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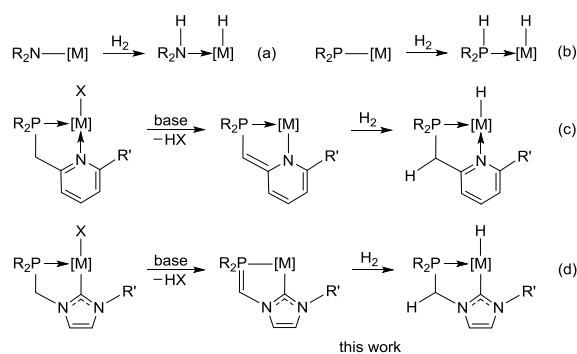
Phosphine-NHC Manganese Hydrogenation Catalyst Exhibiting a Non-Classical Metal-Ligand Cooperative H₂ Activation Mode

Ruqaya Buhaibeh,^[a] Oleg A. Filippov,^[b] Antoine Bruneau-Voisine,^[a,c] Jérémy Willot,^[a] Carine Duhayon,^[a] Dmitry A. Valyaev,^{*,[a]} Noël Lugan,^{*,[a]} Yves Canac^{*,[a]} and Jean-Baptiste Sortais^{*,[a,d]}

Abstract: Deprotonation of the Mn(I) NHC-phosphine complex *fac*-[MnBr(CO)₃(κ²P,Ĉ-Ph₂PCH₂NHC)] (**2**) under a H₂ atmosphere readily gives the hydride *fac*-[MnH(CO)₃(κ²P,Ĉ-Ph₂PCH₂NHC)] (**3**) via the intermediacy of the highly reactive 18-e NHC-phosphinomethanide complex *fac*-[Mn(CO)₃(κ³P,C,Ĉ-Ph₂PCHNHC)] (**6a**). DFT calculations revealed that the preferred reaction mechanism involves the unsaturated 16-e mangana-substituted phosphonium ylide complex *fac*-[Mn(CO)₃(κ²P,Ĉ-Ph₂P=CHNHC)] (**6b**) as key intermediate able to activate H₂ via a non-classical mode of metal-ligand cooperation implying a formal λ⁵-P - λ³-P phosphorus valence change. Complex **2** is shown to be one of the most efficient pre-catalysts for ketone hydrogenation in the Mn(I) series reported to date (TON up to 6200).

Cooperative activation of inert chemical bonds is a topical concern in modern chemistry and homogeneous catalysis. Since the discovery of Shvo-type catalysts,^[1] a wide variety of transition metal complexes bearing non-innocent ligands was exploited for E–H bond activation,^[2] recently supplemented by related reactivity of frustrated Lewis pairs^[3] and main-group ambiphiles.^[4] Among all these transformations, the activation of H₂ is of utmost importance because of its essential role in catalytic [transfer] hydrogenation^[5] and hydrogen borrowing^[6] processes relevant in fine chemicals industry. While the seminal contribution of Noyori and coll. involving an amide/amine interplay in the coordination sphere of transition metals (Scheme 1, (a)) still is the most ubiquitous system for heterolytic H₂ splitting,^[7] similar transformations implying phosphorous analogues remain scarce (Scheme 1, (b)).^[8] By contrast, the association of N- and P-moieties for such application was more developed (Scheme 1, (c)). In this regard, as mostly demonstrated in pincer-type series, the species resulting from deprotonation of the methylene bridge in phosphine-pyridine complexes are capable to activate H₂ across the metal and the

ligand arm though a mechanism in which the rearomatization of the pyridine moiety actually plays a key role (Scheme 1, (c)).^[9] We report herein that a non-classical metalla-substituted phosphonium ylide obtained upon C–H deprotonation of a chelating NHC-phosphine ligand in the Mn coordination sphere can easily activate H₂ (Scheme 1, (d)), thus providing the first evidence of the involvement of λ⁵-P species in metal-ligand cooperation. Thanks to this non-classical mode of H₂ activation, the NHC-phosphine Mn(I) complex behaves as a powerful catalyst for the hydrogenation of ketones.



Scheme 1. H₂ activation by non-innocent ligands via metal-ligand cooperation.

Compassing our recent investigations on the application of Mn(I) complexes supported by bidentate ligands in hydrogenation-type catalysis,^[10] we turned our attention to the use of ligand systems now associating phosphine and NHC donors. Complex **2** was readily obtained in 86% yield from the corresponding phosphine-imidazolium salt [1]OTs^[11] through the sequential addition of KHMDS and [Mn(CO)₅Br] (Scheme 2). According to IR and NMR spectroscopy, the air stable complex **2** forms as a single isomer (δ_P 71.3 ppm (s), δ_C 197.7 ppm (d, ²J_{PC} = 17.5 Hz, C_{N2C}), presenting a facial arrangement of the three carbonyl ligands as confirmed by an XRD study (Figure 1a).^[12]

To explore the chemical behaviour of **2** towards H₂, the latter complex was first reacted with KHMDS in toluene at 0 °C under 1 atm. of H₂. Under these conditions, **2** was rapidly converted into the corresponding Mn(I) hydride complex **3** (Scheme 2, up) isolated in 78% yield, standing up as the first example of a Mn hydride complex bearing a NHC ligand. The ¹H NMR spectrum of **3** displays a doublet at δ_H –7.25 ppm with a ²J_{PH} constant of 53.8 Hz agreeing with the *cis* arrangement of hydride and phosphine moieties. The ³¹P NMR signal of **3** (δ_P 94.2 ppm) was found shifted downfield compared to the bromide precursor **2** (δ_P 71.3 ppm). A similar trend was observed for the carbenic resonance in the ¹³C NMR spectrum (**3**: δ_C 205.4 ppm (d, ²J_{PC} = 14.3 Hz); **2**: δ_C 197.7 ppm (d, ²J_{PC} = 17.5 Hz)). The facial

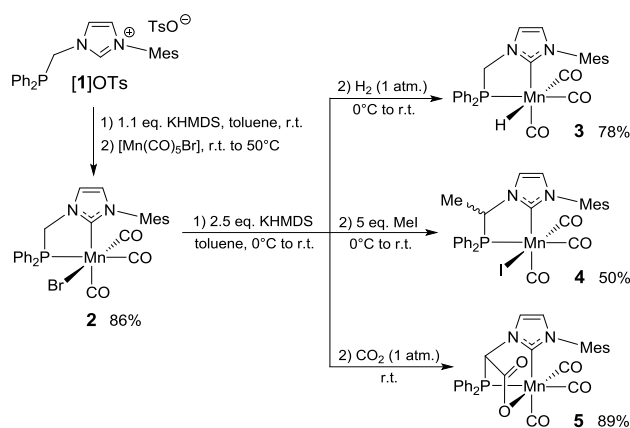
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Scheme 2. Synthesis and reactivity of NHC-phosphine Mn(I) complex **2**.

arrangement of the three carbonyls co-ligands of complex **3** was univocally confirmed by an XRD study (Figure 1b). Noteworthy, performing the previous reaction under D₂ atmosphere led to complex **3**^{D2} with a full incorporation of deuterium at the hydride (Mn–D) and at the CH₂ positions (CH–D, see the S.I.).

In order to further characterize the acidic site in the complex **2**, *i.e.* the one that undergoes the deprotonation reaction, different trapping experiments were carried out. For this purpose, complex **2** was first treated with KHMDS followed by the addition of an excess of classical alkylating agent such as MeI.^[13] The resulting complex **4** showing methylation of the carbon atom linking the phosphine and NHC moieties was isolated as a mixture of two diastereomers (ratio 6:1) differing by the position of the methyl group with respect to the iodine atom (Scheme 2, middle). Both isomers of complex **4** (major isomer: $\delta_{\text{P}} 73.0$ ppm (s); $\delta_{\text{C}} 195.9$ ppm (d, $^2J_{\text{PC}} = 16.6$ Hz, C_{N₂C})) display similar spectroscopic features compared to the bromide precursor **2**. An XRD analysis of **4** evidenced the presence of the *anti*-isomer in the solid state (Figure 1c). In a second time, the deprotonated species was exposed to CO₂ (1 atm.) affording the complex **5** in 89% yield (Scheme 2, bottom) whose solid state structure highlights the existence of a tripodal NHC-phosphine-carboxylate scaffold with a facial arrangement of the carbonyl ligands (Figure 1d).^[14,15] These results clearly indicated that the deprotonation of **2** occurs at the CH₂ bridge forming a sufficiently nucleophilic carbon species to react with electrophiles such as MeI or CO₂.

Yet, after proving the involvement of a deprotonated intermediate **6** of general formulae [Mn(CO)₃(Ph₂PCHNHC)] for the formation of complexes **3-5** from **2**, arose the question of its structure. Despite its relative instability ($t_{1/2}$ of ca. 0.5 h at r.t., decomposition at –30 °C over 16 h), optimization of reaction parameters allowed to prepare suitable samples for complete spectroscopic characterization. The IR spectrum of **6** in toluene exhibits two ν_{CO} bands at 1993 (s) and 1901 (vs) cm⁻¹ consistent with the presence of three CO ligands in a facial arrangement. The ³¹P{¹H} NMR spectrum recorded in a [D₈]toluene solution at –30 °C revealed the complete conversion of **2** ($\delta_{\text{P}} 71.7$ ppm) into **6**, the latter being characterized by a shielded chemical shift at $\delta_{\text{P}} 51.6$ ppm. The deprotonation site was finally revealed by the concomitant presence of doublets at $\delta_{\text{H}} 3.55$ ($^2J_{\text{PH}} = 8.6$ Hz, 1H) and at $\delta_{\text{C}} 22.7$ ppm ($^1J_{\text{PC}} = 18.2$ Hz) in the ¹H and ¹³C{¹H} NMR

spectra respectively, consistent with the presence of a CH group in the α -position of P-atom and confirming that the deprotonation does take place at the CH₂ bridge. Noticeably, while the ¹³C{¹H} NMR spectrum displays three distinct resonances for CO ligands at standard chemical shifts, the carbenic carbon atom appears to be strongly shielded ($\delta_{\text{C}} 178.0$ ppm, d, $^2J_{\text{PC}} = 14.2$ Hz) by ca. 20–25 ppm compared to the antecedent complexes **2-5**.

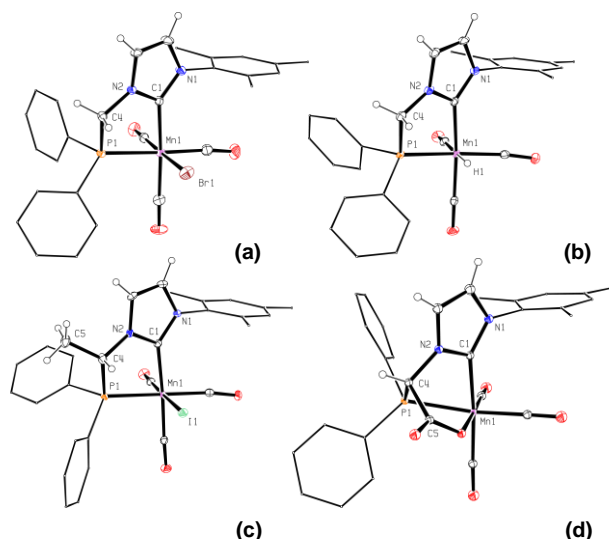


Figure 1. Molecular geometry of complexes *fac-2* (a), *fac-3* (b), *fac-4* (c), and **5** (d) (30% probability ellipsoids, aryl groups represented as a wireframe).

Despite all our efforts, single crystals of complex **6** could not be obtained. Its structure was therefore investigated by theoretical calculations. DFT study at the BP86/def2-TZVP level revealed five minima on the PES. The global minimum corresponds to the strongly distorted octahedral 18-e complex *fac*-[Mn(CO)₃(κ^3 P,C, $\dot{\text{C}}$ -Ph₂PCHNHC)] (**6a**, Figure 2 (left)) featuring a facially coordinated, 5-e donor, NHC-phosphinomethanide ligand.^[16,17] Calculated metrical parameters within the MnPC moiety are comparable to those experimentally found in the related [κ^2 P,C-Ph₂PCH₂)Mn(CO)₄] complex.^[16a] The other minima correspond to the four possible isomers – two *fac* and two *mer* – of square pyramidal 16-e [Mn(CO)₃(κ^2 P, $\dot{\text{C}}$ -Ph₂P=CHNHC)] complex **6b** showing an unusual bidentate NHC-phosphonium ylide ligand

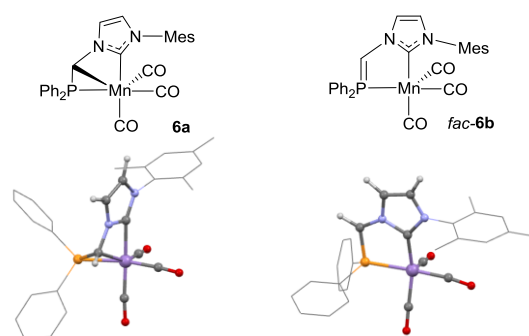


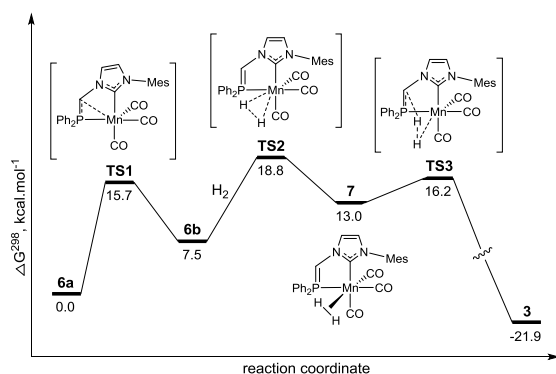
Figure 2. Structures and DFT optimized geometries of complexes **6a** and *fac-6b* (BP86/def2-TZVP, toluene SMD model).

(see the SI for details). The most thermodynamically stable isomer of NHC-ylide complexes *fac*-6b, yet being destabilized by +7.5 kcal.mol⁻¹ relative to **6a**, is depicted in Figure 2 (right). The calculated P–C bond length in *fac*-6b (1.741 Å) is consistent with an ylidic P–C bond, in agreement with experimental values found in a related iron-substituted phosphonium ylide complex (1.766(11) Å)^[18] and in other metal complexes bearing more conventional NHC-ylide ligands (1.750(7)–1.794(8) Å).^[19] According to ETS-NOCV study, the P–Mn bond in *fac*-6b is significantly stronger than that in complexes **2-3** featuring a conventional phosphine-metal dative bond (see the SI for details).

Very significantly, the relatively constrained coordination of the NHC-phosphinomethanide ligand in **6a** results in a strong distortion of yaw angle θ ^[20] for the NHC ligation (**6a**: θ 29.5° vs. **2-4**, **6b**: 6.2–7.2°). Considering that the shielding of the ¹³C NMR chemical shift of carbenic carbon atoms in metal complexes increases as the value of θ ,^[21] the signal recorded at δ_c 178.0 ppm for **6** in solution (*vide supra*) appears to be totally consistent with the most stable structure **6a**. In addition, computed ¹³C NMR chemical shift for the carbenic atom in complex **6a** (δ_c 181.5 ppm) matches well with the experimental value (δ_c 178.0 ppm), a value significantly different from that computed for complex *fac*-6b (δ_c 215.1 ppm) (see Table S5 for details), thus the deprotonation product of **2** was assigned to complex **6a**.

The mechanism of H₂ activation by **6a** was then investigated by DFT calculations. Among the different activation pathways considered, the process showing the lowest energy profile is depicted in Scheme 3 (see the SI for alternative mechanisms). Complex **6a** is first converted into the 16-e NHC-ylide species *fac*-6b with an energy barrier of 15.7 kcal.mol⁻¹ (**TS1**) which then coordinate H₂ to form the dihydrogen complex **7** via a **TS2** of 11.3 kcal.mol⁻¹.^[22] Finally, complex **7** undergoes a facile heterolytic cleavage of the H–H bond through the low-lying transition state **TS3** with an energy barrier of only 3.2 kcal.mol⁻¹ affording finally the experimentally observed-Mn(I) hydride **3**.

Having established that complex **2** could effectively activate H₂ in basic conditions, we next focused our attention on the hydrogenation of ketones as benchmark reaction.^[10a,23] Gratifyingly, at 60 °C, in toluene, in the presence of 1.0 mol% of **2** and 2.0 mol% of KHMDS, acetophenone was fully reduced to 1-phenylethanol (see Table S1 for optimization details). Notably,



Scheme 3. The preferred mechanism of H₂ activation with **6** (BP86/def2-TZVP, toluene SMD model, Gibbs energies are given in kcal.mol⁻¹ and referred to **6a**).

in toluene or *t*-AmOH the loading of **2** could be decreased to 0.1 mol% at 60 °C or even to 0.05 mol% at 100 °C keeping a full conversion. A maximum TON of 6200 was achieved with 0.01 mol% in *t*-AmOH, showing that this catalyst is competitive with the best Mn-based systems for this reaction reported to date.^[23b-c] No reaction took place in the presence of the sole hydride complex **3**, while catalytic activity could be restored in the presence of base, showing its critical role in the catalytic cycle.^[10,23,24]

We then enlarged the synthetic scope of this catalytic transformation (Table 1) and found that a large variety of aryl(alkyl)ketones could be readily reduced (entries 1-18), including sterically hindered representatives (entries 2-4, 7) inaccessible using our previous Mn catalyst based on a chelating phosphine-aminopyridine ligand.^[10c] Interestingly, the reaction is tolerant to aryl groups substituted with halogen atoms (F, Cl, Br, I) and CF₃ moiety (entries 9-14). Aliphatic 2-decanone was hydrogenated in the efficient manner albeit at 100 °C (entry 19). The heterocyclic substrates bearing potentially coordinating groups can also be reduced (entries 20-22) but with lower efficiency.

Table 1. Scope of hydrogenation of ketones catalyzed by Mn complex **2**^[a].

Entry	Substrate	Cat. (%)	Method	Conv. ^[b]	
1		R = Me	0.1	A	>98 (91)
2		R = <i>i</i> -Pr	0.5	A	>98 (89)
3		R = <i>t</i> -Bu	0.5 ^[c]	A	90 (85)
4		R = 2-Me	0.5 ^[d]	A	>98 (93)
5		R = 3-Me	0.2 ^[d]	A	>98 (97)
6		R = 4-Me	0.1	A	>98 (93)
7		R = 2,4,6-Me ₃	0.5 ^[c]	A	>98 (72)
8		R = 4-OMe	0.5 ^[d]	B	>98 (98)
9		R = 4-F	0.1	A	>98 (97)
10		R = 4-Cl	0.5 ^[d]	A	>98 (83)
11		R = 2-Br	0.2 ^[d]	A	94 (81)
12		R = 4-Br	0.2 ^[d]	B	>98 (99)
13		R = 4-I	0.5 ^[e]	A	94 (79)
14		R = 4-CF ₃	0.5 ^[c]	A	>98 (92)
15			0.2 ^[d]	B	90 (65)
16			0.2 ^[d]	A	66 (52)
17			0.2 ^[d]	B	78 (71)
18			0.5 ^[d]	A	50 (37)
19			0.5 ^[c]	A	>98 (98)
20			1.0 ^[f]	A	75
21			1.0 ^[f]	B	40
22			1.0 ^[f]	B	10

[a] Typical procedure: an autoclave was charged with pre-catalyst **2** (0.1 mol%), ketone (2.0 mmol), base (1.0 mol%), **A**: *t*-BuOK, **B**: KHMDS), solvent (2 mL, **A**: *t*-AmOH, **B**: toluene), in this order and then rapidly pressurized with H₂ (50 bar) and heated under stirring at 60 °C for 20h; [b] conversion determined by ¹H NMR, isolated yield in parenthesis; [c] 2% of base, 100 °C; [d] 2% of base; [e] 5% of KOH; [f] 5% of base, 100 °C, 72h

In conclusion, we have shown that a Mn(I) complex of a easily accessible bidentate phosphine-NHC ligand can be selectively deprotonated at the carbon position located between the two donor moieties to afford an original 18-e NHC-phosphinomethanide complex. The latter can serve as a reservoir for an unconventional 16-e NHC-phosphonium ylide complex able to activate H₂ through a metal-ligand cooperation mode based on the formal interplay between λ^5 - and λ^3 -P species. Homogeneous catalysis can take advantage of this new mode of H₂ activation, as demonstrated by the development of one of the most efficient Mn-based catalytic systems for hydrogenation of ketones. Taking into account the ubiquitous presence of the 'R₂PCH₂' motif in transition metal complexes, an awareness of its potential as a non-innocent ligand could now open new perspectives in homogeneous catalysis.

Acknowledgements

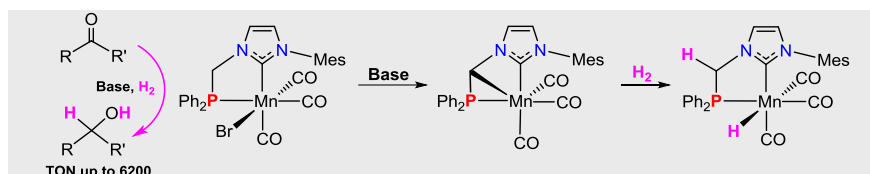
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Keywords: Metal-ligand cooperation • Phosphonium ylides • N-heterocyclic carbenes • Manganese • DFT calculations

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COMMUNICATION



A NHC-phosphine manganese complex in the presence of base is transformed into a NHC-phosfinomethanide derivative capable to easily activate dihydrogen *via* a non-classical metal-ligand cooperative mode. This process is relevant for catalysis providing one of the most efficient Mn-based systems for ketone hydrogenation.

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Phosphine-NHC Manganese Hydrogenation Catalyst Exhibiting a Non-Classical Metal-Ligand Cooperative H₂ Activation Mode