Metal-Ligand Cooperation

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Phosphine-NHC Manganese Hydrogenation Catalyst Exhibiting a Non-Classical Metal-Ligand Cooperative H_2 Activation Mode

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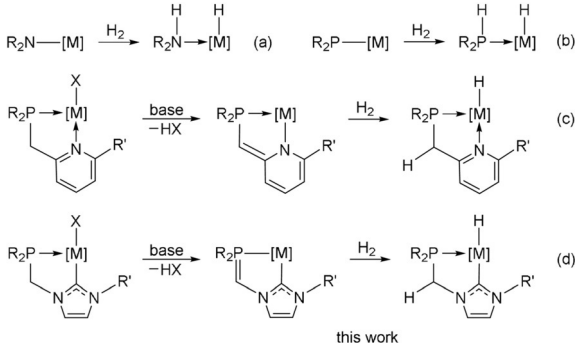
Abstract: *Deprotonation of the Mn^I NHC-phosphine complex fac-[MnBr(CO)$_3$(κ^2P,C-Ph_2PCH_2NHC)] (**2**) under a H_2 atmosphere readily gives the hydride fac-[MnH(CO)$_3$(κ^2P,C-Ph_2PCH_2NHC)] (**3**) via the intermediacy of the highly reactive 18-e NHC-phosphinomethanide complex fac-[Mn(CO)$_3$(κ^3P,C,C-$Ph_2PCHNHC$)] (**6a**). DFT calculations revealed that the preferred reaction mechanism involves the unsaturated 16-e mangana-substituted phosphonium ylide complex fac-[Mn(CO)$_3$(κ^2P,C-Ph_2P=CHNHC)] (**6b**) as key intermediate able to activate H_2 via a non-classical mode of metal-ligand cooperation implying a formal λ^5-P–λ^3-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).*



Scheme 1. H_2 activation by non-innocent ligands via metal-ligand cooperation.

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 H_2 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 1a) still is the most ubiquitous system for heterolytic H_2 splitting,[7] similar transformations implying phosphorous analogues remain scarce (Scheme 1b).[8] By contrast, the association of N- and P-moieties for such application was more developed (Scheme 1c). 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 H_2 across the metal and the ligand arm though a mechanism in which the rearomatization of the pyridine moiety actually plays a key role (Scheme 1c).[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 H_2 (Scheme 1d), thus providing the first evidence of the involvement of λ^5-P species in metal-ligand cooperation. Thanks to this non-classical mode of H_2 activation, the NHC-phosphine Mn^I complex behaves as a powerful catalyst for the hydrogenation of ketones.

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)$_5$Br] (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_{N_2C})), presenting a facial arrangement of the three carbonyl ligands as confirmed by an XRD study (Figure 1a).[12]

To explore the chemical behavior of **2** towards H_2, the latter complex was first reacted with KHMDS in toluene at 0 °C under 1 atm. of H_2. Under these conditions, **2** was rapidly converted into the corresponding Mn^I hydride complex **3**

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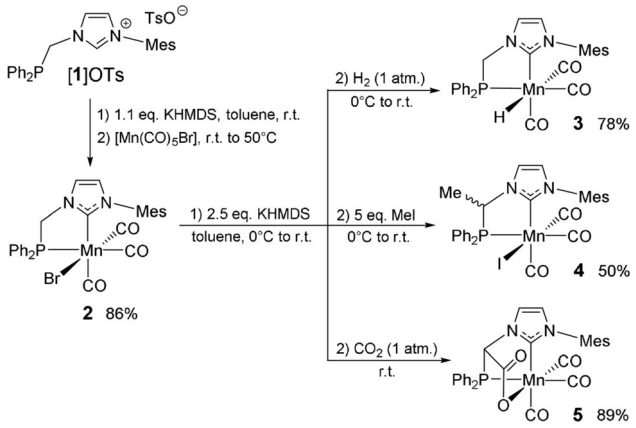


Scheme 2. Synthesis and reactivity of NHC-phosphine Mn^{I} complex **2**.

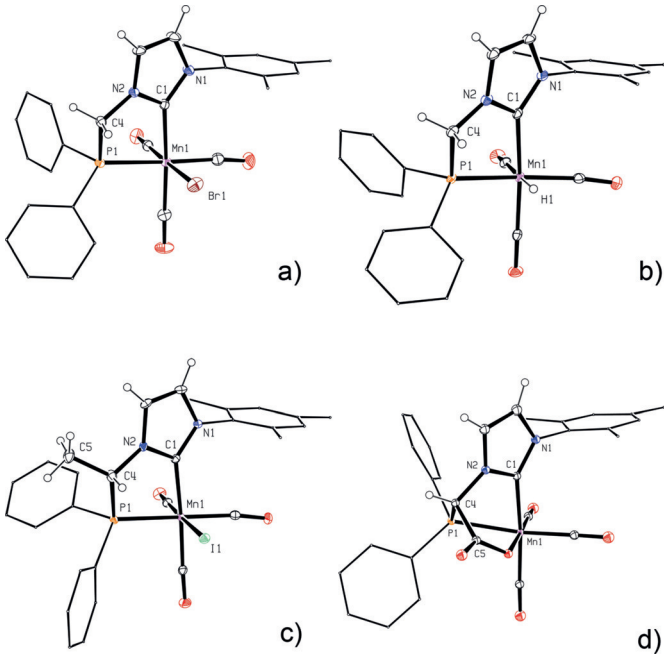


Figure 1. Molecular geometry of complexes *fac*-**2** (a), *fac*-**3** (b), *fac*-**4** (c), and **5** (d) (30% probability ellipsoids, aryl groups represented as a wireframe).

(Scheme 2, up) isolated in 78% yield, standing up as the first example of a Mn hydride complex bearing a NHC ligand. The ^{1}H NMR spectrum of **3** displays a doublet at δ_H −7.25 ppm with a $^{2}J_{PH}$ constant of 53.8 Hz agreeing with the *cis* arrangement of hydride and phosphine moieties. The ^{31}P 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 ^{13}C NMR spectrum (**3**: δ_C 205.4 ppm (d, $^{2}J_{PC}$ = 14.3 Hz); **2**: δ_C 197.7 ppm (d, $^{2}J_{PC}$ = 17.5 Hz)). The facial 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 D_2 atmosphere led to complex $\mathbf{3}^{D2}$ with a full incorporation of deuterium at the hydride (Mn-D) and at the CH_2 positions (CH-D, see the Supporting Information).

In order to further characterize the acidic site in complex **2**, that is 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: δ_P 73.0 ppm (s); δ_C 195.9 ppm (d, $^{2}J_{PC}$ = 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 experiment, the deprotonated species was exposed to CO_2 (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 CH_2 bridge forming a sufficiently nucleophilic carbon species to react with electrophiles such as MeI or CO_2.

Yet, after proving the involvement of a deprotonated intermediate **6** of the general formula [Mn(CO)$_3$(Ph$_2$PCHNHC)] 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 $^{31}P\{^{1}H\}$ NMR spectrum recorded in a [D_8]toluene solution at −30 °C revealed the complete conversion of **2** (δ_P 71.7 ppm) into **6**, the latter being characterized by a shielded chemical shift at δ_P 51.6 ppm. The deprotonation site was finally revealed by the concomitant presence of doublets at δ_H 3.55 ($^{2}J_{PH}$ = 8.6 Hz, 1H) and at δ_C 22.7 ppm ($^{1}J_{PC}$ = 18.2 Hz) in the ^{1}H and $^{13}C\{^{1}H\}$ 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 CH_2 bridge. Noticeably, while the $^{13}C\{^{1}H\}$ NMR spectrum displays three distinct resonances for CO ligands at standard chemical shifts, the carbenic carbon atom appears to be strongly shielded (δ_C 178.0 ppm, d, $^{2}J_{PC}$ = 14.2 Hz) by ca. 20–25 ppm compared to the antecedent complexes **2**–**5**.

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*,*C*-Ph$_2$PCHNHC)] (**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*-Ph$_2$PCH$_2$)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-

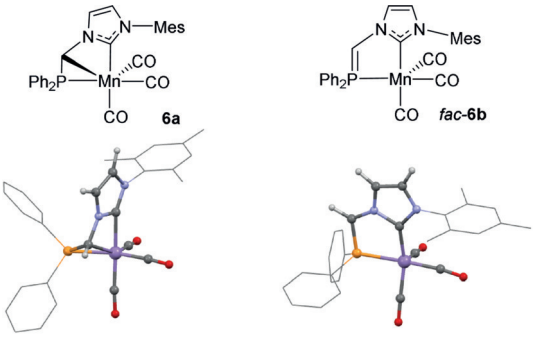
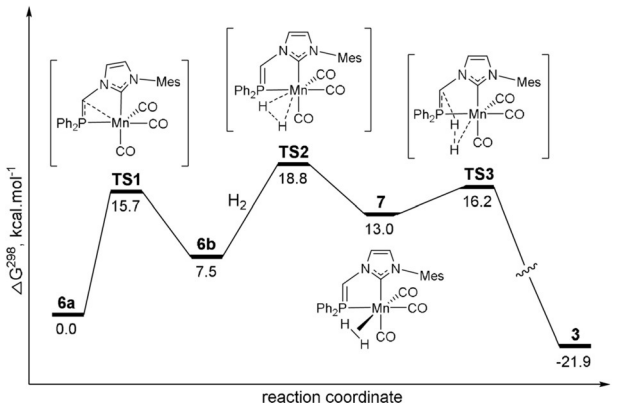


Figure 2. Structures and DFT optimized geometries of complexes **6a** and *fac*-**6b** (BP86/def2-TZVP, toluene SMD model).



Scheme 3. The preferred mechanism of H_2 activation with **6** (BP86/def2-TZVP, toluene SMD model, Gibbs energies are given in kcal mol^{-1} and referred to **6a**.

$(CO)_3(\kappa^2P,C\text{-}Ph_2P{=}CHNHC)]$ complex **6b** showing an unusual bidentate NHC-phosphonium ylide ligand (see the Supporting Information 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 Supporting Information 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**: 29.5° vs. **2**–**4**, **6b**: 6.2–7.2°). Considering that the shielding of the ^{13}C 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 (see above) appears to be totally consistent with the most stable structure **6a**. In addition, computed ^{13}C 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 in the Supporting Information for details), thus the deprotonation product of **2** was be assigned to complex **6a**.

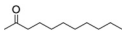
The mechanism of H_2 activation by **6a** was then investigated by DFT calculations. Among the different activation pathways considered, the process showing the lowest energy profile is depicted in Scheme 3 (see the Supporting Information for alternative mechanisms). Complex **6a** is first converted into the 16-e NHC-ylide species *fac*-**6b** with an energy barrier of 15.7 kcal mol^{-1} (**TS1**), which then coordinate H_2 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 H_2 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, 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 CF_3 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.

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 H_2 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 H_2 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 "R_2PCH_2" motif in transition metal complexes, an awareness of its

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*-Pr	0.5	**A**	> 98 (89)
3		R = *t*-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 H_2 (50 bar) and heated under stirring at 60 °C for 20 h; [b] conversion determined by ^{1}H 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, 72 h.

potential as a non-innocent ligand could now open new perspectives in homogeneous catalysis.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: DFT calculations · manganese · metal-ligand cooperation · *N*-heterocyclic carbenes · phosphonium ylides

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