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Bis[diphenylphosphino]methane and its bridge-substituted analogues as chemically non-innocent ligands for H₂ activation

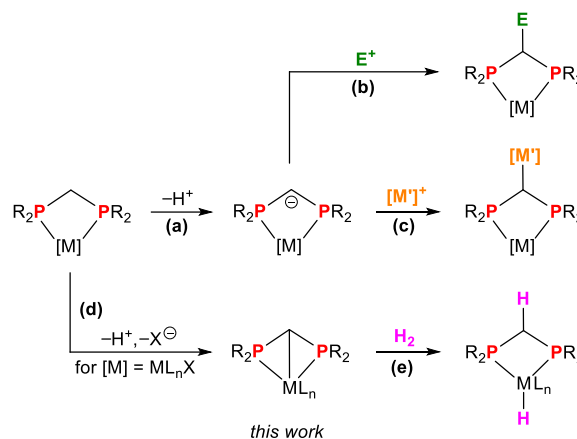
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Deprotonation of *fac*-[(κ²*P,P*-Ph₂PCH(R)PPh₂)Mn(CO)₃Br] (R = H, Me, Ph) produces the corresponding diphosphinomethanide derivatives *fac*-[(κ³*P,C,P*-Ph₂PC(R)PPh₂)Mn(CO)₃], which are prone to activate H₂ to form the hydride complexes *fac*-[(κ²*P,P*-Ph₂PCH(R)PPh₂)Mn(CO)₃H]. Substitution of the *dppm* bridge improves dramatically the reaction efficiency and this was rationalized by DFT calculations.

Since the beginning of 1960's, diphosphinomethanes, including the ubiquitous bis[diphenylphosphino]methane (*dppm*), have been extensively used in transition metal chemistry as ligands capable to exhibit both chelating or bridging coordination modes.¹ While several mononuclear *dppm*-type complexes have found remarkable applications in homogenous catalysis,^{2,3} the chelating *dppm* ligand(s) are generally considered as spectators with the notable exception of the efficient chirality induction brought by P-chirogenic derivatives.⁴ Since the pioneering work of Shaw,⁵ it is well known, however, that the CH₂ bridge of chelating *dppm* can be readily deprotonated to generate anionic bis[diphenylphosphino]methanide (*dppm*⁻) scaffold (Scheme 1, (a)). The nucleophilic character of the bridging carbon atom in such species has later been exploited for the preparation of various bridge-functionalized *dppm* derivatives^{5,6} (Scheme 1, (b)) or bi- or polynuclear compounds⁷ (Scheme 1, (c)). We report herein the first experimental evidence that the deprotonation of *dppm*-type ligands can also lead to neutral cyclometallated κ³*P,C,P*-diphosphinomethanide



Scheme 1. General overview of the chemistry of transition metal diphosphinomethanide (*dppm*⁻) complexes.

complexes relevant for the activation of dihydrogen *via* metal-ligand cooperation^{8,9} (Scheme 1, (d) + (e)).

We have recently reported that the phosphine-*N*-heterocyclic carbene (NHC) ligand in the Mn(I) complex *fac*-[(κ²*P,C*-Ph₂PCH₂NHC)Mn(CO)₃Br] can be readily deprotonated at the methylene bridge to form the NHC-phosphinomethanide derivative *fac*-[(κ³*P,C,C*-Ph₂PCHNHC)Mn(CO)₃], which is able to activate H₂ *via* a non-classical mode of metal-ligand cooperation implying the NHC-phosphonium ylide *fac*-[(κ²*P,C*-Ph₂P=CHNHC)-Mn(CO)₃].¹⁰ In a continuation of this project, we wonder whether the similar reactivity trend could be extended to Mn(I) complexes bearing other chelating R₂PCH₂L ligands and we chose for this study the simple *dppm* and some of its readily accessible bridge-substituted derivatives.

Treatment of Mn(I) complexes *fac*-[(κ²*P,P*-Ph₂PCH(R)PPh₂)Mn(CO)₃Br] (*fac*-**1**^H, R = H; *fac*-**1**^{Me}, R = Me; *fac*-**1**^{Ph}, R = Ph)¹¹ with KHMDS in toluene at room temperature cleanly affords new products *fac*-**2**^R (Scheme 2), which show in IR similar three ν_{CO} patterns shifted by 10–25 cm⁻¹ to lower frequencies being consistent with the formation of neutral metal species. The deprotonation of the methylene (*fac*-**1**^H) or methine (*fac*-**1**^{Me},

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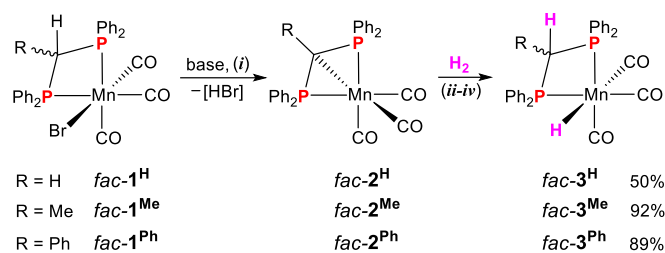
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Scheme 2. Synthesis of Mn(I) diphosphinomethanide complexes *fac-2*^R (R = H, Me, Ph) and their reactivity with dihydrogen. (i) 1.1 equiv. KHMDS, toluene, 25°C; (ii) (R = H): 50 atm. H₂, 50°C, 16h; (iii) (R = Me) 50 atm. H₂, 25°C, 1 h; (iv) (R = Ph): 1 atm. H₂, 25°C, 5 min.

fac-1^{Ph}) bridge within the chelating ligands was unambiguously confirmed by ¹H and ¹³C NMR spectroscopy showing an aliphatic CH fragment as a singlet at δ_H 1.65 ppm, and a strongly shielded triplet at δ_C -10.1 ppm (¹J_{PC} = 5.3 Hz) for *fac-2*^H, and characteristic quaternary carbon atoms at δ_C 0.2 ppm, and δ_C 12.8 ppm (¹J_{PC} = 2.4 Hz) for *fac-2*^{Me} and *fac-2*^{Ph}, respectively. The values of ¹J_{PC} constants within the PCP moiety in complexes *fac-2*^R are anomalously small compared to known Mn(I) κ²P,P-dppm⁻ derivatives^{6,7,12} suggesting the formation of strained P-containing three-membered cycles.¹³ Crystallization of the most stable complex *fac-2*^{Ph} at -20°C (isolated in 60% yield) allowed to establish its structure by X-ray diffraction (Fig. 1).

Diphosphinomethanide ligand in *fac-2*^{Ph} is coordinated to manganese in a tridentate facial κ³P,C,P coordination mode with three carbonyl ligands completing the metal coordination sphere in a distorted octahedral environment. The coordination mode of the phosphorus-containing fragment here is strikingly different from the κ²P,P planar structures typically observed in mononuclear diphosphinomethanide transition metal complexes¹² and has been previously evidenced uniquely in a series of complexes of lanthanides.¹⁴ The PCP unit in *fac-2*^{Ph} is symmetrically bound to Mn and both Mn-P and P-C bond distances are equal within the experimental error (Fig. 1). While Mn-P bonds in *fac-2*^{Ph} are significantly shorter than those observed in the most structurally similar diphosphinomethanide complex [(κ²P,P-dppm^R)Mn(CO)₄]^{12d} (R = 2-(4-methyl)quinolyl, Mn-P: 2.3398(14), 2.3390(15) Å; P-C: 1.738(5), 1.735(5) Å)) P-C bonds within PCP moiety are slightly

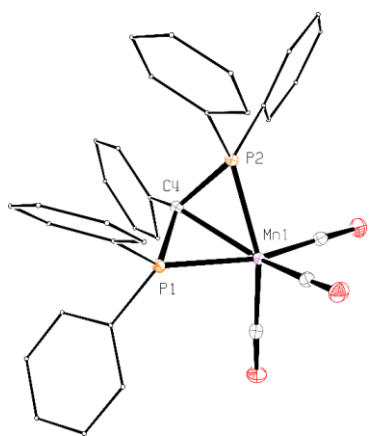


Fig. 1. A perspective view of complex *fac-2*^{Ph} (30% probability ellipsoids, phenyl groups are represented as wireframe). Selected bond lengths (Å) and angles (°): Mn1-P1 2.2255(9), Mn1-P2 2.2222(8), Mn1-C4 2.214(3), P1-C4 1.775(3), P2-C4 1.772(3), P1-C4-P2 103.66(15), P1-Mn1-P2 77.64(3)

longer. Finally, the Mn-C4 bond length is in range of typical Mn(I)-C σ-bonds (CCDC average distance of 2.20 Å for Mn(I) alkyl complexes). Actually, the deprotonation of the methine bridge in *fac-1*^{Ph} induces an intramolecular nucleophilic substitution of the bromide ligand by the resulting carbanion leading to the observed original structure *fac-2*^{Ph} exhibiting 5-electron donor L₂X-type PCP ligand.¹⁵

A first assessment of the reactivity of complexes *fac-2*^R toward dihydrogen was carried out under 1 atm. of H₂ at 25°C. Overnight reaction of complex *fac-2*^H gave an intricate mixture of products (Fig. S15-S16), among which the H₂ activation product *fac*-[(κ²P,P-dppm)Mn(CO)₃H] (*fac-3*^H, Scheme 2), characterized, in particular, by a hydride signal at δ_H -5.10 ppm (td, ²J_{PH} = 43.9 Hz, ⁴J_{HH} = 5.8 Hz), was detected in trace amount. The reactions of *fac-2*^{Me} and *fac-2*^{Ph} were found to be much faster and selective: hydride complex *fac-3*^{Me} was observed as a major product under atmospheric H₂ pressure after one hour at 25°C (Fig. S26-S27) and a selective formation of *fac-3*^{Ph} took place after only few minutes (Scheme 2). The reactions of *fac-2*^H and *fac-2*^{Me} under H₂ pressure (50 atm.) strongly improve the yield of the corresponding hydrides *fac-3*^H and *fac-3*^{Me} isolated in 50 and 92% yield, respectively (Scheme 2). According to NMR data, both complexes *fac-3*^{Me} and *fac-3*^{Ph} exist in solution as a mixture of isomers in a similar ca. 5:1 ratio.¹⁶ 1D NOESY experiments (Fig. S34-35, S46-47) clearly revealed that in both cases the major species correspond to the *fac,anti-3*^R isomer having a *trans* arrangement of the hydride and the proton of the CH(R) bridge. The structure of *fac,anti-3*^{Ph} was further confirmed by a single-crystal X-ray diffraction study. (Fig. 2).

The mechanism of the H₂ activation by complexes *fac-2*^R leading to the hydride complexes *fac-3*^R has been investigated by DFT calculations at the BP86/def2-TZVP level (see the ESI† for details). The first step of the reaction between *fac-2*^R and H₂ involves an heterolytic cleavage of the Mn-C bond *via* the transition state **TS1**^R accompanied by the flipping of dppm^R ligand from the κ³P,C,P to a κ²P,P mode and H₂ coordination to afford the η²-H₂ intermediates *fac-4*^R (Scheme 3).¹⁷ The latter undergo a concerted H-H bond activation process *via* **TS2**^R to form the hydride complexes *fac,syn-3*^R. Interestingly, the activation barriers for these two steps show opposite trends depending on the substituent R on the bridge. While the

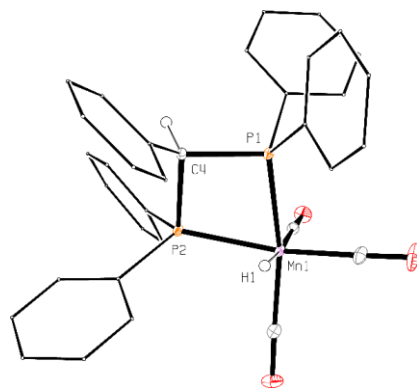
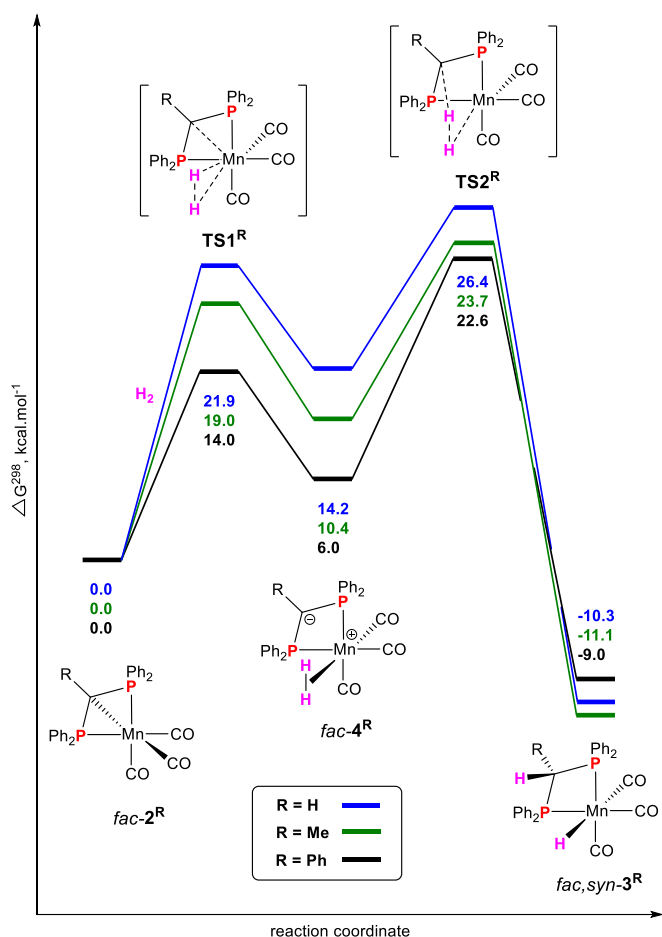


Fig. 2. A perspective view of complex *fac,anti-3*^{Ph} (30% probability ellipsoids, phenyl groups are represented as wireframe). Selected bond lengths (Å) and angles (°): Mn1-P1 2.2549(4), Mn1-P2 2.2830(3), P1-C4 1.8741(12), P2-C4 1.8878(12), Mn1-H1 1.53(2), P1-C4-P2 91.44(5), P1-Mn1-P2 72.808(12).

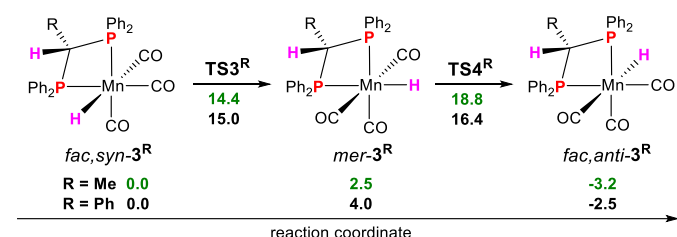


Scheme 3. DFT mechanism of cooperative H₂ activation with complexes *fac-2^R* (BP86/def2-TZVP, toluene SMD model, ΔG^{298} are given in kcal.mol⁻¹ and referred to the reactants (*fac-2^R* + H₂), for the ΔH^{298} profile see Scheme S1 in the ESI).

calculated values for **TS1^R** significantly decrease in the H>Me>Ph order (Scheme 3), the intramolecular proton transfer in *fac-4^R* is more difficult for the phenyl-substituted complex *fac-4^{Ph}* (energy barriers of **TS2^R**: 12.2, 13.3, and 16.7 kcal.mol⁻¹ for *fac-4^H*, *fac-4^{Me}*, and *fac-4^{Ph}*, respectively). The both Gibbs energy span values, namely the differences between the starting complexes *fac-2^R* and the highest transition states **TS2^R**, and the barriers for rate limiting step of H₂ addition (**TS1^R**) are fully consistent with experimentally observed reactivity trend *fac-2^{Ph}* > *fac-2^{Me}* >> *fac-2^H*. A closer inspection of the electronic structure of dppm^{R-} complexes revealed stronger Mn–C bonding in *fac-2^H* with Wiberg bond index (WBI)¹⁸ 0.307 compared to its bridge-substituted analogues *fac-2^{Me}* and *fac-2^{Ph}* (WBI 0.282 and 0.292, respectively), which could indeed contribute to higher **TS1^H** energy value. The potential energy profile of *fac-2^R* upon increasing the dihedral angle Mn–P–C–P to 180° (Figure S54) revealed the enhancement of the ring opening energy in *fac-2^{Ph}* < *fac-2^{Me}* < *fac-2^H* row, thus roughly correlating with the corresponding **TS1^R** energies. This may suggest that in addition to electronic effects, dppm bridge substitution facilitates H₂ coordination step by increasing the strain of the bicyclic [κ^3P,C,P]Mn system in *fac-2^R*.

While the present mechanism account for the formation *fac,syn-3^R* isomers (R ≠ H), experimentally, the *fac,anti* isomers

are actually found to be predominant in solution. According to the DFT calculations the *fac,anti-3^{Me}* and *fac,anti-3^{Ph}* hydride complexes are indeed thermodynamically more stable by 3.2, and 2.5 kcal.mol⁻¹, respectively, than their *fac,syn* analogues. Considering the reaction conditions, such an isomerization could occur through a base-catalyzed epimerization of the bridging chiral carbon. Still, being aware of thermal *fac-to-mer* isomerization known for complexes *fac-[(PR₃)₂Mn(CO)₃X]*,¹⁹ such a possibility in the present case was further investigated by DFT calculations (Scheme 4). As a matter of fact, complexes *fac,syn-3^R* can be readily transformed by a rotation of the entire [Mn(CO)₃H] moiety to the meridional isomers *mer-3^R*, which then can undergo similar rotation to afford *fac,anti-3^R* with activation barriers readily accessible at room temperature (see the ESI† for animated gif files illustrating these steps).



Scheme 4. DFT mechanism of the isomerization of hydride complexes *fac,syn-3^R* into *fac,anti-3^R* (BP86/def2-TZVP, toluene SMD model, ΔG^{298} are given in kcal.mol⁻¹ (green for R = Me, black for R = Ph) and referred to *fac,syn-3^R*). See the ESI† for geometries of transition states and animated gif files for each step of the process.

In order to validate experimentally some mechanistic clues obtained by DFT calculations, we have carried out low temperature NMR monitoring of the reaction between *fac-2^{Ph}* and H₂ (2 atm.) in toluene-*d*₈ (Fig. 3). Unfortunately, we were unable to detect η^2 -H₂ intermediate *fac-4^{Ph}* in –80– –40 °C temperature range. Around –20 °C the formation of *fac,syn-3^{Ph}* as a sole hydride product was evidenced in ³¹P NMR spectrum at δ_P 58.6 ppm. Upon further warming a consumption of starting *fac-2^{Ph}* (δ_P 17.4 ppm) as well as appearance and gradual increase of the signal at δ_P 53.8 ppm belonging to *fac,anti-3^{Ph}* was observed, thus confirming the viability of proposed reaction mechanism.

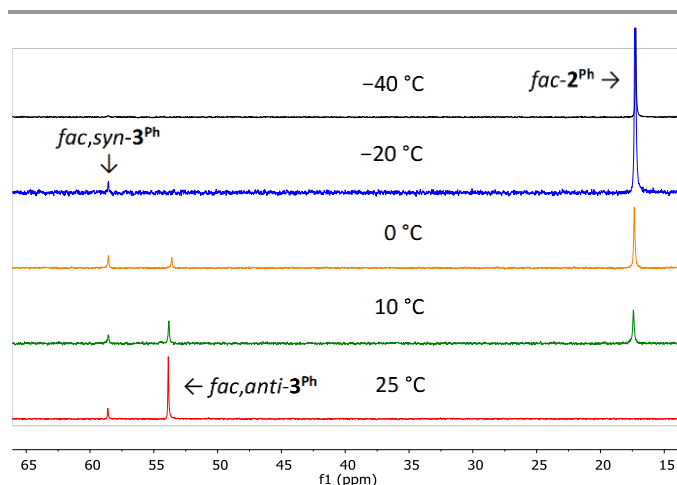


Fig. 3. ³¹P{¹H} NMR monitoring of low temperature reaction of complex *fac-2^{Ph}* with dihydrogen (toluene-*d*₈, 2 atm. of H₂, 242.9 MHz, the time between each temperature point is ca. 25–30 min).

In conclusion, this work unveils the possibility for the simple diphosphinomethane scaffold to act upon deprotonation as a non-innocent ligand for cooperative dihydrogen activation. Additionally, our work provides one more illustrative example how a subtle ligand modification can improve the desired reactivity of transition metal complex. We are currently working on the application of such Mn(I) systems in homogeneous catalysis and expansion of this approach to the cooperative activation of other inert chemical bonds.

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Conflicts of interest

There are no conflicts to declare.

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