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P_4 Coordination

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Intact P_4 Tetrahedra as Terminal and Bridging Ligands in Neutral Complexes of Manganese[**]

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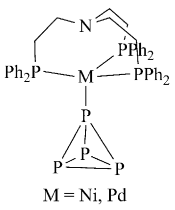
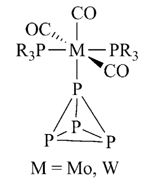
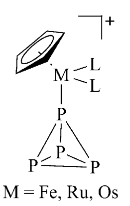
The direct use of white phosphorus to generate organophosphorus compounds is still an unsolved problem,[1] although recently some progress has been achieved by the photolysis of P_4 with neat dienes.[2] A transition-metal mediated conversion is one option for this goal,[3] a mode of activation that first requires coordination of a vertex or an edge of the P_4 tetrahedron at the metal. Looking into the existing compounds that feature end-on P_4 coordination, there are complexes of type **A**, which were synthesized by the Sacconi group.[4] However, these compounds are insoluble in all common solvents, and the other known neutral complexes of type **B** decompose in solution at temperatures above 0 °C.[5]



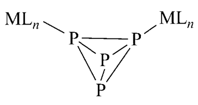
A



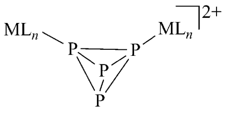
B



C



E



D

So, complexes such as **A** and **B**, do not represent useful starting materials for a subsequent P_4 activation. As Peruzzini et al. have shown, the use of cationic coordination compounds leads to the end-on coordinated P_4 complexes **C**, which are stable in the solid state and in solution.[6,7] An interesting and recently discovered feature is the dynamic process, experienced by a number of P_4 complexes,[6h,i] consisting of tumbling of the P_4 cage while it remains chemically coordinated to the central metal moiety. In addition the P_4 ligand in mononuclear cationic complexes can bind a second metal fragment to give the binuclear dicationic species **D**. If P_4 bridges two Re, or Ru and Pt atoms, dynamic behavior involving the coordinated P_4 has also been detected.[6h,i] In view of the activation of P_4, the second coordination seems to be decisive, since the hydrolysis of type **C** complexes leads to the usual P_4 hydrolysis products. In contrast, the double binding of P_4 in **D** leads by hydrolysis to novel triphosphines and thus to a change of the properties of P_4.[6d] Therefore, the question arises whether neutral complexes with a tetrahedral P_4 ligand can be synthesized, which are stable at room temperature both in the solid state and in solution, and if the missing neutral type **E** complex with a bridging P_4 unit can be isolated?

Both challenges motivated us to use manganese complexes such as $[Cp^RMn(CO)_2(thf)]$ (Cp^R = substituted η-C_5H_5). Interestingly, no unsubstituted E_n (E = Group 15 element) ligand complexes of manganese have been yet synthesized, which provides additional motivation for investigating this chemistry.[8,3] Intensive efforts to use common Cp and Cp* ($Cp^* = \eta$-C_5Me_5) derivatives of cymantrene ($[Cp^RMn(CO)_3]$) failed to coordinate P_4 or even to convert it under thermal or photolytic conditions. So, the design of a novel derivative with a high Lewis acidity was needed.

Herein we report on the synthesis and characterization of $[Cp^{BIG}Mn(CO)_3]$ (**1a**) (Cp^{BIG} = pentakis(4-*n*-butylphenyl)cyclopentadienyl) and its conversion into neutral manganese complexes with a tetrahedral P_4 ligand coordinating in a terminal and in a bridging fashion, and thus to result in the first example of a neutral type **E** complex.

The bulky substituted cymantrene complex **1a** is prepared by the reaction of $[Mn(CO)_5Br]$ with one equivalent $Cp^{BIG}Na$ under high-temperature conditions in THF.[9] Irradiation of a solution of **1a** in THF leads to the elimination of one carbonyl and the formation of $[Cp^{BIG}Mn(CO)_2thf]$ (**1b**). Addition of a solution of **1b** to a solution of five equivalents white phosphorus yields in a quantitative conversion to $[Cp^{BIG}Mn(CO)_2(\eta^1$-$P_4)]$ (**2**) (monitored by ^{31}P NMR spectroscopy; Scheme 1a). Only by using this stoichiometry the isolation of pure **2** is possible (33 % yield). In contrast to the reported neutral η^1-P_4 complexes, **2** is stable not only in the

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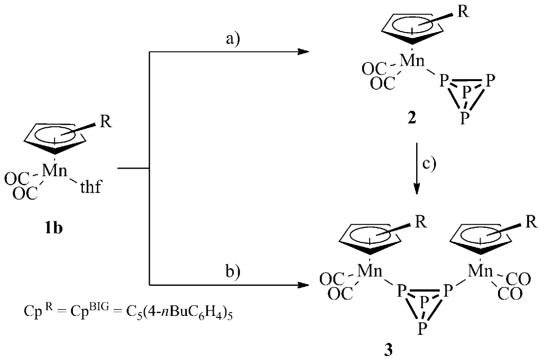

Scheme 1. Synthesis of neutral tetrahedro-P_4 complexes **2** and **3** at room temperature in THF. a) 5 equiv P_4, b) 0.5 equiv P_4, c) 1 equiv **1b**.

solid state but also in solution, even in coordinating solvents such as THF at room temperature. Owing to the *n*-butyl groups of the Cp^{BIG} ligand, it has good solubility in all common organic solvents except acetonitrile.

The molecular structure of **2** (Figure 1) reveals the intact P_4 tetrahedron. The bonds between the apical and the basal P atoms (2.145(2)–2.165(2) Å) are about 7 pm shorter than the basal bonds (2.211(4)–2.232(2) Å). This behavior was also observed for most of the P_4 units in the cationic complexes of Group 8 elements[6a–f] and in the neutral tungsten complex of type **B**.[5] The $^{31}P\{^1H\}$ NMR spectrum of **2** in $[D_8]$toluene at 253 K shows a quartet at $\delta = -305.7$ ppm and a doublet at $\delta = -490.0$ ppm with a $^1J_{PP}$ coupling constant of 224 Hz. At ambient temperature the signals broadened and the quartet splitting was no longer identifiable. The $^{13}C\{^1H\}$ attached proton test (APT) spectrum of **2** in $[D_8]$toluene at 298 K shows a broad signal of the carbonyl groups at $\delta = 226.9$ ppm, three signals in a ratio of 2:1:2 for the cyclopentadienyl carbon atoms ($\delta = 104.6$, 103.2, and 102.8 ppm) and several signals for each of the *n*-butylphenyl carbon atoms,[10] indicating the inequivalency of the five substituents of the ligand. Features of the ^{13}C NMR spectrum (and of ^1H NMR spectrum, see below) suggest that the cyclopentadiene core does not freely rotate about the Cp–Mn axis, but each *n*-butylphenyl group freely rotates about the C_{ipso}–C_{Cp} bond. Based on the remarkable stability of **2** in solution, the question arises whether coordination of a second phosphorus atom is possible. Initial evidence of the existence of the neutral binuclear complex $[\{Cp^{BIG}Mn(CO)_2\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}P_4)]$ (**3**) appears if **1b** is treated with an equimolar amount of white phosphorus at ambient temperatures (Scheme 1), which leads to a mixture of both complexes **2** and **3** with **3** as the main component. The high stability of the products is also indicated by their successful chromatographic separation. Increasing the amount of P_4 shifts the ratio towards **2**, but the formation of the binuclear compound **3** is not totally suppressed until a fivefold excess of phosphorus is used. However, the reaction of **2** with a second equivalent of **1b** leads to the formation of the bridging P_4 complex **3** in 44 % isolated yield (Scheme 1 c; Figure 2).

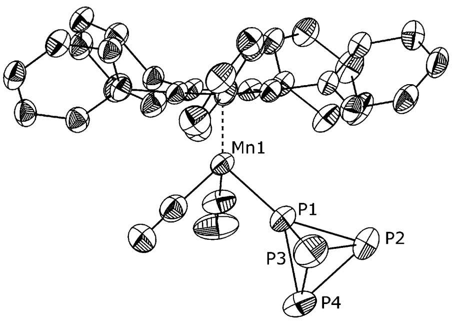

Figure 1. Molecular structure of the neutral complex **2**. H atoms, butyl groups, and solvent molecules are omitted for clarity; thermal ellipsoids set at 50% probability.[15]

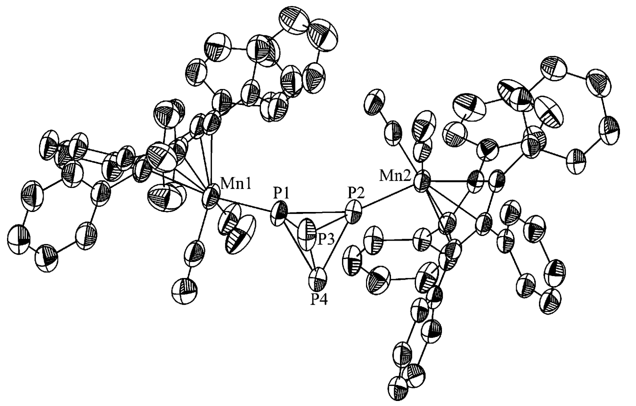

Figure 2. Molecular structure of the neutral complex **3**. H atoms and butyl groups are omitted for clarity; thermal ellipsoids set at 50% probability.[15]

In comparison to the mononuclear complex **2** the formation of the binuclear complex **3** seems to be preferred. Caused by the 'encapsulation' of the reactive sites in **3** by the two Cp^{BIG} ligands a nucleophilic attack of a second P_4 tetrahedron at a manganese complex seems to be hindered.

In addition to the strong coordinative bonds of the P_4 ligand this moiety is encased by the two Cp^{BIG} ligands which enhance the stability of **3**. The Cp^{BIG} ligands are tilted against each other by an angle of 28.6(2)°.

In the molecular structure of **3** the P–P bond lengths show the same tendency as the cationic relatives.[6d–f] The shortest P–P bond is located between the coordinating P atoms (2.149(1) Å), the longest between the non-coordinating ones (2.247(3) Å). The other P–P distances lie between 2.187(2) and 2.200(2) Å). The Mn–P distances in **3** and **2** are identical within the experimental error, so it can be assumed that the coordination of the second P_4 tetrahedron is as strong as the first one.

The $^{31}P\{^1H\}$ NMR spectrum of **3** in $[D_8]$toluene at room temperature shows two broad signals with an integral ratio of 1:1. Upon cooling to 193 K the downfield signal at $\delta = -250.2$ ppm sharpens into a triplet with a $^1J_{PP}$ coupling constant of 159 Hz. Though the signal at $\delta = -478.7$ ppm also gets sharper, it remains a broad triplet. The ^1H NMR spectrum of **3** in C_6D_6 at 298 K shows several signals for each of the *n*-butylphenyl proton. Such a complex pattern seems to indicate that in this case only a limited number of the infinite possible rotamers are present. In fact, beside the conformers arising from hindered rotation about the Mn–Cp axis, the rotamers arising from hindered rotation about the Mn−P bond can be present in solution. In accordance with this view, the $^{13}C\{^1H\}$ APT spectrum of **2** in C_6D_6 at 298 K shows several signals not only for the cyclopentadienyl carbon atoms, but also for the carbonyl carbon atoms.

To ascertain whether the P_4 ligand coordinated to Mn in **2** or **3** is subjected to a dynamic process like those observed for other P_4 complexes,[6h,i] the $^{31}P\{^1H\}$ EXSY and $^{31}P\{^1H\}$ NMR spectra were recorded in [D$_8$]toluene at various temperatures. The $^{31}P\{^1H\}$ EXSY spectrum of **2** at 298 K (Figure 3) shows intense cross peaks between the signals of the basal and coordinated P atoms, indicating that at this temperature the P_4 experiences the tumbling motion discussed above. At 183 K the same experiment did not show any exchange correlation, revealing that at this temperature the P_4 tumbling is slow on the NMR timescale. The $^{31}P\{^1H\}$ EXSY experiment carried out in the presence of free P_4 did not show any exchange peak between free and coordinated P_4, revealing that the mechanism responsible for P_4 motion is not dissociative.

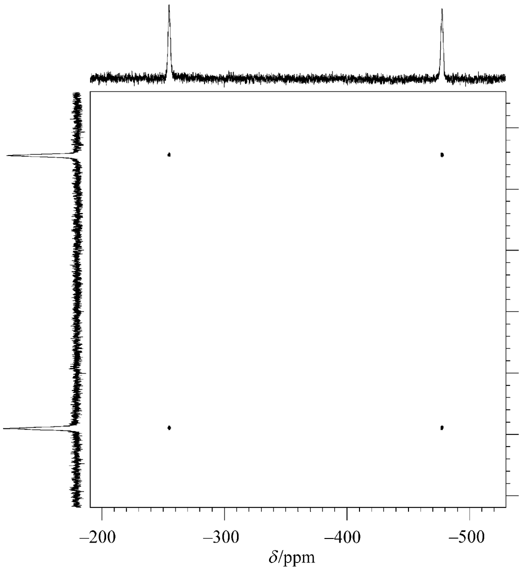

Figure 3. $^{31}P\{^1H\}$ EXSY spectrum of **2** ([D$_8$]toluene, 298 K).

An interesting feature observed recording variable temperature (VT) $^{31}P\{^1H\}$ NMR spectra is that the signals are quite broad at 183 K, then they become sharper at 213 K, and then they progressively broaden again in the range between 233 and 313 K.[10] The broadening in the range between 233 and 313 K has been explained in terms of P_4 tumbling. A likely explanation for the broadening below 213 K can be a hindered rotation of the P_4 cage about the P–M axis. Activation parameters for the P_4 tumbling were calculated by line-shape analysis in the range between 233 and 313 K. The values[10] are similar to those found for *trans*-[Ru(dppm)$_2$(H)(η^1-P$_4$)]BF$_4$ and *trans*-[Ru(dppe)$_2$(H)(η^1-P$_4$)]BF$_4$, and somehow different from those found for [CpRu(PPh$_3$)$_2$(η^1-P$_4$)]PF$_6$, [CpOs(PPh$_3$)$_2$(η^1-P$_4$)]PF$_6$, [Cp*Ru(dppe)(η^1-P$_4$)]PF$_6$, and [(triphos)Re(CO)$_2$(η^1-P$_4$)]OTf (dppe = 1,2-bis(diphenylphosphino)ethane, dppm = bis(diphenylphosphino)methane, OTf = trifluormethane sulfonate, triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane).[6h,i]

Once the motions of the P_4 cage bonded to Mn were elucidated, we tried to gain insights into the possible dynamic behavior of the Cp^{BIG} ligands. The ^{1}H NMR signals of **2**, which are broad already at 298 K, become even broader on lowering the temperature and, more interestingly, appear as the convolution of several quasi-isochronous signals. This evidence confirms that, in contrast to unsubstituted cyclopentadienyl ligands,[11] Cp^{BIG} does not freely rotate about the centroid of the Cp^{BIG}–Mn axis even at room temperature, and the ^{1}H NMR spectrum is the result of the superimposition of all the possible rotamers. Intrigued by this circumstance (i.e. the slow rotation, if any, of Cp^{BIG} at low temperature), we embarked on a heteronuclear Overhauser enhancement study recording ^{31}P-^{1}H HOESY spectra in [D$_8$]toluene at various temperature. The detection of dipolar ^{31}P-^{1}H correlations[12] is a quite demanding job, compared to the more common ^{1}H-^{1}H case, owing to the unfavorable γ_P/γ_H ratio.[13]

Despite these difficulties, the ^{31}P-^{1}H HOESY spectrum of **2** at 273 K in [D$_8$]toluene showed a heteronuclear NOE contact between the basal P atoms of the P_4 cage and the *ortho* H atoms of the Cp^{BIG} phenyl groups (Figure 4).[14] This result confirm that Cp^{BIG} is hindered in rotation while P_4 is rotating quickly and tumbling slowly ($k = 80\ s^{-1}$). Moreover, these data indicate that the P_4 ligand does not exchange its position with that of the carbonyl ligands. The ^{31}P-^{1}H heteronuclear NOE contact was still observable at 283 K

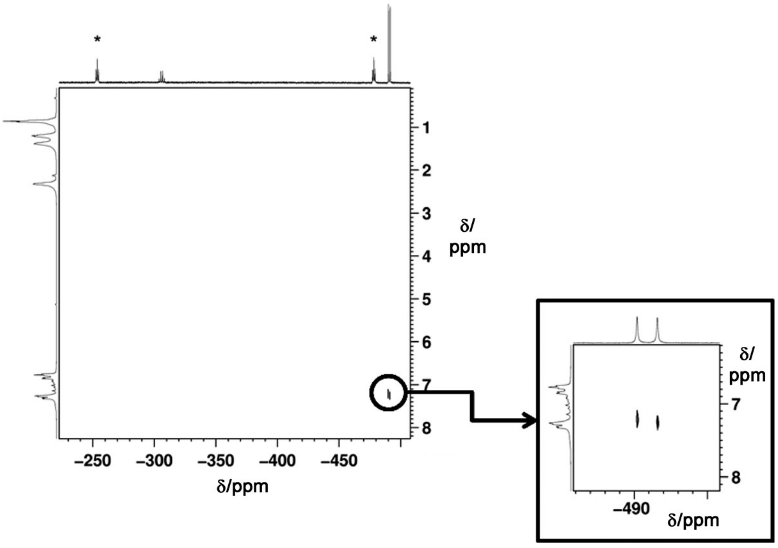

Figure 4. ^{31}P-^{1}H HOESY spectrum of **2** (in mixture with **3**) in [D$_8$]toluene at 273 K showing the correlation between the basal P atoms of the P_4 cage and the *ortho* protons of Cp^{BIG}. Signals marked with asterisks arise from **3**.

and vanished when the same experiment was carried out at 293 K.

As far as the dinuclear complex **3** is concerned, the $^{31}P\{^1H\}$ EXSY spectrum at 298 K[10] showed intense cross peaks between the signals of the coordinated and uncoordinated P atoms, indicating that at this temperature the cymantrene fragment moves around the P_4 cage. The VT $^{31}P\{^1H\}$ NMR spectra showed the same trend observed for **2**, which means that the signals are quite broad at 183 K, become sharper until 253 K, and then progressively broaden again in the range 263–293 K,[10] suggesting that the same sequence of dynamic processes discussed for **2** occur, albeit at different temperatures.[10]

To get a better understanding on the surprising stability of complex **2**, DFT computations were carried out.[10] Thermodynamic characteristics for the gas-phase complex formation for the three η^1-P_4 compounds $\mathbf{B_w}$ (tungsten complex of **B** with R = Cy), $[CpMn(CO)_2(\eta^1\text{-}P_4)]$ (**4**), and **2** were obtained (Table 1, Reactions 1–3). Complex formation enthalpy is only slightly exothermic in case of $\mathbf{B_w}$ (by $-12\ kJ\,mol^{-1}$), but much more exothermic in case of **2** (by $-69\ kJ\,mol^{-1}$) and **4** (by $-93\ kJ\,mol^{-1}$), suggesting stronger Mn–P_4 bonding for **2** and **4**. The entropy disfavors the formation of all three complexes in the gas phase. Complexes **2** and **4** are predicted to be stable with respect to dissociation in solution, while for complex $\mathbf{B_w}$ equilibrium dissociation is expected at room temperature. The processes for the generation of **1b** by CO elimination and thf complex formation (Reactions 4, 5) are highly endothermic (by about $133\ kJ\,mol^{-1}$) and should proceed in non-equilibrium conditions (CO removal). Subsequent substitution of thf by P_4 (Reactions 6, 7) is almost thermoneutral and slightly favorable by entropy, making them exergonic by $3\text{–}4\ kJ\,mol^{-1}$. Note that both CO removal and thf substitution reactions do not depend on the bulkiness of the Cp^R ring (Cp vs Cp^{BIG}).

In summary, we have shown that the variation of the Cp^R substituents in the cymantrene complexes only leads to a high Lewis acidity towards the coordination of P_4 in the case of $[Cp^{BIG}Mn(CO)_2(thf)]$ (**1b**). The two neutral P_4 complexes formed, **2** and **3**, are remarkably stable in the solid state and especially in solution, a feature not observed before for neutral P_4 complexes. Moreover, **3** is the first neutral complex with a P_4 unit in a bridging $\eta^1{:}\eta^1$-coordination mode. The DFT calculations confirm the observed higher stability of the complexes in comparison to complexes of type **B**. Both **2** and **3** show fluxional behavior in solution at room temperature arising from the tumbling of the coordinated P_4. Moreover, at temperatures lower than 283 K the rotation of the Cp^{BIG} about the Mn–Cp axis is hindered and no position exchange between CO and P_4 occurs, as inferred by ^{31}P-^1H HOESY experiments. The introduction of the electronically and sterically special Cp^{BIG} ligand in main-group and transition-metal chemistry opens up possibilities for the stabilization of unprecedented compounds.

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Table 1: Predicted thermodynamic characteristics for the studied gaseous processes at the B3LYP/6-31G* (ECP on W) level of theory. Standard enthalpies $\Delta H°_{298}$ and Gibbs energies $\Delta G°_{298}$ are in $kJ\,mol^{-1}$, standard entropies $\Delta S°_{298}$ in $J\,mol^{-1}\,K^{-1}$.

Entry	Reaction	$\Delta H°_{298}$	$\Delta S°_{298}$	$\Delta G°_{298}$
1	$[W(CO)_3(PCy_3)_2] + P_4 \rightarrow \mathbf{B_w}$	−11.7	−184.2	43.2
2	$[CpMn(CO)_2] + P_4 \rightarrow \mathbf{4}$	−92.5	−140.9	−50.5
3	$[Cp^{BIG}Mn(CO)_2] + P_4 \rightarrow \mathbf{2}$	−69.1	−181.3	−15.0
4	$[CpMn(CO)_3] + thf \rightarrow [CpMn(CO)_2thf] + CO$	133.2	−11.0	136.5
5	$[Cp^{BIG}Mn(CO)_3] + thf \rightarrow \mathbf{1b} + CO$	132.5	2.5	131.8
6	$[CpMn(CO)_2thf] + P_4 \rightarrow \mathbf{4} + thf$	3.0	21.8	−3.5
7	$[Cp^{BIG}Mn(CO)_2thf] + P_4 \rightarrow \mathbf{2} + thf$	2.1	16.1	−2.7

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[13] At a constant internuclear distance in H–X pairs, the heteronuclear dipolar coupling decreases proportionally to coefficient k, calculated by the Equation $k = 0.44(\nu_X/\nu_H)^2 I_X(I_X+1)$ where ν_X and ν_H are the NMR frequencies of X and H nuclei, respectively, and I_X is the spin of X nuclei: V. I. Bakhmutov, *Practical NMR relaxation for chemists*, Wiley, Chichester, **2004**.

[14] On the basis of the interatomic distances observed in the solid state, a correlation between the apical P atom of the cage and the *ortho* H atoms of the Cp^{BIG} phenyl groups should be also expected to be seen in the ^{31}P-^{1}H HOESY spectrum of a [D$_8$]toluene solution of **2** at 273 K. However, the corresponding cross peak is missing, most likely because of to the lower intensity of the signal of the apical P atom.

[15] CCDC 943753 (**2**) and 943754 (**3**) contain the detailed crystallographic information for this manuscript. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..