Hot Paper

Reversible Binding of Hydrogen and Styrene Coordination on a Manganese Phosphenium Complex

Marius Papendick[a] and Dietrich Gudat*[a]

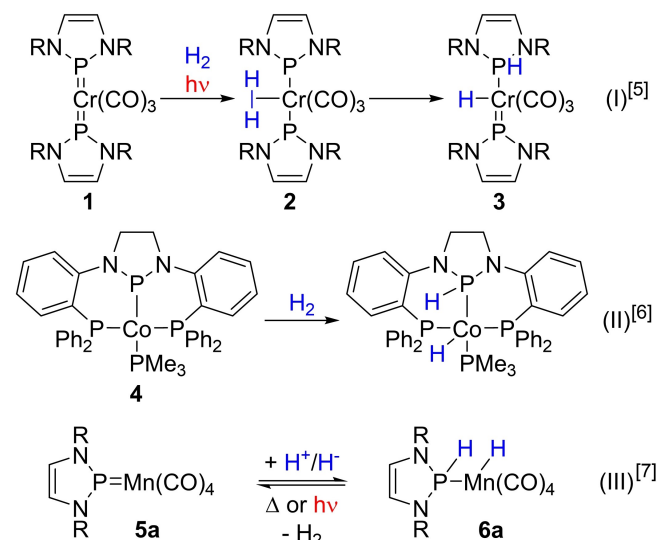*In memory of Edgar Niecke, one of the pioneers of the renaissance of p-block chemistry.*

The reactions of two complexes [(^{R}NHP)Mn(CO)$_4$] (^{R}NHP = N-arylated N-heterocyclic phosphenium) with H$_2$ at elevated pressure (≈ 4 bar) were studied by NMR spectroscopy. Irradiation with UV light initialized in one case (**5a**, R = Dipp) the unselective formation of (^{R}NHP-H)MnH(CO)$_4$) (**6a**) via cooperative addition of H$_2$ across the Mn=P double bond. In the other case (**5b**, R = Mes), addition of H$_2$ was unobservable and the reaction proceeded via decarbonylation to a dimeric species [(^{R}NHP)$_2$Mn$_2$(CO)$_7$] (**7b**) that was isolated and identified spectroscopically. Taking into account the outcome of further reaction studies under various conditions in the absence and presence of H$_2$, both transformations can be explained in the context of a common mechanism involving decarbonylation to **7a,b** as the first step, and the different outcome is attributable to the fact that **7b** is unreactive towards both H$_2$ and CO while **7a** is not. DFT studies relate this divergence to deviations in the molecular constitution and stability arising from a different level of steric congestion. Preliminary studies suggest further that **5a**/H$_2$ as well as **6a** enable the photo-induced hydrogenation of styrene to ethyl benzene, even if the mechanism and possibly catalytic nature of this process remain yet unknown.

Introduction

Catalytic (de)hydrogenation of organic compounds is of crucial importance in academia and industrial chemistry. Potent catalysts are often based on noble platinum group metals, but first-row transition metal complexes[1] or metal-free catalysts based on frustrated Lewis pairs (FLPs)[2] have emerged in recent years as viable alternatives. The mode of action of these systems does not depend on a single active atomic site as in the noble metal complexes, but on cooperative reactivity of the metal and the ligand sphere in first-row transition metal complexes, or a Lewis acid and a Lewis base in FLPs, respectively.[1][2] While the joint participation of metal centers and ligand environment in reactions seems to be familiar in biological catalysis,[3] applying metal-ligand cooperativity (MLC) to promote organic reactions requiring two-electron oxidative addition or reductive elimination steps on synthetic complexes of first-row transition metals, which often prefer one-electron redox steps, is still a new development.[4]

We have recently discovered that a chromium carbonyl complex **1** bearing two N-heterocyclic phosphenium (NHP) ligands is capable of activating dihydrogen (H$_2$) and transferring it to styrene, thus enabling the catalytic hydrogenation of an alkene (Scheme 1, I).[5] Key to this reaction is the photochemical generation of a H$_2$-complex **2**, which relies crucially on the interplay between the metal and the NHP ligands to generate a vacant coordination site in its electronically saturated (18 VE) precursor **1**. Even if the NHP units are not yet directly involved in the binding of H$_2$ at this stage, they act as electron reservoirs[4] that facilitate two-electron reactivity and thus give

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Scheme 1. Reported examples of reactions involving binding a dihydrogen unit on N-heterocyclic phosphenium (NHP) complexes (R = 2,6-iPr$_2$C$_6$H$_2$, Dipp).

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noble character to the non-noble transition metal. Moreover, slow isomerization of **2** to **3** at 40 °C under 8 bar of H$_2$ reveals that the step to heterolytic activation of H$_2$ under fission of the H—H bond and transfer of a hydrogen atom to a NHP ligand is likewise feasible.

The reaction leading to **3** is closely related to the reported[6] 1,2-addition of H$_2$ across the covalent P–Co bond of pincer complex **4** (Scheme 1, II). It was claimed that this transformation proceeds likewise via an intermediate H$_2$-complex, but the fact that the hydrogen molecule absorbed could neither be released (which is feasible in case of **3**) nor transferred to other molecules precluded the application of **4** in hydrogenation catalysis until today. Even so, the reaction is significant in proving that even a single R$_2$P-ligand is sufficient for the activation of H$_2$.

Looking for further phosphenium complexes that might play a role in H$_2$-activation, we focused our attention on manganese complex **5a**.[7] The attachment of two hydrogen atoms under formal 1,2-addition to the Mn≡P double bond is easily achieved via stepwise transfer of a H$^-$/H$^+$ ion pair, and may be reversed by thermolysis or photolysis of the resulting complex **6a** (Scheme 1, III). The course of the dehydrogenation under cooperative elimination of H$_2$ suggests that direct activation of dihydrogen by **5a** (which was unfeasible under ambient conditions) might be possible under more forcing conditions. To verify this hypothesis, we set out to study the behavior of **5a** and its homologue **5b**[8] towards H$_2$ in more detail. The experimental and computational results of this survey and a very preliminary account on the reaction of **5a**/H$_2$ with styrene reported here reveal that the reactions of the NHP complexes display both parallels and differences to the known[9] activation of H$_2$ on dinuclear manganese phosphido complexes.

Results and Discussion

Activation of dihydrogen

Hoping to overcome the reported passiveness of **5a** towards dihydrogen under ambient conditions (room temperature, 1 bar H$_2$),[7] we studied the hydrogenation of this species and its sterically less congested homologue **5b** under increased pressure. High pressure NMR tubes containing solutions of both complexes in C$_6$D$_6$ were pressurized with 4 bar H$_2$, and the progress of the reaction monitored over time by ^{1}H and ^{31}P NMR spectroscopy. Even if the presence of molecular H$_2$ in the solution was clearly proven, the spectra revealed that the desired reaction occurred neither at ambient temperature nor upon heating to 60 °C, and that even after prolonged time exclusively the unchanged starting materials were detectable. However, as in the case of chromium complex **1**,[5] hydrogenation of **5a** could be initiated by irradiation with a xenon arc lamp. NMR spectra recorded after one hour of irradiation confirmed that the starting material had almost quantitatively transformed to a product mixture containing the known metal hydride **6a**[7] as major component (Scheme 2). Even if the reaction was unselective, **6a** was unmistakably identified by its
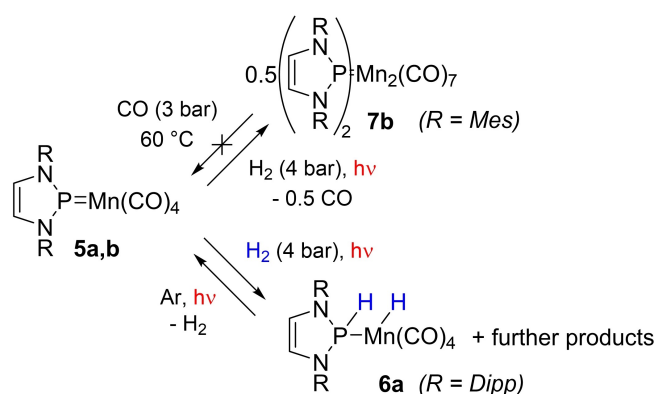
Scheme 2. Reactions of NHP complexes **5a,b** in the presence of H$_2$ (4 bar) under irradiation with a Xe arc lamp. The dehydrogenation of **6a** to **5a** is reported in Ref. [7]. Back conversion of **7b** into **5b** with CO was unobservable (R = Dipp (**5a**, **6a**), Mes (**5b**, **7b**)).

unique spectroscopic data (Figure 1), while the remaining species were neither known nor identifiable. The cooperative dehydrogenation of **6a** having already been demonstrated,[7] this finding proves that the addition of H$_2$ across the Mn≡P double bond is in principle reversible under photochemical conditions, albeit unselective, and that adjusting the partial pressure of H$_2$ allows one to control whether hydrogenation (4 bar H$_2$) or dehydrogenation (H$_2$-free atmosphere) is favored.

A photochemical reaction was also observable for **5b**. NMR spectra of reaction mixtures recorded after several hours of photolysis revealed extensive (>90%) transformation to a single phosphorus-containing species. However, the deshielded ^{31}P NMR signal of the product (δ^{31}P 274 ppm), which indicated the presence of a phosphenium rather than a secondary phosphine complex,[7][8] and the lack of any evidence for the incorporation of a molecule of H$_2$ in the ^{1}H NMR spectra
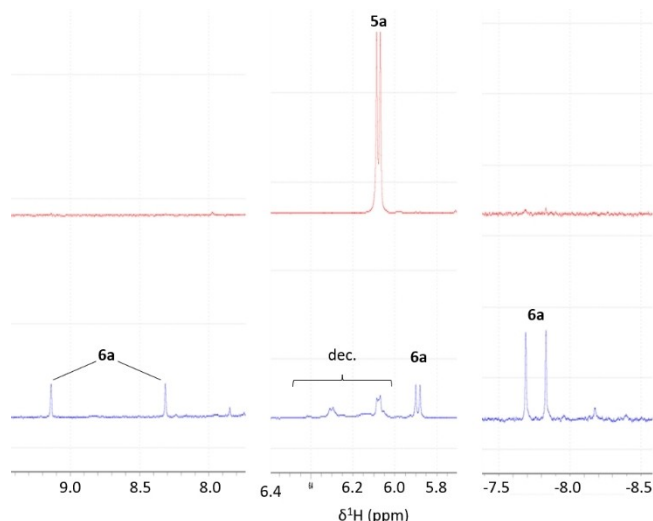

Figure 1. Expansions of the ^{1}H NMR spectrum (400.1 MHz) of a solution of **5a** in C$_6$D$_6$ under H$_2$ atmosphere (4 bar) showing the regions containing signals attributable to P-bound (left), olefinic (middle) and Mn-bound (right) hydrogens before (red trace) and after (blue trace) irradiation with a Xe arc lamp for 60 min. Signals attributable to **5a**, **6a** and unidentified products are labelled. Note that the expansions are drawn using different vertical scales.

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suggested that the reaction had taken a different course as in case of **5a**. The inferred hypothesis that H_2 is not involved at all was corroborated by the discovery that the product is just as well accessible through photolysis of **5b** under argon atmosphere and could be isolated in crude form after adaptation of the reaction conditions (see Experimental Section). Characterization by spectroscopic (IR, NMR) techniques and mass spectrometry allowed us to identify the unknown species as dinuclear complex **7b** (Scheme 2) representing a homologue of **7a** whose preparation from **5a** under similar conditions had already been reported.[7] We want to note that the available NMR data of **7a,b** reveal a remarkable similarity, and that the IR spectra confirm as in the case of **7a** the absence of bridging CO ligands.

The formation of **7b**, like that of **7a**,[7] is readily explained by photo-induced decarbonylation of the original phosphenium complex and successive interception of the resulting product by a second molecule of the starting material (step (i), Scheme 3). However, while conversion between **5a** and **7a**/CO is reversible and the phosphenium complex is slowly restored by recombination of the photolysis products,[7] **7b** proved to be inert toward CO up to 60 °C and CO pressures of 3 bar (Scheme 2). This behavior implies that formation of **7b** is either thermodynamically favored, or its recombination with CO is kinetically inhibited.

The formation of **7b** during photolysis of **5b** under H_2 drew our attention to the possibility that **7a** might also be an intermediate in the corresponding reaction of **5a**. To verify this conjecture, we prepared mixtures of **5a/7a** in high pressure NMR tubes as described by photolyzing solutions of **5a** in C_6D_6 under H_2-free atmosphere,[7] and then pressurized the samples with H_2 (4 bar). An NMR spectroscopic assay disclosed that the composition of these solutions was invariant over several days at room temperature. However, slow conversion of **7a** to **5a** and **6a** could indeed be detected upon prolonged heating to 50 °C, and complete disappearance of **7a** as well as further transformation of **5a** to **6a** was observable upon photolysis (Figure 2). Monitoring the changes in the ^1H NMR spectra revealed that the thermal reaction yields different proportions
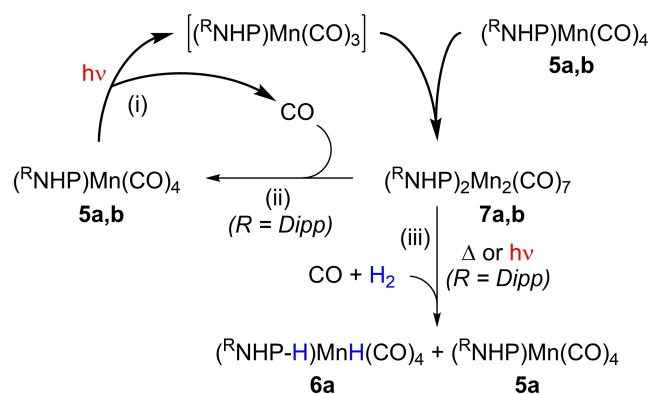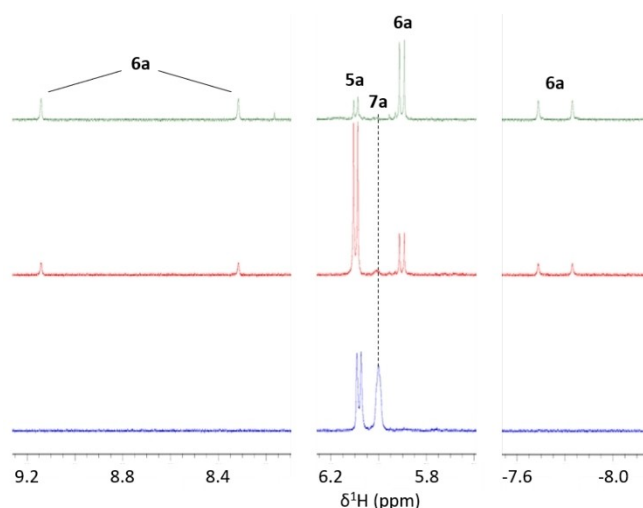
Figure 2. Expansions of the ^1H NMR spectrum (400.1 MHz) of a solution prepared by photolysis of **5a** in C_6D_6 in the absence of H_2 (blue trace), after admission of H_2 (4 bar) and heating for 60 h (red trace) or irradiation with a Xe arc lamp for 1 h (green trace), showing the regions containing the signals of P-bound (left), olefinic (middle) and Mn-bound (right) hydrogens, respectively. The signals attributable to **5a–7a** are labelled.

of **5a** and **6a**, **5a** being the major product and its fraction increasing as the reaction proceeds. Moreover, the eventual decay of the signals of all complexes upon irradiation indicates that the photochemical reaction observed is accompanied by unspecific decomposition.

Additional experiments disclosed that the outcome of the thermal reaction depends delicately on the amount of CO available. Monitoring the evolution of a photochemically generated mixture of **5a/7a**[7] under a mixed atmosphere of H_2 (4 bar) and excess CO (2 bar) at 50 °C revealed that both the overall reaction rate and the proportion of **5a** grew when the partial pressure of CO was increased (86% conversion of **7a** to a 1.5:1 mixture of **5a/6a** after 15 h vs. 38% conversion and product ratio 1.3:1 under autogenous CO pressure; see Figure S9). In contrast, formation of **6a** was completely suppressed when the CO produced during the generation of **7a** was removed (by repeated freeze-pump-thaw cycles) prior to the addition of H_2.

The outcome of all experiments on the thermal conversion of **7a** in the presence of both CO and H_2 can be consistently explained if we assume that two parallel reactions take place, viz. the known interaction of **7a** with CO[7] to give two equivalents of **5a** (step (ii), Scheme 3), and a reaction of **7a** with CO and H_2 to produce a mixture of **5a** and **6a** (step (iii), Scheme 3).

Combining all evidence on the reactivity of **7a,b** towards CO and H_2 gathered so far allows us to rationalize the different outcome of the photolysis of NHP complexes **5a,b** in the presence of H_2 in the context of a common mechanism (Scheme 3). We posit that both transformations are initialized by photolysis of the starting materials to give transient decarbonylated products, which are then preferably quenched by a second molecule of **5a,b** to yield **7a,b** as key intermediates (step (i)). While **7b** does not undergo any further changes, **7a**

Scheme 3. Reaction network accounting for the formation of **7a** by photolysis of **5a** (step (i)[7]) and its reactions with CO (step (ii)) and CO and H_2 (step (iii)), respectively (R = Dipp). Bold arrows denote reactions feasible for both **5a,b**.

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may undergo successive parallel reactions with the previously released CO or with both H_2 and CO to yield **5a** (step (ii)) or **5a** and **6a** (step (iii)), respectively. Any **5a** thus restored can enter another cycle, allowing the process to proceed until all starting material is consumed. Steps (ii) and (iii) can proceed as thermal reactions at elevated temperature, but the accelerated formation of **6a** upon irradiation indicates that photochemical initialization of step (iii) may likewise be feasible. Step (iii) further bears some similarity to the reported thermal activation of H_2 by dinuclear manganese phosphido complexes (Scheme 4),[10] but differs in producing a mononuclear (**6a**) rather than a dinuclear complex as hydrogenation product.

Computational studies on the reactivity of NHP complexes towards H_2 and CO

To gain a deeper understanding of the impact of the divergent reactivity of the dinuclear complexes **7a,b** with CO and H_2 on the outcome of the co-photolysis of **5a,b** and H_2, we computationally modeled presumed reaction steps based on RI-DFT calculations on isolated molecules (gas phase conditions) performed at the RI-ωB97x-D/def2-TZVP//RI-ωB97x-D/def2-SVP level. Calculations were carried out with the program suite TURBOMOLE.[11]

Energy optimization of the molecular geometries of the presumed products **5a,b** and **6a,b** (see Scheme 3) was uncomplicated and yielded conformations that match well with existing computational and experimental data.[7][8] The case of **7a,b** turned out to be more complex as we located in each case
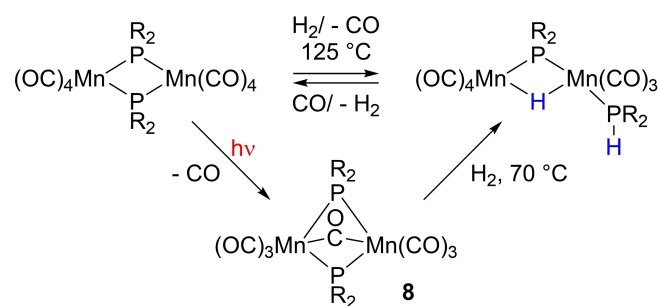
Scheme 4. Reported activation of H_2 by dinuclear manganese phosphide complexes (R = Ph, iPr) according to Ref. [10].
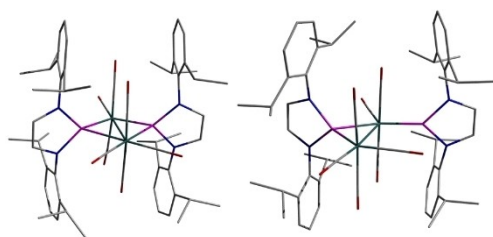
Figure 3. Wireframe representation of the computed molecular structures of **7a**$_{closed}$ (left) and **7a**$_{open}$ (right). Hydrogen atoms were omitted for clarity. The corresponding structures of **7b**$_{closed}$ and **7b**$_{open}$ are shown in Figure S19.

two structural isomers needing further consideration (Figures 3, S19).

The specimens exhibiting the lowest electronic energy contain one $Mn(CO)_3$ and one $Mn(CO)_4$ unit connected by two equivalent, unsymmetrically μ_2-bridging NHP ligands in a similar layout as had been proposed for a NMe-substituted model compound,[7] and are denoted as **7a,b**$_{closed}$. A similar structure was reported for an isolobal dicobalt complex.[12] In the energetically less favored 'open' isomers **7a,b**$_{open}$, a bridging ligand has been shifted to the CO-deficient metal atom, and the molecules now comprise a single μ_2-bridging NHP unit and a terminal phosphenium ligand adopting a similar binding mode as in **5a,b**. Local minimum structures like **8**[10] with bridging carbonyls could not be located.

The gap in electronic energies (*E*) and standard Gibbs free energies (ΔG^{298}) between respective isomers of **7a,b** changes noticeably upon variation of the NHP-ligand (Figure 4a). Formal replacement of N-Mes by bulkier N-Dipp substituents reduces the relative energy of the 'open' form by 6.7 kcal/mol and the Gibbs free energy ΔG^{298} by even 9.4 kcal/mol. The additional sign inversion for ΔG^{298} implies that the thermal equilibrium between both isomers is at room temperature almost entirely on the side of the 'closed' form in case of **7b** (the molar fraction x(**7b**$_{open}$) calculated from ΔG^{298} is ≈ 1 ppm), while **7a** exists as a mixture containing the 'open' isomer as dominant component (x(**7a**$_{open}$) = 0.92). Further interpretation of the thermochemical data suggests that the balance between both isomers is ruled by a combination of energetic and entropic effects. The 'open' form is apparently disfavored by lower electronic bond energy, but profits from an energetically favorable reduction of repulsive interactions and higher conformational mobility increasing the entropy term. While the last issue is not very significant for **7b**, the energetic impact of the 'steric' factors grows with increasing size of the N-aryl groups to make these decisive variables that tip the isomer balance toward the 'open' form in case of **7a**.

The reaction of **7b**$_{closed}$ with CO to yield two molecules of **5b** is calculated as weakly endothermic but exergonic at room temperature, while the analogous reaction of **7a**$_{open}$ (for simplicity, we restrict our survey to the dominant isomers) is predicted to be both exothermic and even more strongly exergonic (Figure 4b). The thermal equilibrium is thus in both cases on the side of the mononuclear complexes **5a,b** regardless of the energetic preferences, which is in accord with the observed inaccessibility of the dimers in a thermally induced reaction. The trends in calculated energies and Gibbs free energies imply that both reactions are again driven by the release of steric strain accompanying the splitting of the dinuclear assemblies, and that the steric interference caused by the bulky N-aryls is sufficiently severe to perceptibly destabilize even the less congested Mn_2-unit with a single μ_2-NHP-ligand in **7a**$_{open}$.

The combination of both **7a**$_{open}$ and **7b**$_{closed}$ with CO and H_2 to give a mixture of **5a,b** and **6a,b** is calculated as both exothermic and exergonic (Figure 4c). Although formation of both hydrogenation products is thus thermodynamically favored at room temperature, it is unlikely to take place in a
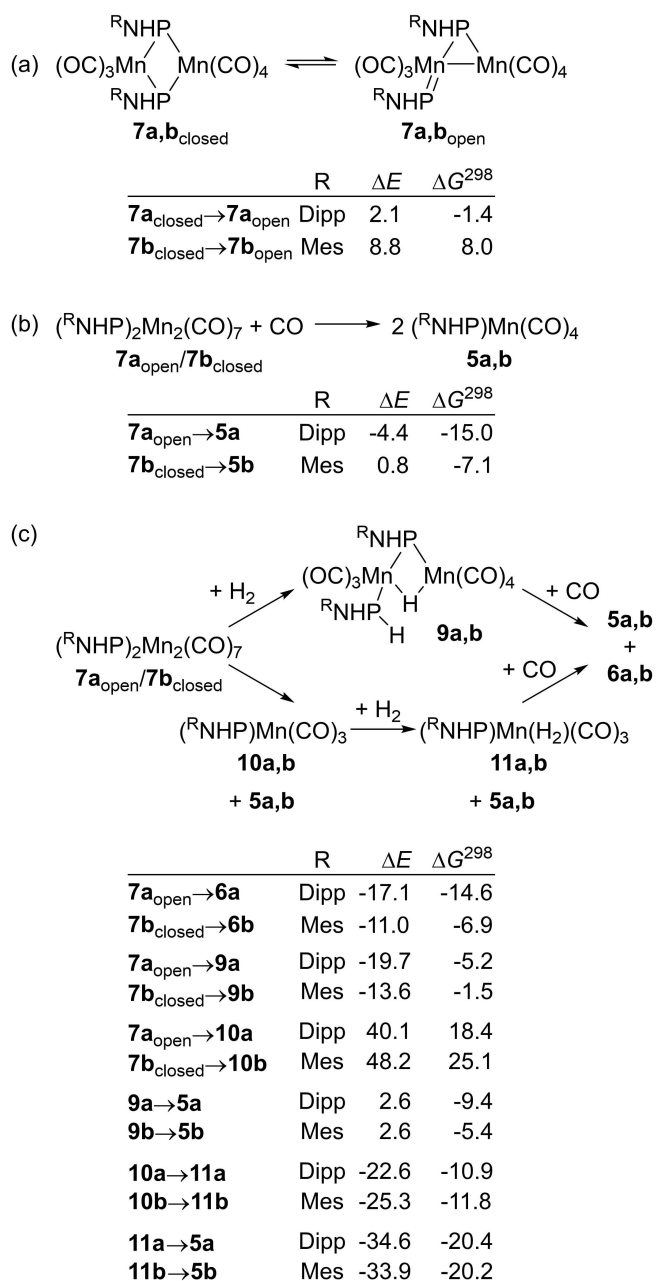
Figure 4. Electronic energies ΔE and standard Gibbs free energies ΔG^{298} (in kcal mol^{-1}) (a) for the isomerization between 'open' and 'closed' forms of **7a,b** and the reactions of the prevailing (in thermal equilibrium at 298 K) isomer (b) with CO, and (c) with H$_2$ and CO, including decomposition of the overall (free) energies into contributions from the individual steps of the reaction scenarios discussed. Further methodologic details are given in the Experimental Section.

single trimolecular step. Assuming that a realistic mechanism is set off by the interaction of the Mn$_2$-complexes with H$_2$ (an initial reaction with CO would produce **5a,b**, which do not undergo a thermally induced reaction with H$_2$), two basic scenarios seem conceivable.

The first scenario is based on the hypothesis that the initial activation of H$_2$ occurs on Mn$_2$-species. Presuming that this reaction takes a similar course as the metal-ligand cooperative activation of H$_2$ by bis-phosphido complexes[10] (Scheme 4), we

formulate the products as complexes **9a,b** containing μ_2-bridging hydride and terminal secondary phosphine ligands. Formation of both species from the appropriate isomer of **7a,b** is predicted to be exothermic and exergonic. Further conversion of **9a,b** with CO to give **5a,b** and **6a,b** is slightly endothermic but still exergonic, thus explaining why the reaction does not stop at the stage of the dinuclear species as in case of the phosphido complexes. A cause for the experimentally observed inertness of **7b$_{closed}$** toward H$_2$ is not immediately evident as its reaction is still predicted as exergonic, albeit with reduced driving force. However, a fair explanation becomes possible if one assumes that the access of H$_2$ to **7b$_{closed}$** is sterically inhibited and the reaction must thus proceed via **7b$_{open}$**. The initial step is then the isomerization of **7b$_{closed}$** to **7b$_{open}$**, which is both endothermic and endergonic and thus suited to increase the kinetic barrier of the whole process.

In the second scenario, it is assumed that the respective isomer of **7a,b** undergoes initial fragmentation to yield a mixture of tetra- and tricarbonyl complexes **5a,b** and **10a,b**, respectively, and the coordinatively unsaturated tricarbonyl complex is then quenched by successive reaction with H$_2$ and CO. The break-up of the Mn$_2$-species is in both cases predicted to be strongly endothermic and endergonic and establishes thus a sizeable kinetic barrier. Hydrogenation of **10a,b**, which is expected to yield dihydrogen complexes **11a,b** as further intermediates, and successive reaction with CO to give **6a,b** are both predicted to be exothermic and exergonic. The deviating reactivity of **7a,b** toward H$_2$ is in this case attributable to the fact that destabilization of **7a$_{open}$** by steric congestion (see above) in combination with a slight stabilization of **10a** by an intramolecular agostic interaction (see Figure S20) facilitate the initial endergonic fragmentation step and thus lower the kinetic barrier for the whole process.

Technically, both scenarios described confirm that activation of H$_2$ by dimanganese complex **7a** is thermodynamically feasible and expected to yield the actual observed complexes **5a** and **6a** as preferred products, and offer as well a reasonable explanation for the deviating behavior of **7a** and **7b**. However, since the available NMR and IR data of **7a,b** do not allow unequivocal distinction between 'open' and 'closed' molecular structures and no further reaction intermediates were experimentally observable, it is not possible at this stage to confirm or rule out a particular pathway. Although the precise reaction mechanism remains thus unresolved for the time being, our calculations nonetheless point out that steric congestion introduced by the bulky N-aryls seems essential for explaining the unique reactivity of **7a** toward H$_2$.

Transfer of hydrogen - reactions with styrene

To elucidate if a molecule of H$_2$ transferred to NHP complex **5a** can be passed on to organic molecules, we studied the reaction of dihydride **6a** resulting from this transfer with excess styrene as model substrate. ^{1}H NMR spectroscopy revealed that the mixture did not react at ambient temperature, but traces of ethyl benzene (EB) were detectable after tempering at 50 °C for

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24 h, and a reaction including almost complete ($>95\%$) consumption of **6a** occurred within 3 h upon continuous irradiation with a xenon arc lamp. The NMR spectra of the reaction mixture unveiled that a substantial quantity of EB had formed, and that **6a** had been converted into a mixture of **5a** ($\approx15\%$), a species later identified as styrene complex **11** ($\approx40\%$), and several unidentified decomposition products ($\approx40\%$, see Scheme 5, (a), Figure S10).

Generation of **6a** being as well feasible in situ via co-photolysis of **5a** and H_2, we further studied the behavior of a solution of styrene and **5a** (28 mol-%) pressurized with 4 bar of H_2 upon irradiation with a xenon arc lamp. Reaction monitoring by NMR spectroscopy revealed that the gradual hydrogenation of **5a** to **6a** took place as expected. In addition, formation of Mn_2-complex **7a** and styrene complex **11** and a steady production of EB throughout the reaction were observable (Scheme 5 (b) and Figure S11). Unfortunately, these reactions were likewise superimposed by a gradual decay of all phosphorus-containing species, which became the dominant process upon prolonged irradiation and eventually resulted in the extensive decomposition to unidentifiable products. The total amount of EB produced exceeding the amount of **5a** originally used by a factor of ≈1.3 gives a first hint that the hydrogenation may be catalytic in NHP-complex, but the decomposition processes precluded quantitative interpretation of the data or an adequate kinetic analysis.

The mutual conversion between **5a**/H_2 and **6a** in the previous reactions arising from photo-induced (de)hydrogenation that had been reported elsewhere[7] or earlier in this work, we posited that photo-decarbonylation of **5a** and trapping of the resulting transient intermediate by styrene could also explain the formation of **11**. Hence, we next explored the reaction of **5a** with excess styrene in the absence of H_2. In accord with our conjecture, formation of the olefin complex along with a small amount of Mn_2-complex **7a** was

observable by NMR spectroscopy after only a few minutes of irradiation with a xenon arc lamp and proceeded within 2 h to reach a steady state in which **11**, **7a**, and unreacted **5a** were present in a 30:1:10 ratio (Scheme 5 (c)).

Even though **11** is not formed entirely selectively, its constitution is clearly deduced from 1D- and 2D NMR spectra of the reaction mixture. The ^{31}P NMR signal displays the large chemical shift ($\delta^{31}P$ 236.1 ppm) and linewidth (due to unresolved spin coupling with the ^{55}Mn nucleus) typical of a phosphenium complex.[7][8] The greatly increased shielding of the ^1H and ^{13}C NMR signals of the vinylic hydrogen (δ^1H 2.46, 2.78, 4.54 ppm) and carbon atoms ($\delta^{13}C$ 61.6, 30.7 ppm) compared to free styrene imply side-on coordination of the double bond, while the signals of the phenyl protons (δ^1H 7.0–7.2 ppm) are similar as in the free ligand and indicate that the aromatic ring does not interact with the metal. Since the styrene ligand renders the two N-Dipp-substituents unequal, the ^1H and ^{13}C NMR spectra display distinguishable signals of two methine and four methyl groups.

The presence of the $Mn(CO_3)$ moiety cannot be unmistakably deduced from the IR spectrum of the mixture, since one of the three expected bands is superimposed by a band from **5a** and is only assigned with reservations. However, it can be established from a study of the reaction of **7a** with excess styrene in the absence of H_2 and free CO. NMR spectroscopy revealed that at room temperature only the unchanged reactants are detectable even after 24 h, while a largely complete conversion to equimolar amounts of **5a** and **11** is observable after heating to 50 °C for 27 h (Scheme 5 (d)). An additional CO source being absent, the mass balance of the reaction permits to deduce the presence of three CO ligands in **11**. The coexistence of **11** with **7a** and styrene under ambient conditions further implies that the formation of the olefin complex upon co-photolysis of **5a** and styrene cannot be explained by photochemically generated **7a** undergoing a subsequent thermally induced reaction with the olefin, as this step would only be possible at elevated temperature. Rather, we assume that the olefin complex is produced either from **7a** or directly from **5a**, respectively, via photo-induced ligand substitution.

While the formation of **5a**–**7a** and **11** observed in the previously described experiments can be reasonably accounted for, the complexity of the reaction network and the instability of the NHP complexes under reaction conditions currently prevent us from identifying a specific pathway for the actual hydrogen transfer to styrene. For the moment, it must thus remain undecided whether this step is truly catalytic and whether it is mediated by one of the NHP complexes or a decomposition product. Catalytic alkene hydrogenation using manganese phosphido complexes is to the best of our knowledge unknown to date, but semihydrogenation of alkynes with dinuclear hydride phosphides as pre-catalysts has recently been reported.[13] Even if this reaction is thermally rather than photochemically initialized and its proposed mechanism relies to a large extent on dinuclear intermediates, which seem to be less important for the complexes studied here, its occurrence
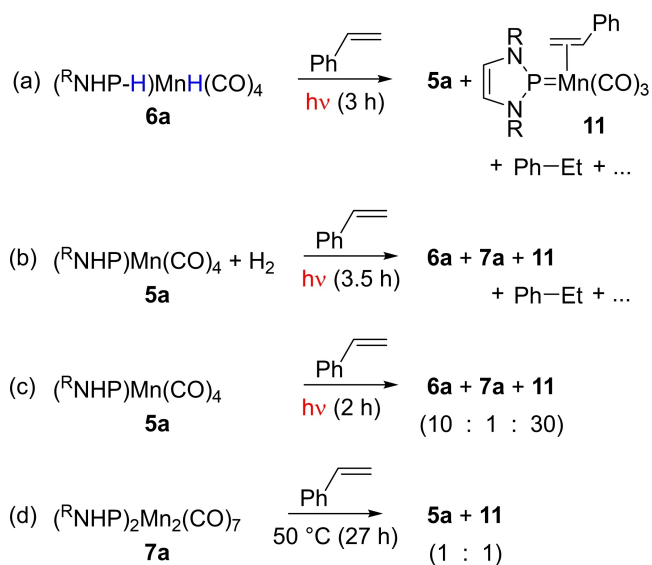
Scheme 5. Reactions of **5a**–**7a** or **5a**/H_2 with styrene (R = Dipp). Products were analyzed by NMR spectroscopy.

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provides a first indication that catalytic hydrogenation of olefins by NHP-complexes may also be possible.

Conclusions

We have established that hydrogenation of the manganese-phosphorus double bond in a phosphenium complex is not only achievable via stepwise H^+/H^- transfer as previously described,[7] but also via the direct addition of H_2 across the double bond after photolytic initialization. By combining this and previous results,[7] proof of principle is provided that the cooperative addition of H_2 across the metal-phosphorus double bond in a simple mono-phosphenium complex is reversible under photochemical conditions, and that the forward and reverse transformation can be addressed by adjusting the H_2 pressure. As in the case of dinuclear phosphido complexes of manganese,[10] the H_2-activation is triggered by initial cleavage of a CO ligand rather than photoinduced coordination isomerization of the NHP-ligand reported for a bis-NHP-complex of chromium,[5] and its success is intimately connected with the stability and chemical reactivity of a dinuclear bis-NHP-complex that appears to be a key intermediate. Computational studies suggest that the prevailing constitution of this species and its reactivity depend decisively on the steric congestion introduced by bulky N-aryl substituents on the NHP ligand, and that the same steric factors can also explain the preferred formation of mononuclear instead of dinuclear products as in analogous reactions[10] of manganese phosphido complexes. Preliminary studies indicate further that mixtures of a sterically congested NHP-complex and H_2 enable the photo-induced hydrogenation of styrene to ethyl benzene. However, although formation of a mixed NHP/olefin complex in this reaction could be shown, the instability of the NHP-complexes under reaction conditions precludes to date a mechanistic interpretation. Further studies on the catalytic aspects of this reaction would seem rewarding once the stability problem can be resolved.

Experimental Section

Manipulations were carried out under an atmosphere of inert argon inside glove boxes or by using standard vacuum line techniques unless stated otherwise. Solvents were dried by published procedures.[16] NMR spectra were recorded on Bruker Avance 250 (^{1}H 250.0 MHz, ^{31}P 101.2 MHz) or Avance 400 (^{1}H 400.1 MHz, ^{13}C 100.5 MHz, ^{31}P 161.9 MHz) instruments at 293 K. ^{1}H Chemical shifts were referenced to TMS using the signals of the residual protons of the deuterated solvent (C_6D_6, δ^1H 7.15) as secondary reference. Spectra of heteronuclei were referenced using the Ξ-scale[17] with TMS ($\Xi = 25.145020$ MHz, ^{13}C) and 85% H_3PO_4 ($\Xi = 40.480747$ MHz, ^{31}P) as secondary references. The syntheses of **5a,b** and **7a** were carried out as reported.[7][8] Reactions under elevated gas pressure were carried out in C_6D_6 using commercially available NMR tubes (Norell© Extreme Series) that could be flange-mounted to home-built apparatuses for the admission of H_2 or CO, respectively, under inert conditions. The gas pressure was adjusted at room temperature by controlling the total pressure in the apparatus determined by means of a manometer. Carbon monoxide (purity 3.7) was used as is, while hydrogen (purity 5.0) was purified using a SAES Pure

Gas© (MC50-904F) unit. Irradiation experiments were performed using an LSB523 150 W Xe OF xenon arc lamp in conjunction with an LSH102 air-cooled enclosure with LSC121 amplifying mirror purchased both from LOT Quantum Design. Further details on instruments and methods used for spectroscopic characterization, the synthesis of **7b**, and the procedures used for carrying out and evaluating the various reaction studies are included together with the appropriate data in the Supporting Information.

RI-DFT calculations were carried out on the bwForCluster Justus2 with the TURBOMOLE program suite (version 7.5.2020).[11] Energy optimization of molecular structures and calculation of harmonic frequencies was carried out using the ωB97x-D functional,[14] whose suitability for describing molecular structures of the NHP-complexes had already been shown,[5,7] with a def2-SVP basis set[15] on isolated molecules, simulating gas phase conditions. The stationary points located were identified as local minima on the energy hypersurface by harmonic vibrational frequency calculations at the same level. Electronic energies at the stationary points were recalculated with a def2-TZVP basis set[15] and are given at the RI-ωB97x-D/def2-TZVP// RI-ωB97x-D/def2-SVP level. Standard Gibbs free energies ΔG^{298} were calculated using the def2-TZVP energies with the corrections obtained from the frequency calculations with the smaller basis set.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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