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COMMUNICATION

Bis[diphenylphosphino]methane and its bridge-substituted analogues as chemically non-innocent ligands for H_2 activation

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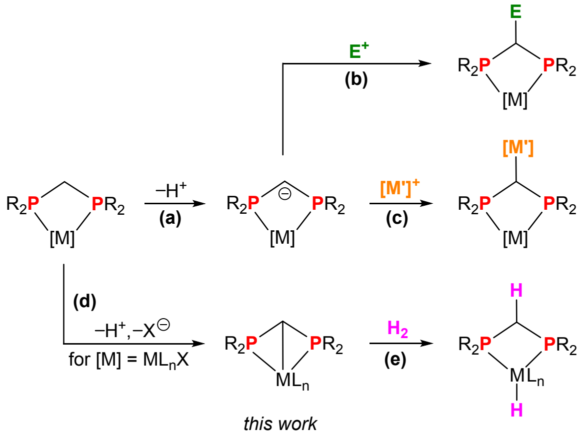
Deprotonation of *fac*-[(κ^2*P*,*P*-Ph$_2$PCH(R)PPh$_2$)Mn(CO)$_3$Br] (R = H, Me, Ph) produces the corresponding diphosphinomethanide derivatives *fac*-[(κ^3*P*,*C*,*P*-Ph$_2$PC(R)PPh$_2$)Mn(CO)$_3$], which are prone to activate H_2 to form the hydride complexes *fac*-[(κ^2*P*,*P*-Ph$_2$PCH(R)PPh$_2$)Mn(CO)$_3$H]. 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 CH_2 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 polymetallic compounds[7] (Scheme 1, (c)). We report herein the first experimental evidence that the deprotonation of dppm-type ligands can also lead to neutral cyclometallated κ^3*P*,*C*,*P*-diphosphinomethanide complexes relevant for the activation of dihydrogen *via* metal-ligand cooperation[8,9] (Scheme 1, (d) + (e)).



Scheme 1. General overview of the chemistry of transition metal diphosphinomethanide (dppm$^-$) complexes.

We have recently reported that the phosphine-*N*-heterocyclic carbene (NHC) ligand in the Mn(I) complex *fac*-[(κ^2*P*,$\hat{C}$-Ph$_2$PCH$_2$NHC)Mn(CO)$_3$Br] can be readily deprotonated at the methylene bridge to form the NHC-phosphinomethanide derivative *fac*-[(κ^3*P*,*C*,$\hat{C}$-Ph$_2$PCHNHC)Mn(CO)$_3$], which is able to activate H_2 *via* a non-classical mode of metal-ligand cooperation implying the NHC-phosphonium ylide *fac*-[(κ^2*P*,$\hat{C}$-Ph$_2$P=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 R$_2$PCH$_2$L 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*-[(κ^2*P*,*P*-Ph$_2$PCH(R)PPh$_2$)-Mn(CO)$_3$Br] (*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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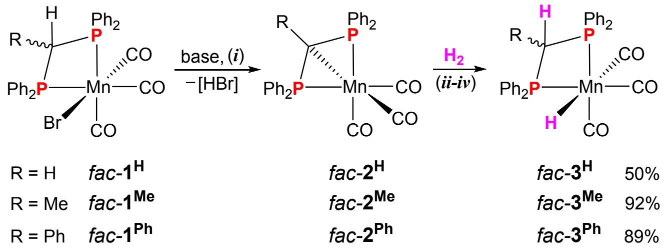

Scheme 2. Synthesis of Mn(I) diphosphinomethanide complexes *fac*-**2**^{R} (R = H, Me, Ph) and their reactivity with dihydrogen. (*i*) 1.1 eqiuv. KHMDS, toluene, 25°C; (*ii*) (R = H): 50 atm. H_2, 50°C, 16h; (*iii*) (R = Me) 50 atm. H_2, 25°C, 1 h; (*iv*) (R = Ph): 1 atm. H_2, 25°C, 5 min.

fac-**1**^{Ph}) bridge within the chelating ligands was unambiguously confirmed by ^{1}H and ^{13}C 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) κ^2*P*,*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 κ^3*P*,*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 κ^2*P*,*P* planar structures typically observed in mononuclear diphosphinomethanide transition metal complexes[12] 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 [(κ^2*P*,*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 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 L_2X-type PCP ligand.[15]

A first assessment of the reactivity of complexes *fac*-**2**^{R} toward dihydrogen was carried out under 1 atm. of H_2 at 25°C Overnight reaction of complex *fac*-**2**^{H} gave an intricate mixture of products (Fig. S15-S16), among which the H_2 activation product *fac*-[(κ^2*P*,*P*-dppm)Mn(CO)$_3$H] (*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 H_2 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 H_2 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 H_2 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 H_2 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 κ^3*P*,*C*,*P* to a κ^2*P*,*P* mode and H_2 coordination to afford the η^2-H_2 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

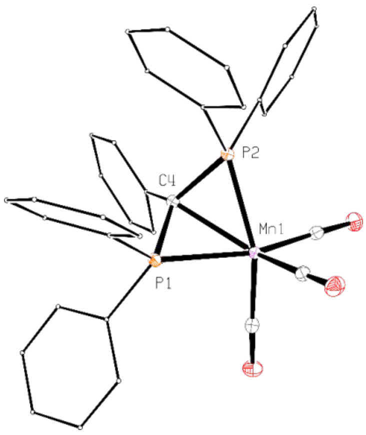

Fig. 1. A perspective view of complex *fac*-**2**^{Ph} (30% probability ellipsoids, phenyl groups are represented as wireframe). Selected bond lengths (Å) and angles (°): Mn1–P1 2.2255(9), Mn1–P2 2.2222(8), Mn1–C4 2.214(3), P1–C4 1.775(3), P2–C4 1.772(3), P1–C4–P2 103.66(15), P1–Mn1–P2 77.64(3)

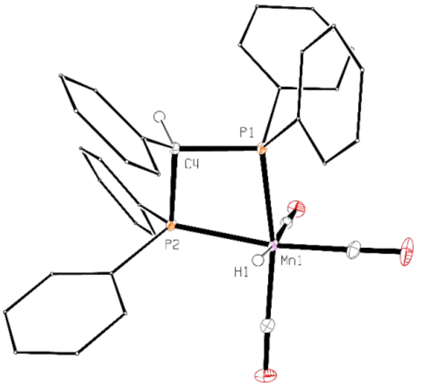

Fig. 2. A perspective view of complex *fac,anti*-**3**^{Ph} (30% probability ellipsoids, phenyl groups are represented as wireframe. Selected bond lengths (Å) and angles (°): Mn1–P1 2.2549(4), Mn1–P2 2.2830(3), P1–C4 1.8741(12), P2–C4 1.8878(12), Mn1–H1 1.53(2), P1–C4–P2 91.44(5), P1–Mn1–P2 72.808(12).

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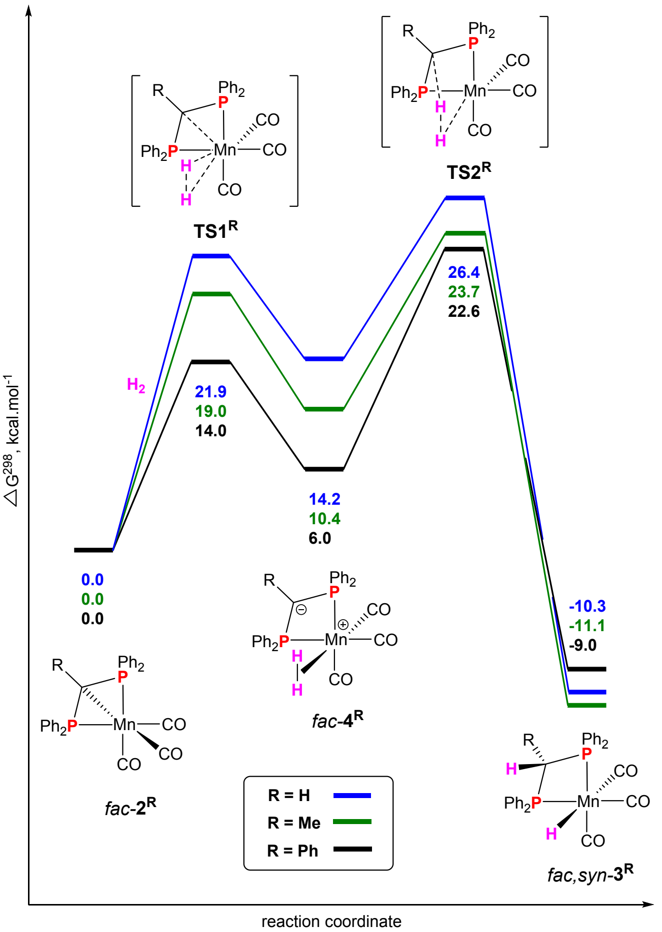
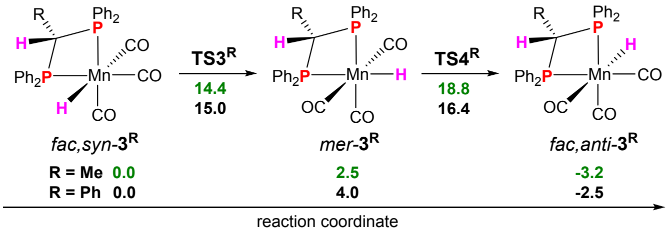


Scheme 3. DFT mechanism of cooperative H_2 activation with complexes *fac*-**2**^{R} (BP86/def2-TZVP, toluene SMD model, ΔG^{298} are given in kcal.mol^{-1} and referred to the reactants (*fac*-**2**^{R} + H_2), for the ΔH^{298} profile see Scheme S1 in the ESI).

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 H_2 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°C (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 H_2 coordination step by increasing the strain of the bicyclic [κ^3*P,C,P*]Mn system in *fac*-**2**^{R}.

While the present mechanism account for the formation *fac,syn*-**3**^{R} isomers (R $\neq$ 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*-[$(PR_3)_2Mn(CO)_3X$],[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 H_2 (2 atm.) in toluene-d_8 (Fig. 3). Unfortunately, we were unable to detect η^2-H_2 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 ^{31}P 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.

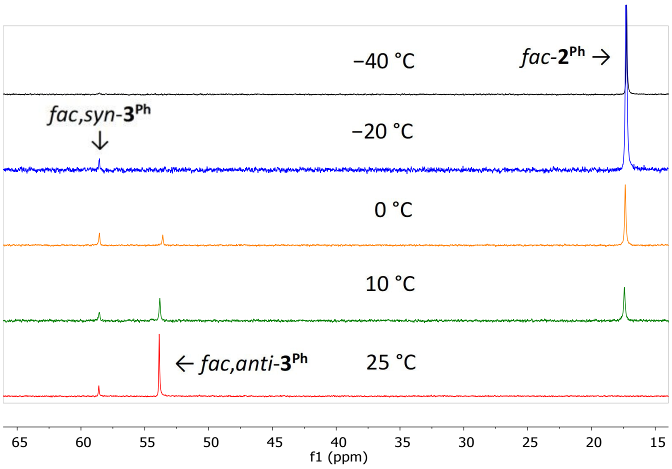


Fig. 3. $^{31}P\{^1H\}$ NMR monitoring of low temperature reaction of complex *fac*-**2**^{Ph} with dihydrogen (toluene-d_8, 2 atm. of H_2, 242.9 MHz, the time between each temperature point is *ca.* 25-30 min).

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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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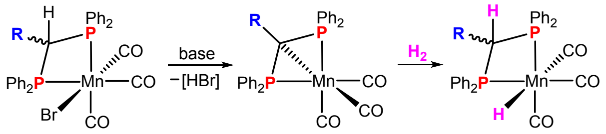

R = H (50 atm. H_2, 50 °C, 16 h) *vs.* R = Ph (1 atm. H_2, 25 °C, 5 min)

Dppm bridge substitution dramatically improves reactivity!

Interconversion between coordinated diphosphinomethane and diphosphinomethanide moieties can be used as a new tool for metal-ligand cooperation.