ by Ginsberg and Lindsell in 1971,[3] and proceeds through an as yet unfinished string of key discoveries. Milestones in this story include, among others, Sacconi's reporting of $[(NP_3)Ni(\eta^1\text{-}P_4)]$ [$NP_3 = N(CH_2CH_2PPh_2)_3$], the first coordination compound exhibiting an intact *tetrahedro*-tetraphosphorus ligand,[4] and the spectacular complexes $[\{Cp^*Mo\}_2(\mu,\eta^6{:}\eta^6\text{-}P_6)]$[5] and $[Cp^*Fe(\eta^5\text{-}P_5)]$[6] prepared by Scherer and co-workers. These compounds, respectively containing the unprecedented hexaphosphabenzene and pentaphosphacyclopentadienyl ligands, bolstered confidence in the hypothesized approach based on building up polyphosphorus ligands through the well-known isolobal relationship between P atoms and CH groups.[7] Of course, there were many other breakthroughs in the coordination chemistry of naked phosphorus atoms and units, and dozens of other relevant contributions from the groups led by Sacconi,[8] Scherer,[9] Scheer,[10] Dahl,[11] Markó,[11a,12] Goh,[13] Wachter,[14] Huttner,[15] Stoppioni,[16] Schrock,[17] Cummins,[18] and others[19] have contributed to the rapid metamorphosis of white phosphorus coordination chemistry. Outstanding reviews describing the coordination chemistry of white phosphorus have also appeared in recent literature.[20]

In contrast, studies addressing the reactivity of these complexes have until recently seldom been considered, and remain quite rare in the literature. In addition, many of these early studies have been limited to the straightforward addition of electrophilic metal fragments − generally $M(CO)_5$ (M = Cr, Mo, W) − to the residual electron pair of the unsubstituted phosphorus atom.[21] An excellent recent survey by Whitmire deals with the chemistry of main group/transition metal cluster compounds, but addresses the reactivity of these complexes only to a limited extent,[20b] and does not cover the chemistry related to the metal-mediated hydrogenation of white phosphorus. This microreview is intended to fill this gap and focuses on the metal-mediated formation of P−H bonds, with particular emphasis on those reactions in which the P−H bond is produced starting from the P_4 molecule or fragments thereof.

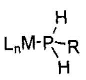
2. Formation of P−H Bonds from Naked P Atoms and Units Bonded to Transition Metal Complexes

2.1. A Survey of Transition Metal Complexes Incorporating P−H Bonds

Unlike that of nitrogen, the reaction of white phosphorus with hydrogen has received comparably little attention, and the possibility that H_2 might directly react with P_4 is still a matter of debate.[22] Thus, the sparse reports on this subject, indicating that a reaction could take place only under high H_2 pressure at elevated temperature (> 360 °C), should be carefully considered.[23]

Although a bewildering variety of binary phosphorus-hydrogen compounds (phosphanes) have been described in the last thirty years,[24−26] transition metal complexes containing phosphorus hydrides are practically limited to the numerous complexes containing primary (**1**) and secondary (**2**) phosphanes (or phosphites) or their simple derivatives, particularly bridging phosphido species (**3**).[27,28] There also exist a small number of transition metal complexes incorporating one or more PH_3 ligands,[29] but homoleptic species, such as $[Ni(PH_3)_4]$ (**4**), are extremely rare.[30] PH_3 complexes are in turn a suitable starting point for the preparation of terminal and bridging phosphido (PH_2) complexes,[31] and some μ-phosphinidene derivatives, such as $[\{Cp^*Mn(CO)_2\}_2(\mu\text{-}PH)]$ (**5**)[32] and $[\{Co(CO)_4\}_2\{Cr(CO)_3\}(\mu_3\text{-}PH)]$ (**6**)[33] have also been prepared from PH_3 precursors.

Clusters featuring μ_3-PH or μ_4-PH capping phosphinidene ligand are also well known.[33,34] Such compounds can be prepared by direct interaction of PH_3 with polymetallic clusters[34c] or by treating a preformed PH_3 metal complex with a carbonyl cluster.[33] However, the best synthetic approach to phosphinidene clusters is the hydrolysis of silylphosphinidene clusters. A neat application of this preparative methodology has recently been reported by Schauer and co-workers, who synthesized the biphosphinidene cluster $[Fe_3(CO)_9(\mu_3\text{-}PH)_2]$ (**7**) by controlled hydrolysis of P−Si bonds.[35] The reactivity of **7**, which is largely centered on the P−H functionality, has been investigated thoroughly. Remarkably, the reaction chemistry at one P−H functional site is effectively transferred to the second P−H site through the trimetallic $Fe_3(CO)_9$ core.



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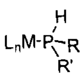

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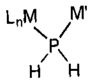

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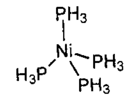

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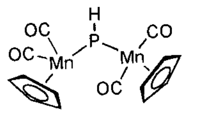

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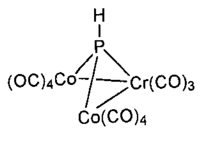

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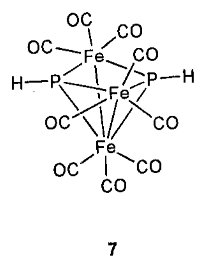

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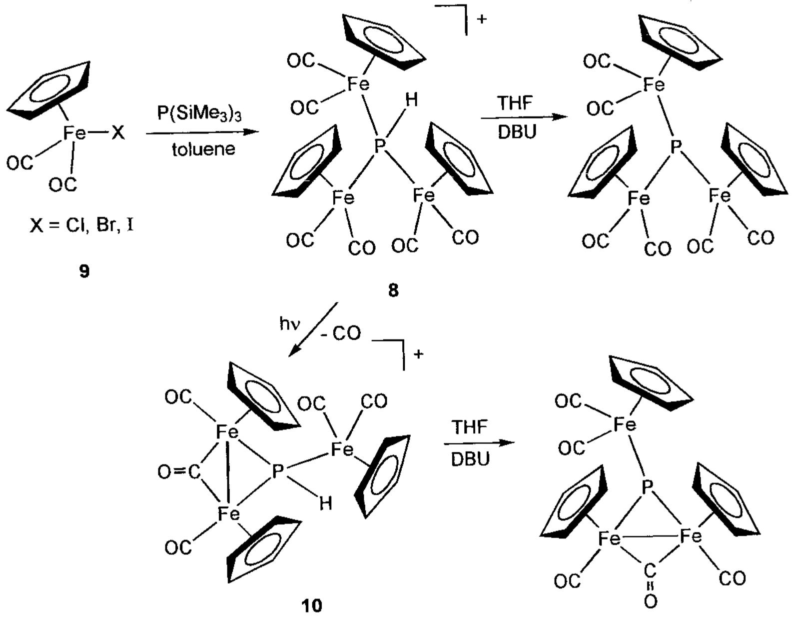
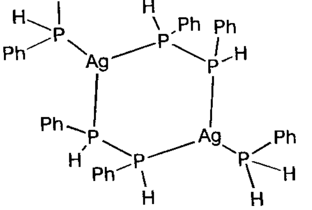
Stable triorganometallic phosphonium salts of formula $[\{Cp(CO)_2Fe\}_3(\mu_3\text{-}PH)]_n$ X (**8**) (n = 1, X = halide; n =2, X = $FeCl_4$) have been prepared by Lorenz and co-workers by in situ methanolysis of P−Si bonds. Thus, **8** has readily been obtained as reddish brown microcrystals by treatment of $[CpFe(CO)_2X]$ (**9**) with $P(SiMe_3)_3$ at room temperature in toluene followed by crystallization in the presence of methanol.[36] UV irradiation induced the transformation of the tetrachloroferrate salt $[\{Cp(CO)_2Fe\}_3(\mu_3\text{-}PH)]_2[FeCl_4]$ into the *closed-Fe,Fe*-triferriophosphonium derivative $[\{Cp(CO)_2Fe\}\{(\mu\text{-}CO)[Cp(CO)_2Fe]_2\}(\mu_3\text{-}PH)]_2[FeCl_4]$ (**10**) by means of elimination of one CO ligand and formation of an Fe−Fe bond supporting a bridging carbonyl ligand.[37] Notably, the PH protons in both the triferriophosphonium derivatives **8** and **10** can easily be removed with DBU (1,8-diazabicyclo[5.4.0]undecene) in THF. Scheme 1 summarizes these transformations.



Scheme 1

Of the other phosphanes, including the long-known P_2H_4, no transition metal derivative has yet been reported; unsurprising in view of the hyperreactivity of these molecules and their marked tendency to disproportionate.[24−26] However, complexes of substituted diphosphanes are known, and some of them, such as the dinuclear silver complex $[\{(PH_2Ph)Ag\}_2(\mu,\eta^1\text{:}\eta^1\text{-}P,P'\text{-}P(H)PhP(H)Ph)_2](AsF_6)_2$ (**11**), featuring two bridging diphenyldiphosphane ligands, have been authenticated by X-ray methods.[38] The coordination chemistry of substituted diphosphenes (P_2R_2) has also been studied, but the stabilization of diphosphene complexes usually requires bulky substituents. An outstanding review by Weber highlights the coordination chemistry of these ligands, also including the very few compounds containing P−H bonds.[39] At present, four complexes containing the parent diphosphene ligand (P_2H_2) have been reported. Two of these, $[Cp_2Mo(\eta^2\text{-}P_2H_2)]$ (**12**) and $[Cp_2TaH(\eta^2\text{-}P_2H_2)]$ (**13**), were prepared from direct treatment of metal hydrides with white phosphorus[40,41] and will be discussed in detail in the next section. The formation of the kinetic intermediate $[(dcpe)Ni(\eta^2\text{-}P_2H_2)]$ (**14**) (dcpe = $Cy_2PCH_2CH_2PCy_2$) during the methanolysis of $[(dcpe)Ni(\eta^2\text{-}P_2(SiMe_3)_2)]$ (**15**) en route to the formation of the diphosphorus dimetallic species $[\{(dcpe)Ni\}_2(\mu,\eta^2\text{:}\eta^2\text{-}P_2)]$ (**16**) (Scheme 2) was briefly mentioned by Schäfer and co-workers.[42] Although **14** was not stable enough to be isolated, it was observed at low temperature and its ^{31}P and ^1H NMR spectra were recorded. At 0 °C in toluene, it slowly decomposed, yielding **16** and phosphane (PH_3). However, no details about this intriguing decomposition reaction, in which both P−P and P−H bonds were broken and reassembled, were provided.



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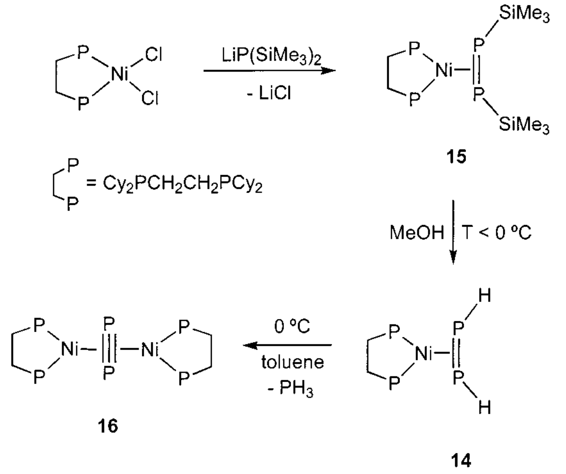
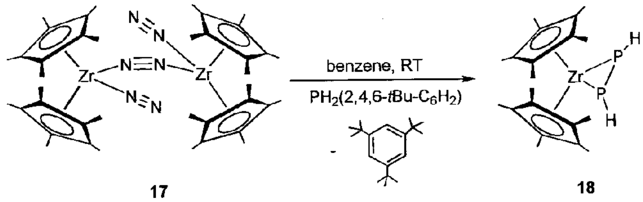
The only other known diphosphene complex was prepared by Stephan and co-workers by treatment of $[\{Cp^*{}_2Zr(N_2)\}_2(\mu\text{-}N_2)]$ (**17**) with the primary phosphane $PH_2(2,4,6\text{-}t\text{Bu-}C_6H_2)$.[43] The reaction proceeded smoothly in benzene at room temperature to afford the diphosphene complex $[Cp^*{}_2Zr(\eta^2\text{-}P_2H_2)]$ (**18**) and 2,4,6-$t\text{Bu}_3\text{-}C_6H_3$ in excellent yield (Scheme 3). The formation of **18** was associated with a P−C bond activation reaction at the sterically congested Zr−P system, which forms in the presence of a bulky primary phosphane. Such P−C bond activation



Scheme 2

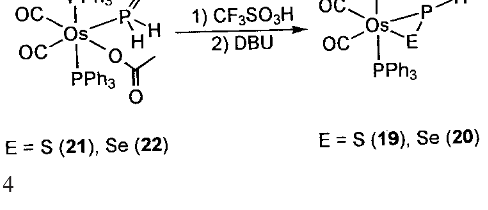


Scheme 3

methodology has successfully been used to synthesize several substituent-free P_x complexes of zirconium.[43]

It is worth mentioning that the parent diphosphene (P_2H_2) molecule, which in the four derivatives mentioned above was stabilized by complexation with low-valent organometallic metallocenes, has never been isolated in the free state. Such a molecule represents the lightest member of the P_nH_n family of phosphorus hydrides, the heavier members of which ($n > 2$) are known in the form of monocyclic phosphanes,[24–26,44] or, for $n = 2$, have been isolated by stabilization with bulky organic substituents. Theoretical investigations of P_2H_2 model complexes, such as $[(PH_3)_2Pd(P_2H_2)]$[45] and $[(CO)_5Cr(P_2H_2)]$[46] predict that the side-on η^2-coordination mode is the preferred one, with a short elongation of the diphosphene ligand P−P bond relative to that in the free molecule.[47]

Also relevant to this survey are the thioxophosphane and selenoxophosphane osmium complexes $[Os(\eta^2\text{-PHE})(CO)_2(PPh_3)_2]$ (E = S, **19**; Se, **20**), which were elegantly prepared by Roper and co-workers by stepwise addition of triflic acid and DBU to the thiophosphido and selenophosphido derivatives $[Os\{PH_2(E)\}(\eta^1\text{-}O\text{-OOCCH}_3)(CO)_2(PPh_3)_2]$ (E = S, **21**; Se, **22**) (Scheme 4).[48]



Scheme 4

Apart from these sparse examples, there does not exist any other homogeneous group of low-valent phosphorus transition metal complexes hosting the P−H functionality. This is particularly surprising if one considers that the number of known phosphorus hydrides is only exceeded by that of hydrocarbons[25] and that, notwithstanding the difficulties of directly utilizing higher phosphorus hydrides as starting reagents for preparative purposes, there should be at least three reliable synthetic strategies for incorporation of P−H bonds within the coordination polyhedron of a transition metal complex:

(a) the direct reaction of white phosphorus with transition metal hydrides,

(b) the electrophilic hydrogenation (addition of protic acids) of neutral transition metal species incorporating P_x units,

(c) the nucleophilic hydrogenation (addition of hydride reagents) of transition metal complexes incorporating P_x units.

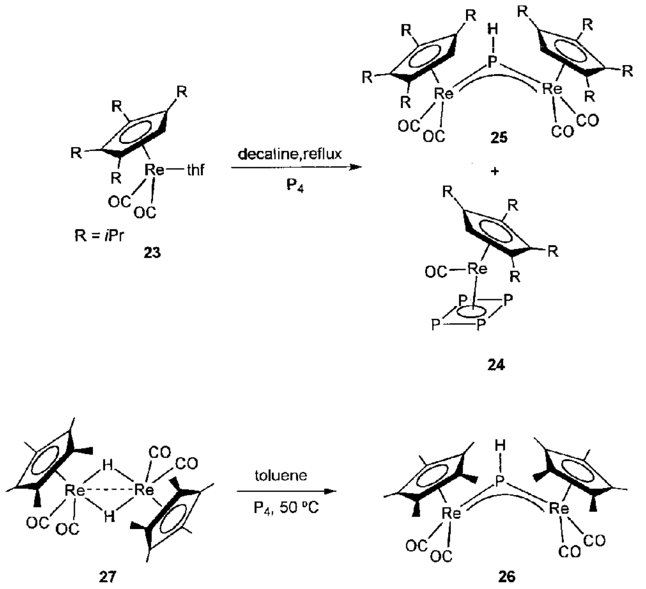
Although the above strategies should be broadly useful for the synthesis of transition metal complexes with P−H ligands in several preparative contexts, these methods have only been exploited to a very limited extent.

Treatment of white phosphorus with organometallic complexes may sometime result in the direct formation of P−H species even in the absence of suitable hydrogen donor sources. Adventitious water is generally considered to be responsible for the formation in these unpredictable reactions of species containing P−H. A pleasing example of this chemistry is provided by the study of the reaction of the sterically demanding rhenium metallocene $[(1,2,3,4\text{-}i\text{Pr}_4C_5H)Re(CO)_2(thf)]$ (**23**) with excess P_4.[49a] After prolonged reflux in decalin and chromatographic workup, a mixture was obtained, from which the tetraphosphacyclobutane $[(1,2,3,4\text{-}i\text{Pr}_4C_5H)Re(CO)(\eta^4\text{-}P_4)]$ (**24**) and μ-phosphinidene $[\{(1,2,3,4\text{-}i\text{Pr}_4C_5H)Re(CO)_2\}_2(\mu\text{-PH})]$ (**25**) complexes were separated (Scheme 5). A similar phosphinidene complex $[\{Cp^*Re(CO)_2\}_2(\mu\text{-PH})]$ (**26**) was obtained by treatment of $[\{Cp^*Re(CO)_2\}_2(\mu\text{-}H)_2]$ (**27**) with P_4 in toluene. However, no details of the mechanism leading to **26** were given.[49b] The two dirhenium phosphinidenes exhibit NMR resonances shifted strongly to low field (^{31}P: $\delta = 505/512$, and ^1H: $\delta = 15.5/14.8$), with direct P−H coupling constants (191/187 Hz) typical of $^1J_{PH}$ couplings.[50]

2.2. Reaction of White Phosphorus with Transition Metal Hydrides

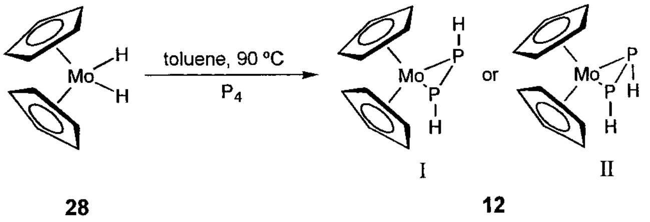
2.2.1. Reactions of White Phosphorus with Hydrido-Metallocenes

The reaction of white phosphorus with a transition metal complex was first described as early as 1974, by Green and co-workers. In a short note it was reported that the molybdenum dihydride $[Cp_2MoH_2]$ (**28**) reacted smoothly with P_4 in hot toluene at 90 °C to yield, after chromatographic workup on alumina, deep red crystals; these were assigned the stoichiometry $[Cp_2Mo(\eta^2\text{-}P_2H_2)]$ (**12**) on the basis of MS analysis, molecular mass determination, and ^1H and



Scheme 5

^{31}P NMR spectroscopy (Scheme 6).[40] However, spectroscopic methods alone were not capable of distinguishing between the two possible stereoisomers of the diphosphene ligand in **12** [*trans* (I) or *cis* (II)], which were preferred to the planar arrangement because of stereochemical arguments. The P_2H_2 ligand in **12** is believed to supply two electrons to the Mo^{II} complex, thus paralleling the bonding behavior of ethene in the related $[Cp_2Mo(C_2H_4)]$.



Scheme 6

Confirmation of Green's formulation of **12**, was provided soon after by Cannillo et al., who determined the molecular structure of **12** using X-ray methods. A view of the structure of Green's complex is presented in Figure 1.[51]

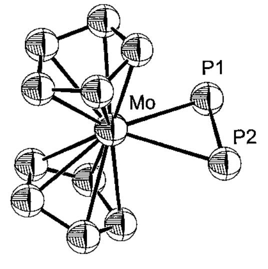
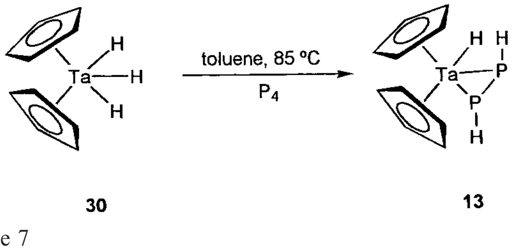


Figure 1. Crystal structure of $[Cp_2Mo(\eta^2\text{-}P_2H_2)]$ (**12**)

The most intriguing feature of the structure is the presence of a *quasi*-isosceles, triangular MoP_2 moiety, featuring a P−P separation of 2.146 Å, shorter than that found in black or white allotropes of phosphorus and in the diphosphane P_2H_4, but longer than the P=P bond length measured for P_2 molecules in the gas phase by electron diffraction.[52] The two P−H hydrogen atoms could not be located in the electron density map, but their presence was confidently inferred from spectroscopic measurements. In particular, the ^1H NMR spectrum exhibited an AA′XX′ multiplet at $\delta = 0.19$ with a $J_{PH} + J_{PH'}$ separation of ca. 160 Hz, while the corresponding multiplet in the proton-coupled ^{31}P NMR spectrum appeared at $\delta \approx 203$.[53] A sharp band at 2240 cm^{-1} in the IR spectrum was assigned to the stretching mode of the P−H bond.

No convincing information about the process which results in the assembling of the $Mo(P_2H_2)$ moiety from MoH_2 and excess P_4 has been provided, and the whole mechanism transforming the MoH_2 unit into the $Mo(P_2H_2)$ unit remains obscure. In situ monitoring of the originally reported "one-pot synthesis" of **12** by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy was not informative in retrospect.[54] The initial formation of **12** was already observed at 40 °C, but the transformation of **28** into the diphosphene complex was completed within a reasonable time only at temperatures higher than 60 °C. No intermediate species en route to the diphosphene was observed. In our hands, the formation of **12** was confirmed by the appearance in the $^{31}P\{^1H\}$ NMR spectrum ([D$_8$]toluene) of a singlet resonance at $\delta = -194.6$, paralleled by the rising in the proton spectrum of a doublet of doublets at $\delta \approx 0.44$ [$^1J(H,P) = 91.5$ Hz, $^2J(H,P) = 67.7$ Hz].[53] These NMR spectroscopic data, which confirm those given by Green with a lower field instrument, differ from those reported by Stephan and coworkers for $[Cp^*_2Zr(\eta^2\text{-}P_2H_2)]$,[55] but are in line with the NMR spectroscopic data given by Schäfer et al. for the thermally unstable $[(Cy_2PCH_2CH_2PCy_2)Ni(\eta^2\text{-}P_2H_2)]$.[56]

The reaction of primary phosphanes with $[Cp_2MH_3]$ (M = Nb, **29**; Ta, **30**) was thoroughly studied by Stephan and co-workers, who synthesized a variety of hydrido-diphosphene complexes $[Cp_2MH(\eta^2\text{-}P_2R_2)]$ (R = Ph, Cy) using this procedure.[41] In order to prepare unsubstituted diphosphene species, the reaction of white phosphorus with the tantalum trihydride **30** was successfully investigated. Thus, **30** and white phosphorus reacted in toluene at 85 °C to yield colorless crystals of $[Cp_2TaH(\eta^2\text{-}P_2H_2)]$ (**13**) after workup (Scheme 7).

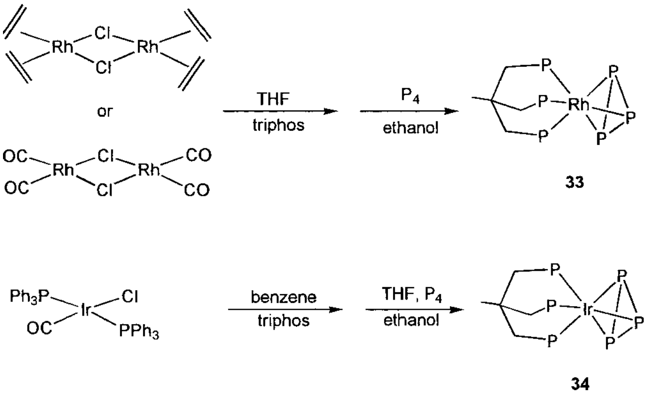


Scheme 7

Compound **13** was characterized by NMR spectroscopy and X-ray crystallography; the structural data revealed geometric features similar to those of **12**, with two cyclopentadienyl rings and a diphosphene ligand coordinated to the metal center. The three-membered MP_2 ring is tightly bonded to tantalum, with P−Ta−P angles ranging from 47.6 to 48.4°. A crystallographically located, but stereochemically inactive, hydride ligand completes the coordination sphere about the metal center. As for **12**, the two diphosphene hydrogen atoms were not located by X-ray methods and their disposition in the complex remains unclear. Theoretical calculations and analogy with the *transoid* disposition adopted by other crystallographically characterized disubstituted diphosphenes of formula [$Cp_2MH(\eta^2\text{-}P_2R_2)$] (M = Nb, Ta; R = Ph, Cy), gave credence to the view that the P_2H_2 ligand in **13** also adopts a *transoid* disposition. In particular, an energy difference of only 1−2 kcal mol^{-1} for the two optimized structures was computed by EHMO methods. A series of variable-temperature NMR experiments were consistent with the *transoid* structural assignment. Particularly informative was the analysis of the NOE enhancements observed at 193 K between the two P_2H_2 protons and the protons of the two inequivalent Cp rings. Compound **13** is stereochemically non-rigid, but the occurrence of a fluxional process exchanging *cisoid* and *transoid* isomers by inversion of both diphosphene ligand PH moieties could not be confirmed from analysis of the low-temperature NMR spectra. As with the molybdenum derivative **12**, no mechanism for the formation of **13** was provided.

2.2.2 Reactions of White Phosphorus with Hydrido-Polyphosphanes

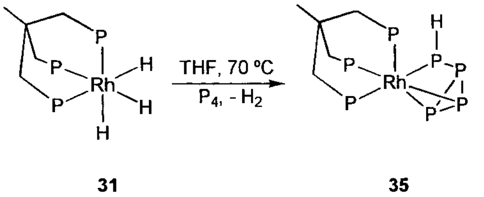
Notwithstanding Green's breakthrough in metal-assisted P−H chemistry and the continuous and impressive burgeoning of P_4-coordination chemistry during the last two decades,[57] studies dealing with the reactivity of transition metal hydrides with white phosphorus remained almost ignored until a couple of years ago, when we decided to investigate the reactivity of white phosphorus with transition metal hydrides stabilized by tripodal polyphosphanes. Our attention focused first on the known trihydrides [(triphos)RhH_3] (**31**)[58] and [(triphos)IrH_3] (**32**),[59] which had been successfully used by Bianchini and co-workers as hydrogenating catalysts for a variety of organic unsaturated substrates such as alkenes,[60] alkynes,[61] and thiophene derivatives,[62] including the highly HDS-resistant dibenzothiophene.[63] One of the most important reasons for choosing these hydrides at the very beginning of our investigation, apart from the general knowledge of their chemistry and the effectiveness of their catalytic performances in hydrogenation processes, was that the reactivity of both (triphos)Rh and (triphos)Ir systems towards white phosphorus was well known from Sacconi's studies, dating back to 1979.[64] Indeed, irrespective of the rhodium(I) or iridium(I) precursor,[65] the combination of triphos, M^I and white phosphorus resulted in the formation of the air- and moisture-stable complexes [(triphos)$M(\eta^3\text{-}P_3)$] as lemon yellow (M = Rh, **33**) or off-white (M = Ir, **34**), crystalline materials in moderate yields (Scheme 8).[64][66] Complexes **33** and **34** belong to the extensively studied family of *cyclo*-triphosphorus complexes [(triphos)$M(\eta^3\text{-}P_3)]^{n+}$ (n = 0, M = Co, Rh, Ir; n = 1, M = Ni, Pd, Pt) containing the P_3 unit *trihapto*-coordinated to the transition metal center.[67] The reactivity of these complexes has been widely investigated.[21,68]



Scheme 8

The generally accepted mechanism that governs the chemistry of both **31** and **32** involves the thermal reductive elimination of dihydrogen to produce the highly reactive species [(triphos)MH]. Once formed, the 16-electron fragment may be blocked by two-electron donor ligands, such as CO, or may reform an M^{III} complex by promoting the oxidative addition of different addends. In no case was removal of the residual hydride observed, although in a few instances it might selectively be delivered onto one of the oxidatively added atoms.[69] On all of these premises, it was of interest to see how the thermally generated fragments [(triphos)MH] would react with white phosphorus.

In keeping with our expectations, treatment of **31** with white phosphorus in THF at about 70 °C under nitrogen did not produce, at least directly, the *cyclo*-triphosphorus species **33**, but afforded an orange solution from which dark yellow microcrystals of the novel complex [(triphos)$Rh(\eta^1\text{:}\eta^2\text{-}HP_4)$] (**35**) were obtained after solvent removal under reduced pressure (Scheme 9).[70]



Scheme 9

Although the solid structure of **35** has not yet been verified by X-ray crystallography, the solution structure of the complex was substantiated by intensive multinuclear and multidimensional NMR experiments, which unequivocally demonstrated the presence of the rhodium-bonded $\eta^1\text{:}\eta^2$-HP_4 ligand, acting as a six-electron donor towards the (triphos)Rh fragment.

Key points of the NMR spectroscopic characterization lending credence to the proposed structure for **35** were the temperature-invariant $^{31}P\{^1H\}$ NMR spectrum, exhibiting a well-resolved ABCDEFGX spin system (confirmed by computer simulation and fitting), and the $^{31}P,^{31}P$-2D COSY NMR spectrum. In particular, it was possible to disentangle the not trivial pattern of P,P connectivities from an analysis

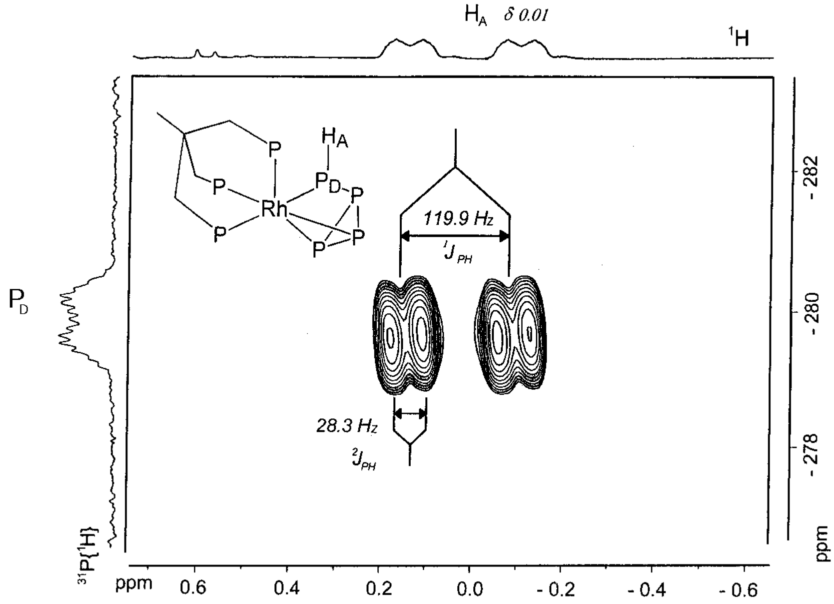
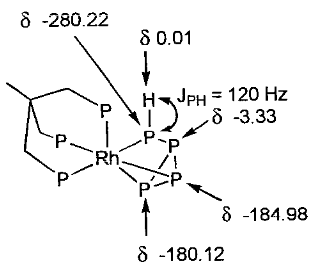


Figure 2. Contour plot of a section of the ^1H,^{31}P-2D NMR spectrum of [(triphos)Rh(η^1:η^2-HP_4)] (**35**), showing the relevant cross peak between the P_D atom and the P−H hydrogen atom

of the homonuclear correlation spectrum, and eventually to confirm the proposed structure for the phosphorus skeleton originating from the P_4 tetrahedron. The presence of the P−H ligand was underscored by a weak absorption at 2213 cm^{-1} in the IR spectrum (disappearing in the deuterated isotopomer [D_1]-**35**), by ^{31}P-DEPT NMR polarization transfer experiments (DEPT-90 and DEPT-135), and by ^1H,^{31}P-HMQC heteronuclear correlation NMR experiments. Inspection of the heterocorrelated spectrum made evident the presence of a cross-peak signal correlating the phosphorus multiplet centered at $\delta = -280.22$ and a doublet of broad doublets resonating at $\delta \approx 0.01$ in the ^1H NMR spectrum. A relevant section of the contour-plot diagram, illustrating the one-bond P−H correlation, is presented in Figure 2.

Although the assemblage of the HP_4 ligand from white phosphorus and a transition metal hydride and its incorporation into a metal complex framework is unprecedented, the existence of an HP_4 anion had previously been demonstrated by Baudler and co-workers, who in 1988 prepared the alkaline salts M(HP_4) (**36**: M = Li, Na, K) by treatment of white phosphorus with metal naphthalenide as reducing reagent in 1,2-dimethoxyethane at −78 °C.[71] Unlike **35**, which is stable at room temperature under nitrogen or argon in both solid state and in solution, Baudler's derivatives could not be stored even at low temperature, decomposing in a few days at −78 °C, thus indicating that stabilization of highly reactive intermediates, even in phosphorus hydrido chemistry, can be achieved by means of metal coordination. A comparison of the NMR parameters of **35** with those of Baudler's salt reflects the substantial spectroscopic differences occurring upon stabilization of the tetraphosphorus monohydrido anion by metal coordination, but, noticeably, shows an almost identical value for the two one-bond P−H coupling constants [119.9 Hz for **35** vs. 129 Hz for K(HP_4)]. The P_4H units in both **35** and **36** can be formally considered as monodeprotonated anions derived from the known tetraphosphorus dihydride P_4H_2. This phosphane, which has been identified by mass spectrometry, is the simplest member of the low-hydrogen phosphanes of formula P_nH_{n-2}.[72] These exhibit structural motifs based on condensed polyphosphorus ring systems, and in the case of P_4H_2 a bicyclo-[1.1.0]tetraphosphane structure (**37**) has been proposed.[24−26,72] In terms of their structural layouts, both the tetraphosphane **37** and the derivatives **35** and **36** can be traced back to the few known derivatives containing the tetraphosphabicyclobutane skeleton (P_4^{2-}). Complexes of



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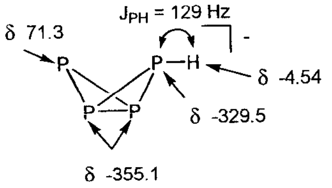

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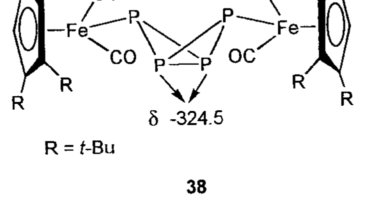


38

this class, featuring a butterfly MP_4M array, have been directly obtained either by cothermolysis of P_4 with $[\{Cp'(CO)_2Fe\}_2]$ – one example is $[\{Cp'(CO)_2Fe\}_2(\mu,\eta^1:\eta^1\text{-}P_4)]$ (**38**) (Cp′ = 1,2,4-tBu$_3$-C$_5$H$_2$)[73] – or by reaction of the diphosphene complex $[Cp^*(CO)_2Fe(P{=}PCp^*)]$ with $[\{Cp^*(CO)_2Fe\}_2]$ – one example is $[\{Cp^*(CO)_2Fe\}_2(\mu,\eta^1:\eta^1\text{-}P_4)]$ (**39**).[74]

Now the task at hand was to understand the mechanism leading to **35** and to explore the chemical reactivity of the HP_4 ligand. To address the first point, we decided to follow the reaction of P_4 and **31** by in situ NMR spectroscopy in order to observe some intermediates preceding the formation of the HP_4 ligand. Thus, when a 5-mm NMR tube (sealed under nitrogen) containing a [D$_8$]THF solution of **31** and white phosphorus (1:2) was heated in the NMR probe, a slow reaction took place at ca. 40 °C, selectively producing **35** as the only phosphorus-containing complex, without providing any evidence for intermediate species. The transformation was very slow at this temperature; after 4 h, less than 25% of **31** had been converted into the HP_4 compound. Inspection of the ^1H NMR spectrum revealed that dihydrogen had also been released (singlet at $\delta \approx 4.75$). Heating the probe-head to ca. 70 °C resulted in the fast (2 h) disappearance both of the **31** doublet at $\delta \approx 29$ and of the set of resonances due to **35**, and led to the formation of a doublet of quadruplets at $\delta \approx -269$, which was attributed to the *cyclo*-triphosphorus complex **33** by comparison with an authentic specimen.[64] The formation of **33**, which is almost quantitative after 2 h at 70 °C, was accompanied by the disappearance of the H_2 resonance in the proton spectrum and by the progressive development in the $^{31}P\{^1H\}$ NMR spectrum of a singlet resonance at $\delta = -244.77$, which was attributed to the formation of PH_3. In agreement with this assignment, this singlet transformed into a narrow quadruplet, with $^1J(H,P) = 186.9$ Hz, in the proton-coupled NMR spectrum. Figure 3 illustrates these transformations and highlights these experiments.

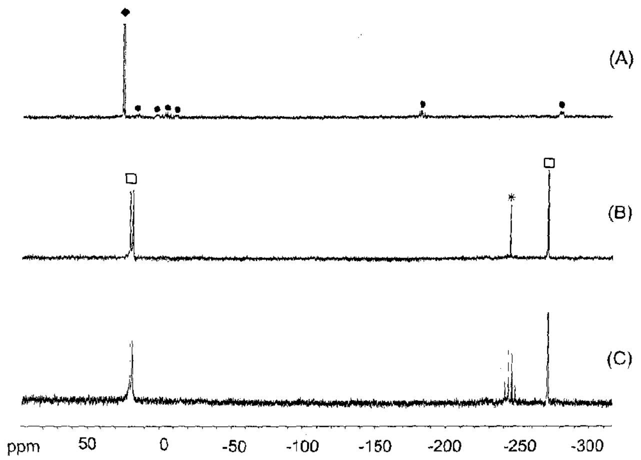
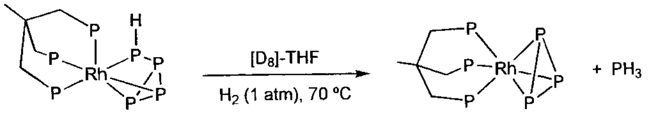


Figure 3. Monitoring of the reaction of [(triphos)RhH$_3$] (**31**) with P$_4$ (2:1) in [D$_8$]THF: (A) $^{31}P\{^1H\}$ spectrum after 1 h heating at 40 °C; (B) $^{31}P\{^1H\}$ spectrum after 2 h heating at 70 °C; (C) ^{31}P spectrum after 2 h heating at 70 °C; (◆) [(triphos)RhH$_3$] (**31**); (•) [(triphos)Rh(η^1:η^2-HP$_4$)] (**35**); (□) [(triphos)Rh(η^3-P$_3$)] (**33**); (*) PH$_3$

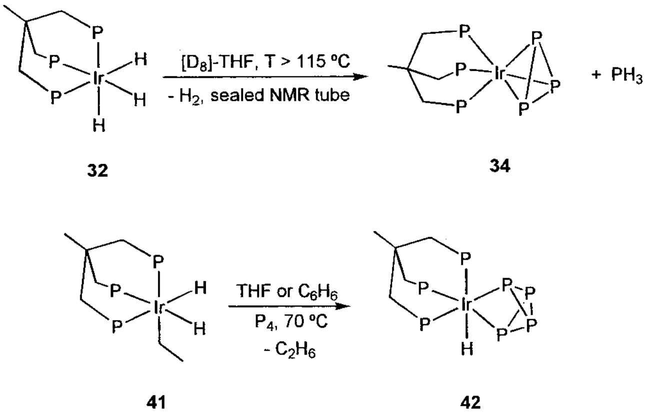
The reaction described above is remarkable because it provides the first evidence that *at least one of the four P atoms of white phosphorus can be hydrogenated to phosphane by a metal-assisted reaction*. It is also worth mentioning that all of the three hydride ligands in **31** are selectively transferred to the same phosphorus atom, while the three remaining phosphorus units in the P_4 molecule are efficiently scavenged in the form of the thermally robust *cyclo*-triphosphorus moiety in complex **33**. A separate NMR experiment carried out with the perdeuterated trihydride [D$_3$]-**31** confirmed the total incorporation of deuterium into the phosphane molecule, thus indicating that the three hydrogen atoms were transferred from the rhodium center to the same phosphorus atom. Addition of H_2 (1 atm) to a [D$_8$]THF solution of **35** at 70 °C transformed the HP_4 species into PH_3 and **33** (Scheme 10), but under N_2 the thermal reaction was difficult to control and the formation of **33** (< 70%) was accompanied by extensive decomposition. No compound arising from the formally produced "phosphinidene" (PH) species was identified and, because of the complexity of the reaction mixture, no experiment aimed at trapping this highly reactive fragment was attempted.



35 **33**

Scheme 10

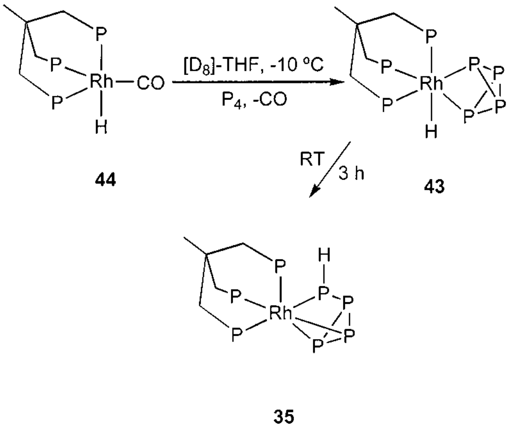
As NMR monitoring of the reaction of **31** with P_4 did not provide definitive mechanistic information, we turned our attention to the kinetically more inert and thermally more robust iridium complex **32.** As expected, and in keeping with the general behavior of **32**, the reaction of the iridium trihydride with P_4 did not differ from that of its rhodium congener. However, the reaction needed a greater degree of activation to start, taking place only at temperatures higher than 115 °C. At this temperature, the formation of PH_3 and **34** from the undetected complex [(triphos)Ir(η^1:η^2-HP$_4$)] (**40**) should occur very rapidly, and thus did not allow for the detection of any intermediate species during an in situ NMR experiment (sealed NMR tube) (Scheme 11). However, having established that the [(triphos)IrH] fragment is well suited as a platform for carrying out the hydrogenation reaction of P_4 to PH_3 and *cyclo*-P$_3$, it was an obvious step to look through the variety of organometallic complexes available in our laboratory and therefore to turn our attention to the cognate iridium complex [(triphos)Ir(H)$_2$Et] (**41**).[75] Compound **41** thermally eliminates ethane, rather than H_2, under milder conditions (ca. 70 °C) and, irrespective of the solvent medium (benzene, THF, acetone, acetonitrile, etc), gives the fragment [(triphos)IrH]. This, in the absence of any external reagent, brings about C–H bond activation of the solvent, yielding octahedral Ir^{III} complexes of formula [(triphos)Ir(H)$_2$R] [R = C_6H_5, C_4H_7O, $CH_2C(O)CH_3$, CH_2CN, etc.]. However, when a solution of **41** in THF or benzene was brought to reflux in the presence of elemental phosphorus (Ir/P_4 = 1:2), no solvent activation took place, and a bright yellow solution was obtained, from which pale yellow microcrystals of the novel compound [(triphos)IrH(η^2-P_4)] (**42**) separated.[76] Compound **42** was characterized by elemental analysis, mass spectrometry and IR spectroscopy [IR: medium-intensity ν(Ir−H) band at 2061 cm^{-1}], as well as by multinuclear NMR spectroscopy.



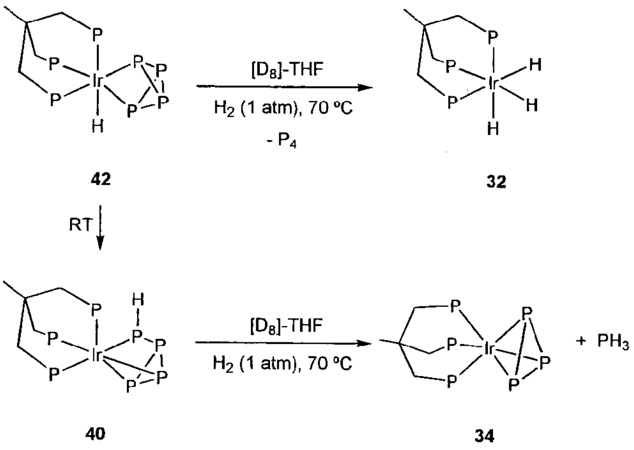
Scheme 11

Complex **42** is a member of the well-known family of transition metal complexes containing the bicyclotetraphosphane ligand[77] and, in keeping with this hypothesized structure, it shows in the $^{31}P\{^1H\}$ NMR spectrum a slightly second-order-perturbed ABB′CDEE′ spin system. Probably, **42** forms by oxidative addition of P_4 to the unsaturated [(triphos)IrH] fragment. This can reasonably be assumed as the first basic step of the reaction of P_4 with both **31** and **32**. In contrast to the easy synthesis of **42**, no analogous rhodium compound could be detected in the reaction of **31** with P_4. However, a species showing NMR parameters in line with that of the anticipated [(triphos)RhH(η^2-P_4)] (**43**) was generated in a 5-mm NMR tube by treating a cold [D_8]THF solution of the hydrido-carbonyl complex [(triphos)RhH(CO)] (**44**)[58] with one equivalent of P_4, dissolved in the same solvent. At room temperature, the transformation of **43** into **35** is sufficiently slow to allow the hydridobicyclotetraphosphane complex to be isolated. On standing of the solution at room temperature, **43** was transformed quantitatively into **35** within 3 h (Scheme 12).[78] On the basis of this finding, it is quite probable that **43**, which initially forms at the temperature required to eliminate H_2 thermally from **31**, undergoes a quick transformation into **35** without being observable by NMR experiments.

Compound **42** is kinetically stable and could be isolated in the solid state in pure form. Nevertheless, in a THF solution standing at room temperature in a sealed NMR tube, it spontaneously tautomerized within days into the HP_4 derivative [(triphos)Ir(η^1:η^2-HP_4)] (**40**) (Scheme 13). The reaction was not selective and a number of unknown iridium species and some decomposition products accompanied the formation of **40**, which could not be obtained in a yield higher than 25%. Hydrogenation of **40**, in a [D_8]THF solution heated at about 70 °C, cleanly produced PH_3 and the iridium *cyclo*-P_3 complex **34**. Remarkably, when pressurized with dihydrogen, **42** did not produce PH_3 and **34**, because the reductive elimination of P_4 became competitive with the hydrogenation reaction of the activated P_4 ligand. Thus, after exposure of **42** to H_2 and heating at ca. 70 °C, the trihydride **32** was quantitatively recovered (Scheme 13). Nevertheless, this result is valuable from a mechanistic viewpoint as it underlines that *the functionalization of the activated P_4 ligand by selective delivery of one hydride from the metal center to the phosphorus atom is mandatory for accomplishing the complete hydrogenation of one P atom to PH_3.*



Scheme 12



Scheme 13

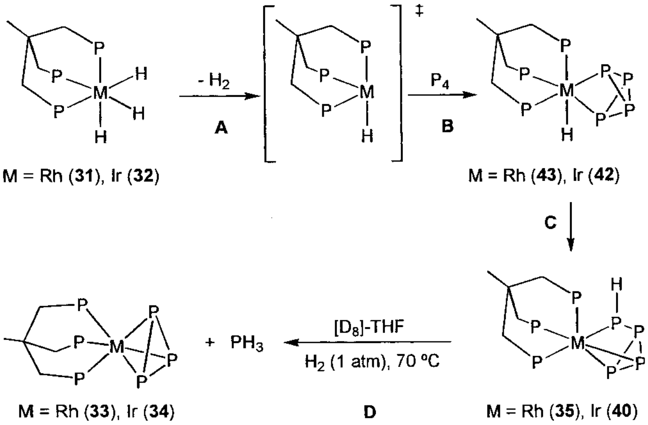
A perusal of the large body of collected experimental information about the reaction with white phosphorus of **31** and **32** provides convincing evidence with which to propose a plausible mechanism for the hydrogenation of one phosphorus atom in white phosphorus to phosphane. Fundamental key points of the proposed mechanism, which is depicted in Scheme 14 are:

(**A**) the thermal elimination of H_2 from the rhodium or iridium trihydride is the preparative step necessary to generate the highly reactive fragment [(triphos)MH],

(**B**) the P_4 oxidative addition occurs by P−P bond activation and results in the formation of the octahedral hydridobicyclotetraphosphanes **42** and **43**. The iridium complex **42** is endowed with enough stability to be isolated in the solid state, but the rhodium analogue **43** could not be intercepted under the experimental conditions used. It has been synthesized at lower temperature by alternative routes,[78]

(**C**) the unprecedented HP_4 complexes **35** and **40** are obtained from the irreversible intramolecular tautomerization $M(H)(\eta^2\text{-}P_4) \rightarrow M(\eta^1{:}\eta^2\text{-}HP_4)$ by hydride migration from the metal to one of the proximal P atoms of the η^2-P_4 ligand. This step is a prerequisite for the following hydrogenation reaction,

(**D**) in the absence of H_2, the reaction stops at the HP_4 complex, but when dihydrogen is added, or when the reaction is carried out in a closed system, complete hydrogenation of the hydrogenated phosphorus atom in the HP_4 ligand takes place. Notably, the hydrogenation step is accompanied by concomitant P−P bond cleavage with release of PH_3.



Scheme 14

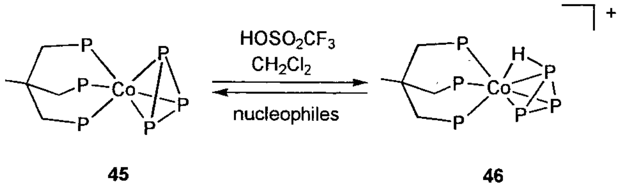
The final hydrogenation step, conveying two hydrogen atoms to the PH group in the HP_4 ligand, is currently under study. A possible mechanism accounting for the formation of PH_3 involves the metal-mediated, heterolytic splitting of a molecular hydrogen ligand, followed by stepwise addition of H^+ and H^- to the hydridotetraphosphorus ligand. Convincing chemical evidence supporting the heterolytic mechanism comes from the observation that electrophiles like H^+ and Me^+ selectively attack the hydrogen-substituted P atom in **35** (vide infra),[79] and that both (triphos)Rh and (triphos)Ir systems are capable of coordinating H_2, forming the highly fluxional, nonclassical hydrides $[(triphos)Rh(\eta^2\text{-}H_2)(H)_2]^+$ [80] and $[(triphos)Ir(\eta^2\text{-}H_2)(H)_2]^+$.[81]

Now there remains the crucial point of turning the stoichiometric hydrogenation of white phosphorus into a catalytic process. In this regard, we think that the formation of **33**, which accompanies the assemblage of PH_3 from **35** and H_2, represents a dead-end, because the triphos *cyclo*-triphosphorus complexes are extremely robust and cannot return the rhodium precursor to the reaction system under any realistic conditions. Experimentally, we have not yet been able to observe any catalytic reaction, and only a stoichiometric amount of phosphane was produced when a solution of **31** and white phosphorus (Rh/P_4 = 1:10) in [D8]THF was pressurized with up to 30 atm of H_2 in a sapphire NMR tube and heated up to 90 °C (high-pressure NMR experiment). Harsher reaction conditions caused extensive decomposition of the rhodium complexes without increasing the PH_3 yield.[82]

Nonetheless, we think it possible to accomplish the catalytic hydrogenation of P_4, providing that hydrogen transfer from the transition metal hydride to phosphorus is carried out using a metal hydride capable of coordinating and activating P_4, but unable to form stable complexes with the released P_x fragment (i.e. *cyclo*-P_3 in the case at hand). In order to verify this hypothesis, we are currently expanding the range of transition metal hydrides to be treated with white phosphorus. Particularly, we are looking at hydrides stabilized by polydentate ligands capable of easily dissociating one arm (hemilabile ligands), which should make coordination of H_2 to the intermediate P_4-activated complexes possible.[82]

2.3. Electrophilic Hydrogenation of P_x Units Incorporated into Transition Metal Complexes

Electrophilic hydrogenation (addition of protic acids) of neutral transition metal species incorporating P_x units is a simple method for generating the P−H bond functionality in a metal-stabilized polyphosphorus P_x unit. However, this synthetic procedure has scarcely been used and the only well-documented literature example related to such reaction was reported by Stoppioni and co-workers in 1991.[83] By straightforward addition of two equivalents of triflic acid to a suspension of $[(triphos)Co(\eta^3\text{-}P_3)]$ (**45**) in dichloromethane, a rapid dissolution of the starting compound occurred, giving an orange solution from which orange crystals of composition $[(triphos)Co(\eta^3\text{-}HP_3)](OSO_2CF_3)_2{\cdot}(H_5O_2)$ (**46**) were obtained after layering with benzene at room temperature (Scheme 15).



Scheme 15

The reaction is reversible, and even mild nucleophiles such as acetone, ether and ethanol can deprotonate **46**, giving back the *cyclo*-triphosphorus complex **45**. NMR analysis of the complex did not clarify the solution structure of the $[(triphos)Co(\eta^3\text{-}HP_3)]^+$ cation. However, the observation in the ^1H NMR spectrum of a temperature-invariant broad hump at $\delta \approx -13.7$ points to the presence of a hydrogen atom with a rather prominent hydride character.[84] The solid-state structure of **46** consists of triflate anions, $H_5O_2^+$ and $[(triphos)Co(\eta^3\text{-}HP_3)]^+$ cations in a 2:1:1 ratio. Noticeably, the co-crystallized molecules of triflic acid and adventitious water found by the X-ray diffraction analysis do not show any short contacts with the complex cation. The addition of a proton to the tetrahedral array of the parent CoP_3 cluster causes only moderate distortions, resulting in a slight lengthening of the Co−P bonds from 2.301 Å in **45** to 2.396 Å [$d(\text{Co-P})_{\text{ave}} = 2.343$ Å] in **46** (Figure 4). A rationale for the location of the crystallographically undetected proton was obtained, in view of the distorted solid-state geometry, by theoretical analysis using both a semiempirical extended Hückel approach and ab initio DFT calculations.[85]

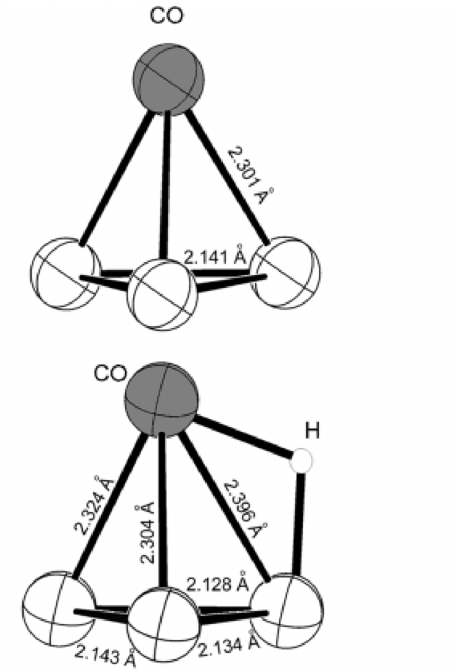
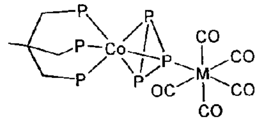


Figure 4. Comparison of the inner cores of $[(\text{triphos})\text{Co}(\eta^3\text{-P}_3)]$ (**45**) (top) and $[(\text{triphos})\text{Co}(\eta^3\text{-HP}_3)]^+$ (**46**) (bottom); the H atom in **46** has been inserted in a calculated position

Among the four different preferential sites of attack of the H$^+$ to the CoP$_3$ moiety, the optimized structure for the CoHP_3^+ cation entails the added H atom forming a bridge between one of the phosphorus atoms of the P$_3$ ring and cobalt. The calculated minimized geometry was found to be in very good agreement with that proposed on the basis of the experimentally observed crystallographic distortions for **46** and has been attributed to the minimal steric requirements of the H$^+$. In keeping with the existence of slightly higher minima in the energy profile associated with the electrophilic alkylation of **45**,[85] the electrophilic addition of sterically more demanding fragments to **45** results in the formation of geometrically distinct $\text{Co}(\eta^3\text{-P}_3\text{R})^{n+}$ (n = 0, 1) adducts, in which the added electrophile may bind one CoP$_3$ core phosphorus atom as an exocyclic ligand, such as in $[(\text{triphos})\text{Co}(\eta^3\text{-P}_3\{\text{M(CO)}_5\})]$ (**47**),[21b,86] and $[(\text{triphos})\text{Co}(\eta^3\text{-P}_3\text{Me})]\text{PF}_6$ (**48**),[87] or may be bound to a pair of phosphorus atoms of a slightly elongated P−P edge, such as in the mononuclear mercury adduct $[(\text{triphos})\text{Co}(\eta^3\text{-P}_3\{\text{HgPh}\})]\text{PF}_6$ (**49**),[68e] or in the binuclear species with a coinage metal cation bridging two CoP$_3$ fragments, $[\{(\text{triphos})\text{Co}(\eta^3\text{-P}_3)\}_2(\mu_4\text{-M})]\text{PF}_6$ (M = Cu, Ag, Au) (**50**).[68d,68g]



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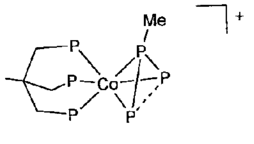

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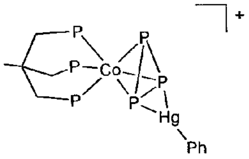
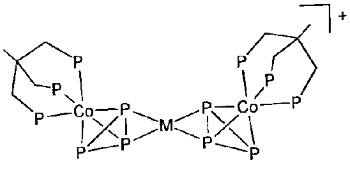
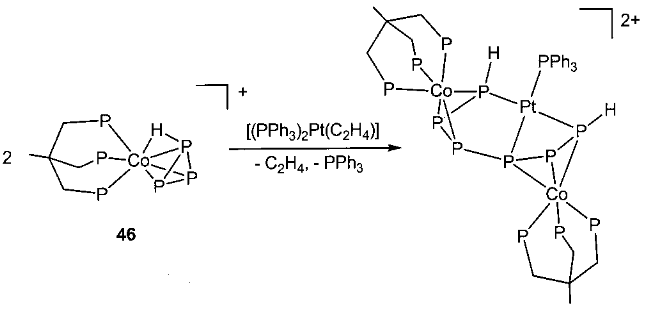


49



50

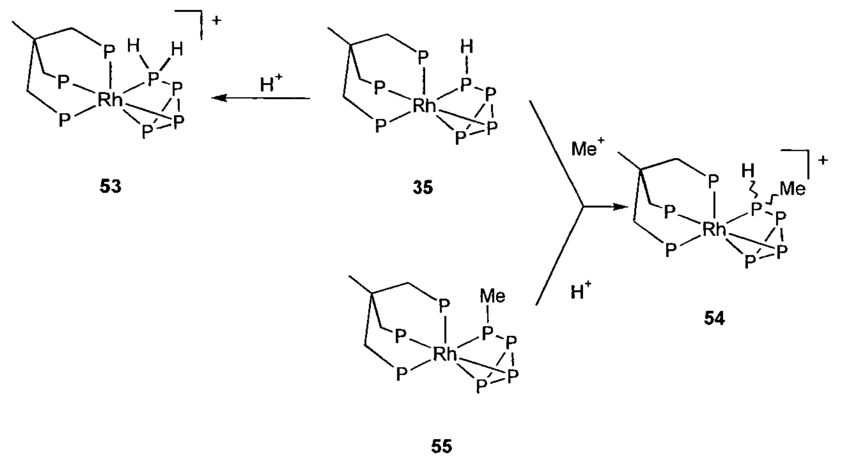
The protonated complex **46** was successfully used by Di Vaira and Stoppioni as the starting material for the construction of an unprecedented open-chain P$_6$H$_2$ ligand by reaction with $[(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)]$ (**51**).[88] Thus, addition of **51** to a dichloromethane solution of **46** gave dark brown crystals of $[\{(\text{triphos})\text{Co}\}_2(\eta^3,\eta^3,\eta^3\text{-P}_6\text{H}_2)\{\text{Pt}(\text{PPh}_3)\}](\text{OSO}_2\text{CF}_3)_2\cdot 2\text{C}_6\text{H}_6$ (**52**), authenticated by X-ray methods (Scheme 16).



Scheme 16

The cationic complex **52** results from the coming together of two $[(\text{triphos})\text{Co}(\eta^3\text{-HP}_3)]^+$ cations and a Pt(PPh$_3$) moiety. The P$_6$H$_2$ fragment is generated by P−P bond formation from two different $\text{Co(HP}_3)^+$ units, while during the reaction the labile ethene and one triphenylphosphane ligand are removed from the platinum center. This metal center exhibits the usual square-planar geometry, formed by the residual PPh$_3$ ligand and by three phosphorus atoms of the assembled P$_6$H$_2$ fragment. Although the presence of two triflate anions implies the existence of two protons, as required for charge balance, these could not be located either by structural investigation, or by spectroscopic techniques (IR and ^{1}H NMR). However, the narrow distribution of the six Co−P bonds in **52** [$d(\text{Co-P})_{\text{ave}} = 2.305$ Å] would rule out a bridging Co−H−P location for the skeletal hydrogen atoms in **52**. Similarly, theoretical EH calculations do not indicate any electrophilic privileged target between the six P atoms of the P$_6$H$_2$ ligand, but rather point to an appreciable amount of negative charge spread over the six positions in the hexaphosphorus chain.[88]

Addition of electrophiles to $[(\text{triphos})\text{Rh}(\eta^1{:}\eta^2\text{-HP}_4)]$ (**35**) was briefly considered in order to shed some light on



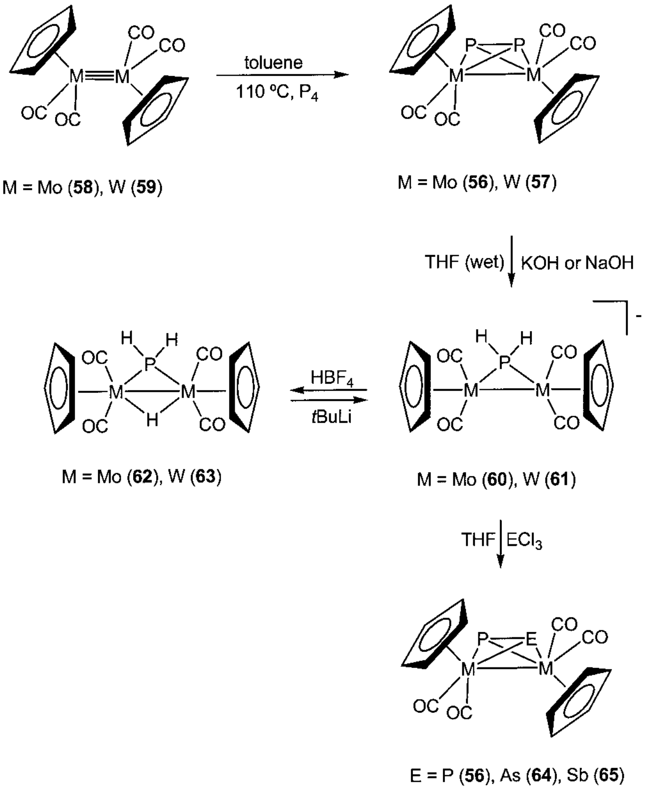
Scheme 17

the reaction mechanism that transforms **35** into PH_3 and **33** (vide supra).[79] Thus, in a series of dedicated in situ experiments, it was demonstrated that the phosphorus atom bearing the P−H functionality is the selected target of electrophilic reagents H^+ or Me^+. As a result, the cationic derivatives $[(triphos)Rh(\eta^1{:}\eta^2\text{-}H_2P_4)](BF_4)$ (**53**) and $[(triphos)Rh(\eta^1{:}\eta^2\text{-}H(Me)P_4)](OSO_2CF_3)$ (**54**), which were characterized by NMR spectroscopy, were synthesized. Notably, the signal of the phosphorus atom, that underwent the addition of the second substituent, experienced a significant downfield shift, moving − for example − from $\delta = -280.22$ in **35** to -172.83 in **54**. Conclusive evidence confirming the regioselectivity of the electrophilic attack on the RP_4 ligands was obtained by comparing the reaction of **35** with $MeOSO_2CF_3$ and the cross reaction in which one equivalent of HBF_4 or $HOSO_2CF_3$ was added to a solution of the methylated complex $[(triphos)Rh(\eta^1{:}\eta^2\text{-}MeP_4)]$ (**55**).[78,79] Irrespective of the starting $[(triphos)Rh(RP_4)]$ substrate and the electrophile used, the final products of the cross reactions exhibited identical NMR properties, and may therefore be assigned as the cationic $[(triphos)Rh(\eta^1{:}\eta^2\text{-}H(R)P_4)]Y$ (R = H, **53**; R = Me, **54**). Scheme 17 summarizes these reactions.

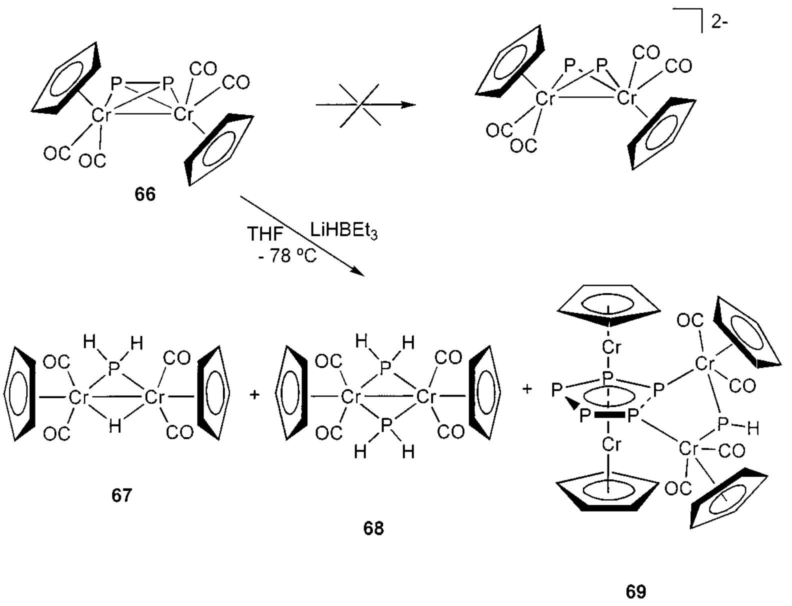
2.4 Nucleophilic Hydrogenation of P_x Units Incorporated into Transition Metal Complexes

The "nucleophilic hydrogenation"[89] of transition metal complexes incorporating P_x units is a synthetic methodology that can be successfully used to introduce a P−H functionality into the framework of a transition metal complex. This route to species containing P−H was first adopted by Mays and co-workers, who have recently undertaken a thorough investigation of the reactivity of transition metal complexes featuring a bridging diphosphorus ligand. As a provisional result of these ongoing studies, it has been demonstrated that transition metal species with bridging P_2 ligands have a high synthetic potential as precursors to very unusual and frequently otherwise inaccessible organophosphorus ligands.[90]

As a key contribution to this chemistry, the Cambridge team investigated the reactivity of the easily accessible M_2P_2 tetrahedranes $[\{CpM(CO)_2\}_2(\mu,\eta^2,\eta^2\text{-}P_2)]$ [M = Mo (**56**); W (**57**)], originally prepared by Scherer et al., by cothermolysis of white phosphorus and $[CpM(CO)_2]_2$ [M = Mo (**58**); W (**59**)] in refluxing toluene.[91] Thus, treatment of **56** (or **57**) with a large excess of NaOH or KOH in wet THF afforded the new anionic phosphido complexes $[\{CpM(CO)_2\}_2(\mu\text{-}PH_2)]^-$ [M = Mo (**60**); W (**61**)] as air-sensitive, purple solutions.[92] The two complexes were not isolated as solids, but after addition of a slight excess of $HBF_4{\cdot}OEt_2$, orange crystals of the new neutral derivatives



Scheme 18



Scheme 19

[{CpM(CO)$_2$}$_2$(μ-PH$_2$)(μ-H)] [M = Mo (**62**); W (**63**)] were obtained in fairly good yield (Scheme 18). As well as by straightforward spectroscopic and FABMS characterization, the molybdenum derivative **62** was authenticated by X-ray diffraction analysis, confirming the presence of an essentially planar MoHMoP core.

The formation of **62** was reversible and the purple color of **60** could be restored by adding one equivalent of *t*BuLi in THF. Solutions of **60** were extremely reactive towards halogenated compounds.[93] Quite remarkable is the reaction with ECl$_3$ (E = P, As, Sb), which immediately produced orange solutions from which the air-stable tetrahedranes [{CpMo(CO)$_2$}$_2$(μ,η^2,η^2-PE)] [E = P (**56**); As (**64**); Sb (**65**)] were obtained. Crystallographic analysis of **64** and **65** confirmed the presence of rare examples of hetero-μ,η^2:η^2-PAs and -μ,η^2:η^2-PSb ligands.

A relevant breakthrough in this chemistry has recently been provided by the German group led by Scheer, which has studied the reactivity of the chromium derivative [{CpCr(CO)$_2$}$_2$(μ,η^2:η^2-P$_2$)] (**66**) towards main-group hydrides.[94] The work of Scheer et al. was aimed at breaking the P−P bond of the Cr$_2$P$_2$ tetrahedrane to generate a dianionic moiety (Cr$_2$P$_2$$^{2-}$) suitable for use as building block for the formation of new metal-bridged oligomers (a P atom is isolobal with a CH group[7]) (Scheme 19). Surprisingly, the addition of two equivalents of "superhydride" to a THF solution of **66** did not afford the expected dianion,[95] but yielded a mixture of P−H compounds which were separated by column chromatography on silica gel.[96]

The major product was the dichromium complex [{CpCr(CO)$_2$}$_2$(μ-H)(μ-PH$_2$)] (**67**), which shares most of its spectroscopic and structural parameters with Mays' derivatives **62** and **63**. The chromium dimer [{CpCr(CO)$_2$}$_2$(μ-PH$_2$)$_2$] (**68**) and a singular tetrachromium derivative [{CpCr(CO)$_2$}$_2$(μ-PH)}{(CpCr)$_2$(μ,η^1:η^1:η^5:η^5-P$_5$)}] (**69**) were also formed as minor products. Complex **68** consists of two CpCr(CO)$_2$ units held together by two phosphido (μ-PH$_2$) bridges, while the paramagnetic complex **69** exhibits a unique triple-decker sandwich structure in which the middle *cyclo*-P$_5$ ligand additionally coordinates the chromium metal center of an external [{CpCr(CO)$_2$}$_2$(μ-PH)] moiety with two contiguous P atoms. The *cyclo*-P$_5$ ligand is unusually distorted in comparison to other triple-decker complexes with the *cyclo*-P$_5$ ligand,[97] and its bonding properties have been interpreted by supposing a partition of the P$_5$ ligand into a allylic P$_3$ and a P$_2$ subunit.[98]

3. Concluding Remarks

This review summarizes the chemistry of transition metal complexes containing P−H bonds, and specifically highlights the possibility of establishing one or more P−H bonds in a transition metal center by hydrogenation of white phosphorus or polyphosphorus ligands. In examining the wealth of knowledge so far collected about reactions involved in the metal-assisted formation of P−H bonds from P$_4$ or P$_x$ ligands, it has become evident that a first step has been made in the direction of metal-assisted P$_4$ hydrogenation, but it is also evident that there remain many unresolved questions requiring additional synthetic efforts in order to accomplish a second, more important and probably definitive, step in such a direction. Clearly, further studies aimed at unraveling the intimate mechanism of the stoichiometric hydrogenation reactions of white phosphorus described here would be highly desirable in view of the industrial relevance associated with the as yet unaccomplished hydrogenation of the P$_4$ molecule.

The first industrial production of synthetic ammonia from nitrogen and hydrogen was begun at BASF in Ludwigshafen, Germany, in 1913, using a revolutionary catalytic process combining N$_2$ and H$_2$ at high pressure. At present, we do not yet know when the catalytic production of PH_3 from white phosphorus and hydrogen will be written about in future chemical textbooks, but certainly we now know that transition metal complexes can bring about such intriguing processes.

Acknowledgments

This work was supported by the EU through the inco Copernicus project ERB IC15CT960746 and COSTD17 Action. The authors wish to express their gratitude to their colleagues, H. Butenschön (Hannover, Germany), L. Y. Goh (Singapore), H. Grützmacher (ETH, Zürich, Switzerland), O. J. Scherer (Kaiserslautern, Germany), R. R. Schrock (MIT, MA, USA), D. W. Stephan (Windsor, Canada) and P. Stoppioni (Florence, Italy) for preprints of unpublished results or for answering specific questions about their researches in this area. The authors are indebted to colleagues H. M. Lee (Hong Kong) and M. Ehses (INM, Saarbrücken, Germany) for reading the manuscript and for the helpful suggestions and P. Barbaro (Florence, Italy) for running ^{2}D-NMR spectra. I. R. thanks the Spanish "Ministerio de Educacion y Cultura" for the postdoctoral fellowship granted.

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Received June 16, 2000
[I00237]