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P–C *versus* C–H bond cleavage in coordinated bis(dimethylphosphino)methane: controlled access to either phosphinite or functionalized diphosphine complexes

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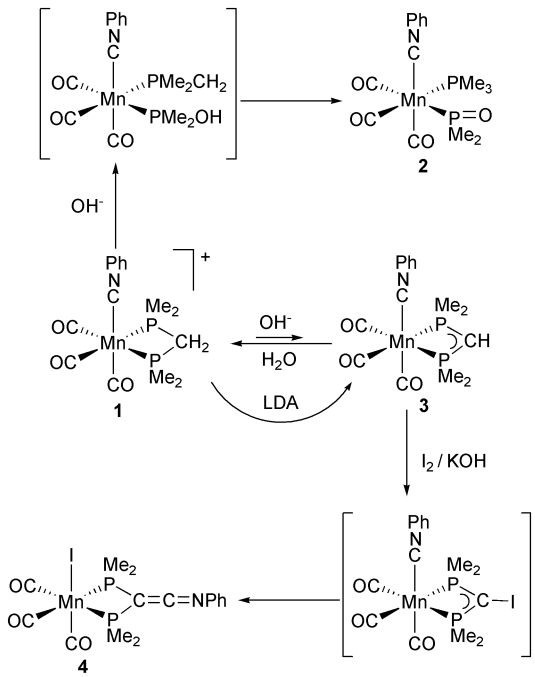
Treatment of *fac*-[Mn(CNPh)(CO)$_3$(dmpm)]ClO$_4$ (1) with KOH affords neutral phosphinite complex *fac*-[Mn(PMe$_2$O)(CNPh)(CO)$_3$(PMe$_3$)] (2) as a result of P–C bond cleavage on the dmpm ligand, whereas when carrying out the reaction in the presence of iodine the diphosphinoketenimine derivative *fac*-[MnI(CO)$_3$-{(PMe$_2$)$_2$C=C=NPh}] (4) is obtained after deprotonation and further functionalization of the central carbon atom of the diphosphine.

Basic treatment of complexes containing diphosphinomethane ligands usually produces deprotonation of the central carbon atom with formation of diphosphinomethanide derivatives,[1] which are useful reagents for the synthesis of functionalized diphosphines.[2] Moreover, it has been reported that basic treatment of [PtCl$_2$dppm] produces the cleavage of a P–C bond of the diphosphine leading to different polynuclear species containing phosphinite ligands depending upon the conditions employed.[3] It is of note that P–C bond cleavage plays an important role in deactivation pathways of phosphine complexes used as homogeneous catalysts[4] and is an active field of work.[5] In this communication, we report the first example of a coordinated diphosphine in which both C–H and P–C bond cleavages can be achieved selectively by choosing the appropriate reaction conditions, providing controlled access to either phosphinite complexes or diphosphinomethanide derivatives.

Reaction of *fac*-[Mn(CNPh)(CO)$_3$dmpm]ClO$_4$ (**1**)[6]† with an excess of KOH in CH_2Cl_2 produces, after 2 h of stirring at room temperature, the scission of a P–C bond of dmpm affording neutral phosphinite complex *fac*-[Mn(PMe$_2$O)(CNPh)-(CO)$_3$(PMe$_3$)] (**2**), a process which has no precedent in the case of alkylic diphosphines. As shown in Scheme 1, a mechanism can be assumed for this reaction involving nucleophilic attack of OH^- anion to a phosphorus atom, forming a transient complex containing hydroxydimethylphosphine and dimethylphosphinomethanide ligands, followed by intramolecular proton transfer from oxygen to carbon. Alternatively, treatment of **1** with a non-nucleophilic strong base such as lithium diisopropylamide (LDA) in THF instantaneously produces deprotonation of dmpm to give the diphosphinomethanide derivative *fac*-[Mn(CNPh)(CO)$_3${(PMe$_2$)$_2$CH}] (**3**). Compounds **2** and **3** were characterised by spectroscopic methods. The ^{31}P NMR spectrum of **2** displayed two signals, corresponding to dimethylphosphinite (δ 80.2) and trimethylphosphine (δ 12.5) ligands at usual chemical shifts, whereas the ^{13}C NMR spectrum showed signals for each methyl group of dimethylphosphinite ligand (δ 29.6, $^2J_{P-C}$ = 27 Hz; δ 29.9, $^2J_{P-C}$ = 27 Hz) according with their diasterotopic character, in addition to that of trimethylphosphine ligand (δ 18.7, $^2J_{P-C}$ = 30 Hz). Nature of **2** was unambiguously confirmed when the structure of the closely related *fac*-[Mn(PMe$_2$O)(CN*t*-Bu)(CO)$_3$(PMe$_3$)] (**2a**) was determined by X-ray analysis.‡ **2a** was prepared in an analogous procedure to that employed for **2** starting from *fac*-[Mn(CN*t*-Bu)(CO)$_3$dmpm]ClO$_4$(**1a**), but, unlike **2**, yields suitable crystals for X-ray analysis. Two molecules of **2a** were found in the asymmetric unit featuring very similar structural parameters. A view of one of them is presented in Figure 1 together with selected bond lengths and angles



Scheme 1

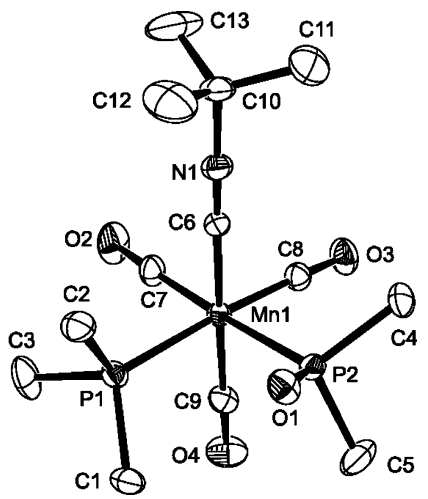


Fig. 1 ORTEP drawing of **2a**; hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Mn(1)–P(1) 2.328(5), Mn(1)–P(2) 2.341(2), P(1)–C(1) 1.795(6), P(1)–C(2) 1.799(6), P(2)–C(4) 1.794(6), P(2)–O(1) 1.492(4); P(1)–Mn(1)–P(2) 91.3(1), O(1)–P(2)–C(4) 109.5(3), O(1)–P(2)–C(5) 106.7(3), C(4)–P(2)–C(5) 98.8(4).

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Complex **3** is extremely sensitive to protonation, so that traces of water revert it to **1**, avoiding the obtention of solid pure samples of this compound. Nevertheless, the low values of the ν(CNPh) (2128 cm^{-1}) and ν(CO) (2000, 1930 cm^{-1}) frequencies, together with the appearance of a characteristic high field singlet (δ −27.2) in the ^{31}P NMR spectrum, strongly support the proposed formulation for **3**. Diphosphinomethanide ligands can be readily converted to functionalized diphosphines by reaction with electrophiles. Thus, the treatment of **3** with iodine in the presence of KOH afforded the diphosphinoketenimine derivative *fac*-[MnI(CO)$_3${(PMe$_2$)$_2$C=C=NPh}] (**4**), after formation of diphosphinoiodomethanide derivative [Mn(CNPh)(CO)$_3${(PMe$_2$)$_2$CI}] and subsequent C–C coupling of the coordinated isocyanide and the diphosphinocarbene fragment [(PMe$_2$)$_2$C:] (Scheme 1), in a parallel process to that described for the analogous dppm complexes.[7] In fact, complex **4** is easily and quantitatively obtained by direct treatment of **1** with KOH and I_2 in CH_2Cl_2 (10 min of stirring at room temperature). This result clearly shows that C–H bond cleavage in **1** by KOH may occur much faster than P–C bond cleavage, even though in the reaction of **1** with KOH no spectroscopic evidence was found of the presence of **3**, probably due to traces of moisture in the solvent. The IR spectrum of **4** showed a lack of bands corresponding to coordinated isocyanide, and ν(CO) (2011, 1952, 1908 cm^{-1}) frequencies according with a neutral *fac*-tricarbonyl derivative, whereas ^{31}P NMR spectrum showed that phosphorous atoms remain equivalents (δ 5.1). To our knowledge, the diphosphine in **4** constitutes the first example of a *P*-alkyl phosphinoketenimine[8] and it should be noted that the related [(PPh$_2$)$_2$C=C=NPh] has proved to be a valuable reagent for the synthesis of novel phosphaheterocycles.[9] It is expected that, owing to the high basicity of the methanide carbon atom, the diphosphinomethanide complex **3** may allow the synthesis of a great variety of functionalized alkylic diphosphines by carrying out the reaction of **1** and KOH in the presence of different electrophiles.

In summary, coordinated dmpm can be an appropiate entry to either phosphinite or functionalized diphosphine complexes, mediated by selective P–C or C–H bond cleavage, depending upon the reaction conditions chosen.

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Notes and references

† Satisfactory elemental analyses were obtained for **1**, **2** and **4**.

Data for **1**: IR (CH_2Cl_2, cm^{-1}): 2150 (m) ν(CNPh), 2037 (vs), 1977 (s) ν(CO); ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.54 (br, 5H, *Ph*), 3.85 (dt, 1 H, $^2J_{HH}$ = 19, $^3J_{PH}$ = 12, P$_2$C*H*$_2$), 3.56 (dt, 1 H, $^2J_{HH}$ = 19, $^3J_{PH}$ = 12, P$_2$C*H*$_2$), 1.86 (m, 12H, (P(C*H*$_3$)$_2$)$_2$); ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = −2.0 (s, br, (*P*(CH$_3$)$_2$)$_2$).

Data for **2**: IR (CH_2Cl_2, cm^{-1}): 2130 (m) ν(CNPh), 2009 (vs), 1937 (s) ν(CO); ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.45 (m, 5H), 1.71–1.60 (m, 15H); ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = 80.2 (s, br, *P*(CH$_3$)$_2$O), 12.5 (s, br, *P*(CH$_3$)$_3$); ^{13}C{^{1}H} NMR (75.47 MHz, CH_2Cl_2/D_2O): δ = 219.2 (br, *C*O), 178.9 (s, *C*NPh), 130.1–126.2 (m, Ph), 29.9 (d, $^1J_{PC}$ = 27, P(*C*H$_3$)$_2$O), 29.6 (d, $^1J_{PC}$ = 27, P(*C*H$_3$)$_2$O), 18.7 (d, $^1J_{PC}$ = 30, P(*C*H$_3$)$_3$).

Data for **3**: IR (THF, cm^{-1}): 2128 (m) ν(CNPh), 2000 (vs), 1930 (s) ν(CO); ^{31}P{^{1}H} NMR (121.5 MHz, THF/D_2O): δ = −27.2 (s, br, *P*(CH$_3$)$_2$).

Data for **4**: IR (CH_2Cl_2, cm^{-1}): 2011 (vs), 1952 (s), 1908 (m) ν(CO); ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.47–7.32 (m, 5H, *Ph*), 2.00–1.86 (m, 12H, (P(C*H*$_3$)$_2$)$_2$); ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = 5.1 (s, br, (*P*(CH$_3$)$_2$)$_2$).

‡ *Crystal data* for **2a** ($C_{13}H_{24}MnNO_4P_2{\cdot}H_2O$): M = 393.23, crystal size 0.46 × 0.46 × 0.20 mm, a = 10.526(2), b = 14.56(1), c = 14.59(3)Å, α = 108.43(8), β = 98.3(1), γ = 98.58(7)°, V = 2054(5) Å^3, ρ_{calcd} = 1.272 g cm^{-3}, μ = 0.816 mm^{-1}, Z = 4, triclinic, space group $P\bar{1}$, λ = 0.71073 Å, T = 293(2) K, θ_{max} = 25.97, independent reflections = 8009, refined parameters = 411, $R1$ = 0.0438, $wR2$ = 0.1103, largest diff. peak and hole 0.50 and −0.52 e $Å^{-3}$. CCDC 210714. See http://www.rsc.org/suppdata/cc/b3/b305316d/ for crystallographic data in .cif or other electronic format. Two molecules of the complex were found in the asymmetric unit. Both molecules have very similar structural parameters, with differences arising from the presence of two molecules of water displaying O–H···O hydrogen bonds with the oxygen atom of the phosphinite ligand in one of them.

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