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Metal-Assisted Synthesis of dppm-Derived Diphosphines Involving the Formation of Three New Types of Frameworks around Carbon: P_2CHX, $[P_2CX]^-$, and P_2CX_2 (X = Halogen)

Javier Ruiz, René Arauz, Víctor Riera,* and Marilin Vivanco
Instituto de Química Organometálica, Universidad de Oviedo, 33071 Oviedo, Spain
Santiago García-Granda and Amador Menéndez-Velázquez
Departamento de Química Física y Analítica, Universidad de Oviedo, 33071 Oviedo, Spain

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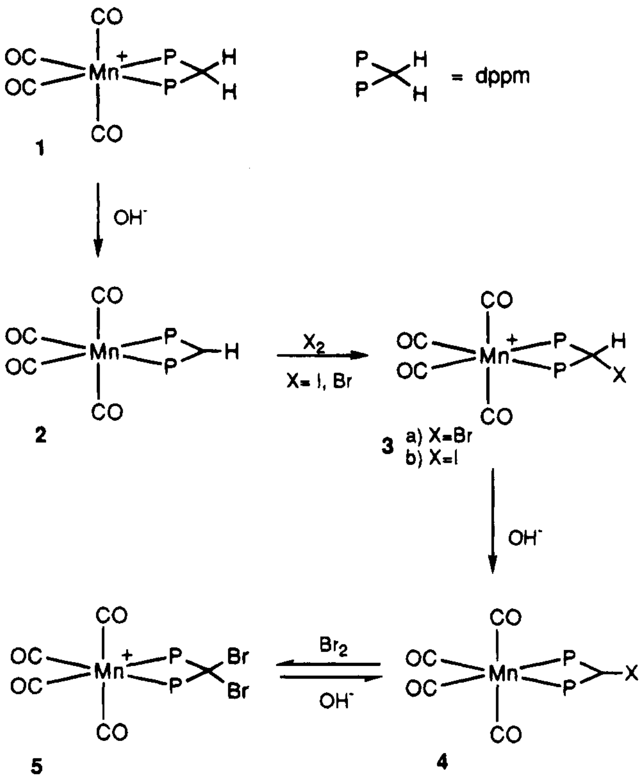
Summary: The new halogenated diphosphines [$(PPh_2)_2C(H)(X)$], [$(PPh_2)_2CX_2$], and the anion [$(PPh_2)_2CX]^-$, coordinated to manganese(I), have been obtained by using a suitable sequence of deprotonation−halogenation reactions on [$Mn(CO)_4(dppm)]ClO_4$ (1). This implicates the formation of three new basic cores around carbon: P_2CHX, $[P_2CX]^-$, and P_2CX_2.

The importance in coordination chemistry of diphosphine ligands, e.g. bis(diphenylphosphino)methane (dppm),[1] is now widely recognized, due to their ability to stabilize mono- and binuclear metallic complexes in a variety of oxidation states as well as to the application of these complexes in the field of homogeneous catalysis.[2] In this respect it is always a fundamental goal to accomplish the synthesis of new diphosphines displaying different steric and electronic features. In this context we report here the preparation of new general types of halogenated diphosphines derived from coordinated dppm, having the heretofore unknown basic cores P_2CHX, $[P_2CX]^-$, and P_2CX_2.

Our synthetic approach is illustrated in Scheme 1. Halogenation of dppm in the octahedral complex [$Mn(CO)_4(dppm)]ClO_4$ (**1**)[3] is performed by previously transforming it into the corresponding bis(diphenylphosphino)methanide derivative **2** by treatment with KOH. We have already made use of the nucleophilic character at the central carbon atom of the methanide in **2** to prepare a number of heterometallic species.[4,5] We have now found that **2** can also react with dihalogen molecules (I_2, Br_2) to promote a heterolytic cleavage of the halogen−halogen bond, giving rise to the halogenated derivative **3**.[6] In order to prevent the formation of a considerable amount of **1** and **4**, by means of a proton transfer from **3** to **2**, an excess of halogen must be used.

Scheme 1



Coordinating with manganese through the phosphorus makes the halogenation reaction of the diphosphinomethanide ligand chemoselective on the carbon atom, preventing halogenation from taking place on the phosphorus atoms, as occurs in free tertiary phosphine ligands.[7] In this respect it has been shown that the treatment of $Li^+[(PPh_2)_2CH]^-$ with electrophiles generally gives mixtures corresponding to attack on carbon and phosphorus atoms.[8]

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1994.

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[3] (a) Carriedo, G. A.; Riera, V. *J. Organomet. Chem.* **1981**, *205*, 371. (b) Data for **1**: FTIR (CH_2Cl_2) ν(CO) 2094 (m), 2027 (m), 2014 (s), 1999 (sh) cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 5.24 (t, $^2J_{H-P} = 12$ Hz, P_2CH_2).

[4] Ruiz, J.; Riera, V.; Vivanco, M.; García-Granda, S.; García-Fernández, A. *Organometallics* **1992**, *11*, 4077.

[5] For other recent publications on diphosphinomethanide chemistry, see: (a) Ruiz, J.; Riera, V.; Solans, X.; Tauler, E. *J. Chem. Soc., Dalton Trans.* **1990**, 1607. (b) Ruiz, J.; Araúz, R.; Riera, V.; Vivanco, M.; García-Granda, S.; Pérez-Carreño, E. *J. Chem. Soc., Chem. Commun.* **1993**, *9*, 740. (c) Laguna, A.; Laguna, M. *J. Organomet. Chem.* **1990**, *394*, 743. (d) Karsch, H. H.; Deubelly, B.; Grauvogl, G.; Lachmann, J.; Muller, G. *Organometallics* **1992**, *11*, 4245. (e) Karsch, H. H.; Grauvogl, G.; Kawecki, M.; Bissinger, P. *Organometallics* **1993**, *12*, 2757. (f) Karsch, H. H.; Grauvogl, G.; Kawecki, M.; Bissinger, P.; Kumberger, O.; Schier, A.; Muller, G. *Organometallics* **1994**, *13*, 610. (g) Karsch, H. H.; Farazin, G.; Steigelmann, O.; Kooijman, H.; Hiller, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1739. (h) Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; López-de-Luzuriaga, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 87.

[6] Synthesis of **3a**: A solution of {$Mn(CO)_4[(PPh_2)_2CH]$} (**2**; 0.20 g, 0.36 mmol) in 20 mL of CH_2Cl_2 was added dropwise to an excess of bromine (0.13 mL, 2.54 mmol) at room temperature with continuous stirring. The solvent was then evaporated to dryness and the residue washed with *n*-hexane (30 mL). A yellow crystalline solid was obtained (0.30 g, 96%). The product can be recrystallized from CH_2Cl_2/*n*-hexane. Synthesis of **3b**: This was similarly prepared from {$Mo(CO)_4[(PPh_2)_2CH]$} (**2**; 0.20 g, 0.36 mmol) and an excess of iodine (0.64 g, 2.54 mmol). After it was washed with *n*-hexane (3 × 20 mL), the red solid obtained was recrystallized from CH_2Cl_2/*n*-hexane. Yield: 0.29 g (76%).

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The conductivity values for compounds of type **3** are in the range for 1:1 electrolytes, and the analytical data are consistent with their formulation as $[X_3]^-$ salts.[9] The structure of the complex cation was unambiguously established by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopy.[10] Notably, in the proton spectrum of **3** the P_2CHX hydrogen appears as a triplet at higher frequency (about 1 ppm) than the P_2CH_2 hydrogens in **1**.[3] Moreover, the IR spectra of **3** show higher values for the ν(CO) absorptions than those of **1**.[3] All these data indicate that the remaining P_2CHX hydrogen atom in **3** has an enhanced acidic character. Consequently, a further deprotonation reaction can easily be carried out by treatment with KOH to give **4**,[10,11] a neutral complex containing the remarkable halodiphosphinomethanide anion $[(PPh_2)_2C(X)]^-$. In order to fully structurally characterize the new ligand, an X-ray diffraction study has been carried out for **4b**.[12] The molecular structure (Figure 1) shows the manganese in a distorted-octahedral coordination geometry. The MnP_2CI skeleton is planar, and the P(1)−C(1) and P(2)−C(1) distances (1.706(5) and 1.730(5) Å, respectively) are shorter than the corresponding ones in dppm derivatives (1.85 Å),[1a] thus evidencing some double-bond character, as occurs in other diphosphinomethanide derivatives.[5] In accordance with this the C(1)−I distance (2.115(4) Å) is only slightly longer than that in iodoarenes.[13] These structural data are consistent with C(1) adopting an sp^2 hybridization, the negative charge of the methanide ligand being delocalized through the PCP skeleton. Some comparison can be made between the P_2CI unit in **4b** and the N_2CI unit in the 2-iodoimidazolium ion $[C(CH_3){=}C(CH_3)N(Et)C(I)N(Et)]^+$,[14] which also may be regarded as a carbene−I^+ adduct, although in **4b** the P_2CI fragment is electronically richer.

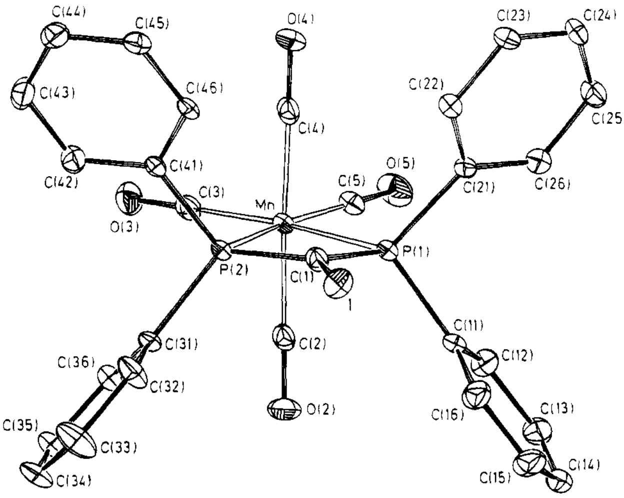

Figure 1. ORTEP drawing of $[Mn(CO)_4\{(PPh_2)_2CI\}]$ (**4b**) showing 30% probability ellipsoids. Selected bond distances (Å) and angles (deg): C(1)−I = 2.115(4), P(1)−C(1) = 1.706(5), P(2)−C(1) = 1.730(5); P(1)−C(1)−P(2) = 103.5(2), P(1)−C(1)−I = 129.5(3), P(2)−C(1)−I = 126.9(3).

Owing to the nucleophilicity at the central carbon atom of the methanide, complex **4a** reacts with an excess of bromine, affording the dihalogenated-dppm cationic derivative **5** in quantitative yield, the counteranion being $[Br_3]^-$.[9,10,15] Efforts to prepare the analogous iodine derivative by treatment of **4b** with iodine resulted in the formation of a complex mixture of species, so far uncharacterized. The diphosphine $[(PPh_2)_2C(Br)_2]$ in **5** is an interesting example in which a tetrahedral carbon atom has only heteroatom substituents. The bromine atoms bonded to the carbon are appreciably electrophilic; thus, by treatment of **5** with KOH the methanide derivative **4a** is obtained.

In conclusion, in this work we have carried out the preparation of new general types of diphosphines having the new basic cores P_2CHX, $[P_2CX]^-$, and P_2CX_2, by using a suitable sequence of deprotonation−halogenation reactions on coordinated dppm. Apart from their inherent significance, an important feature of these ligands is their potential use as starting materials for the synthesis of a variety of functionalized diphosphines.

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Supplementary Material Available: Text giving details of the X-ray crystal structure determination and tables of positional parameters, bond lengths and angles, anistropic thermal parameters, torsion angles, and least-squares planes for **4b** and text giving details of the syntheses of **3a**,**b**, **4a**,**b**, and **5** (14 pages). Ordering information is given on any current masthead page.

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(9) Conductivity (acetone, 5×10^{-4} M) and analytical data for the new compounds are as follows. **3aBr₃**: conductivity 140 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{29}H_{21}Br_4MnO_4P_2$: C, 40.04; H, 2.43. Found: C, 40.37; H, 2.34. **3bI₃**: conductivity 126 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{29}H_{21}I_4MnO_4P_2$: C, 32.92; H, 2.00. Found: C, 32.71; H, 1.93. **4a**: Anal. Calcd for $C_{29}H_{20}BrMnO_4P_2$: C, 55.35; H, 3.20. Found: C, 55.31; H, 3.20. **4b**: Anal. Calcd for $C_{29}H_{20}IMnO_4P_2$: C, 51.51; H, 2.98. Found: C, 51.23; H, 2.80. **5Br₃**: conductivity 132 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{29}H_{20}Br_5MnO_4P_2$: C, 36.71; H, 2.12. Found: C, 36.51; H, 2.08.

(10) Key spectroscopic data are as follows. **3a**: FTIR (CH_2Cl_2) ν(CO) 2097 (s), 2038 (m), 2016 (vs) cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 6.23 (t, $^2J_{H-P}$ = 10 Hz, 1H, P_2CHBr); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 43.7 (t, $^1J_{C-P}$ = 10 Hz, P_2CHBr); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ 41.0 (s, P_2CHBr). **3b**: FTIR (CH_2Cl_2) ν(CO) 2096 (s), 2037 (m), 2015 (vs) cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 6.46 (t, $^2J_{H-P}$ = 11 Hz, 1H, P_2CHI); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 15.2 (t, $^1J_{C-P}$ = 10 Hz, P_2CHI); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ 33.0 (s, P_2CHI). **4a**: FTIR (CH_2Cl_2) ν(CO) 2075 (s), 1995 (vs), 1965 (s) cm^{-1}; ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 1.22 (t, $^1J_{C-P}$ = 50 Hz, P_2CBr); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ 10.1 (very broad, P_2CBr). **4b**: FTIR (CH_2Cl_2) ν(CO) 2074 (s), 1993 (vs), 1965 (s) cm^{-1}; ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ −34.7 (t, $^1J_{C-P}$ = 46 Hz, P_2CI): $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ 5.2 (very broad, P_2CI). **5**: FTIR (CH_2Cl_2) ν(CO) 2100 (s), 2041 (m), 2025 (vs) cm^{-1}; ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 64.4 (t, $^1J_{C-P}$ = 3 Hz, P_2CBr_2); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ 75.0 (s, P_2CBr_2).

(11) Synthesis of **4a**: An excess of KOH (1 g) was added to a solution of **3a** (0.2 g, 0.23 mmol) in 20 mL of CH_2Cl_2. The mixture was stirred until the IR spectrum of the solution showed no bands corresponding to **3a** (2 h approximately). The resulting yellow solution was filtered off and concentrated to 5 mL. Addition of *n*-hexane and cooling (−20 °C) gave yellow crystals of the product (0.12 g, 83%). Synthesis of **4b**: This was similarly prepared from **3b** (0.15 g, 0.14 mmol). Yield: 0.077 g (81%). Pale yellow crystals of **4b**·CH_2Cl_2 for the X-ray diffraction study were obtained by recrystallization from CH_2Cl_2/*n*-hexane.

(12) Crystal data of **4b**·CH_2Cl_2: orthorhombic, space group $P2_12_12_1$, a = 9.038(3) Å, b = 17.673(7) Å, c = 18.972(5) Å, V = 3030(2) Å^3, Z = 4, D_{exptl} = 1.67 g cm^{-3}, Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation (graphite crystal monochromator, λ = 0.710 73 Å), μ = 17.42 cm^{-1}, F(000) = 1504, T = 200 K, final conventional R = 0.025 and wR2 = 0.069 for 2620 "observed" reflections and 448 variables.

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(15) Synthesis of **5**: A solution of **4a** (0.15 g, 0.24 mmol) in 20 mL of CH_2Cl_2 was added dropwise to an excess of bromine (0.061 mL, 1.18 mmol). The resulting mixture was stirred for 10 min, and then the solvent was evaporated to dryness under reduced pressure. The residue was washed with *n*-hexane (20 mL), giving a yellow solid (0.21 g, 93%). The product can be recrystallized from CH_2Cl_2/*n*-hexane.