

Preliminary communication

NEW OCTAHEDRAL BIS(DIPHENYLPHOSPHINO)METHANIDE DERIVATIVES AND HETEROMETALLIC SPECIES FROM MIXED LIGAND ISOCYANIDE-dppm IRON(II) COMPLEXES

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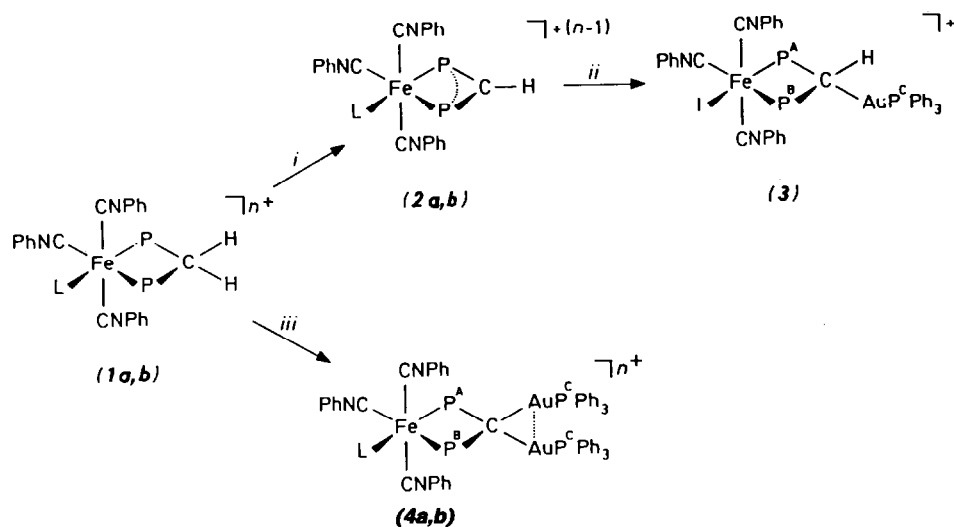
Summary

The cationic complexes $[\text{FeL}(\text{dppm})(\text{CNPh})_3]^{n+}$ (**1a**: L = I, $n = 1$; **1b**: L = CNPh, $n = 2$) are readily deprotonated by KOH to give $[\text{FeL}(\text{dppm-H})(\text{CNPh})_3]^{n-1}$ (**2a** and **2b**). **2a** reacts with $[\text{tHtAuPPh}_3]\text{PF}_6$ to give *mer*- $[\text{FeI}((\text{PPh}_2)_2\text{C}(\text{H})(\text{AuPPh}_3))(\text{CNPh})_3]\text{PF}_6$ (**3**). The new heterotrimetallic species $[\text{FeL}((\text{PPh}_2)_2\text{C}(\text{AuPPh}_3)_2)(\text{CNPh})_3]^{n+}$ (**4a** and **4b**) have been obtained from **1a** and **1b** by treatment with ClAuPPh_3 in the presence of KOH.

Bis(diphenylphosphino)methanide ion (dppm – H), has proved to be a valuable ligand in coordination chemistry. It can act as bidentate or tridentate by bonding to one, two, or three metal atoms through the phosphorus and the central carbon atom [1]. Although the (dppm – H) ligand was originally obtained by deprotonating dppm with strong bases [2], it can be generated much more easily by direct deprotonation of coordinated dppm [3–5].

Thus we have found that treatment of the cationic compounds *mer*- $[\text{FeI}(\text{dppm})(\text{CNPh})_3]\text{I}$ (**1a**) and $[\text{Fe}(\text{dppm})(\text{CNPh})_4](\text{ClO}_4)_2$ (**1b**) [6] with an excess of KOH in CH_2Cl_2 gives the new neutral and cationic derivatives: *mer*- $[\text{FeI}(\text{dppm-H})(\text{CNPh})_3]$ (**2a**) and $[\text{Fe}(\text{dppm-H})(\text{CNPh})_4]\text{ClO}_4$ (**2b**) * (see Scheme 1). Most of previously known compounds containing the ligand dppm–H in a chelating mode are square-planar derivatives, and there are very few examples of octahedral

* Selected spectroscopic data for 2–4: **2a**: IR $\nu(\text{CN})$ (CH_2Cl_2): 2150w and 2102s; $^{31}\text{P}\{^1\text{H}\}$ NMR (CH_2Cl_2) (positive chemical shifts are to high frequency relative to external 85% H_3PO_4): δ 16.3 (d), –18.8 (d), J 46 Hz. **2b**: IR $\nu(\text{CN})$ (CH_2Cl_2): 2180w, 2138s and 2120sh; $^{31}\text{P}\{^1\text{H}\}$ NMR (CH_2Cl_2): δ –8.9(s); ^1H NMR (CDCl_3): δ 2.45 (CH, t, $J(\text{PH})$ 4.7 Hz). **3**: IR $\nu(\text{CN})$ (THF): 2160w, 2120s; $^{31}\text{P}\{^1\text{H}\}$ NMR (CH_2Cl_2): δ 48.5 (dd, P^{A}), 6.0 (dd, P^{B}), 38.7 (t, P^{C}) ($J(\text{AB})$ 66 $J(\text{AC}) = J(\text{BC}) = 11$ Hz). **4a**: IR $\nu(\text{CN})$ (CH_2Cl_2): 2157m, 2115s; $^{31}\text{P}\{^1\text{H}\}$ NMR (CH_2Cl_2): δ 60.0 (dt, P^{A}), 19.1 (dt, P^{B}), 35.7 (t, P^{C}) ($J(\text{AB})$ 64, $J(\text{BC}) = J(\text{AC}) = 9$ Hz). **4b**: IR $\nu(\text{CN})$ (CH_2Cl_2): 2187m, 2145s; $^{31}\text{P}\{^1\text{H}\}$ NMR (CH_2Cl_2): δ 35.7 (t), 27.8 (t), $J = 8$ Hz.



SCHEME 1. (i). excess of KOH; CH_2Cl_2 . (ii). $\text{L} = \text{I}$; $[(\text{tth})\text{AuPPh}_3]\text{PF}_6$ (1 equiv.); thf. (iii). ClAuPPh_3 (2 equiv.); excess of KOH; CH_2Cl_2 .

geometry. Compound **2b** is also the first example of a cationic octahedral dppm-H derivative.

It is known that compounds with dppm-H ligand can be attacked by electrophiles RX ($\text{X} = \text{halogen}$, $\text{R} = \text{Me}$, Et , PhCO , etc.) at the central CH group [7,8], and also react with silver and gold complexes to give heterometallic compounds [9]. Treatment of **2a** with the cationic species $[(\text{tth})\text{AuPPh}_3]\text{PF}_6$ ($\text{tth} = \text{tetrahydrothiophene}$) in thf, readily afforded the bimetallic complex $[\text{FeI}((\text{PPh}_2)_2\text{C}(\text{H})(\text{AuPPh}_3))(\text{CNPh})_3]\text{PF}_6$ (**3**) * (see Scheme 1). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3**, which showed two doublets of doublets (P^A and P^B) and a triplet (P^C) was in accord with this formulation. Reactions of the dppm-H derivatives with organic electrophiles were less clear cut. Thus compounds **2b** and **2b** failed to react with MeI to give C-methyl-substituted complexes, and use of stronger alkylating agents such as $\text{Me}_3\text{O}^+\text{SbCl}_6^-$ resulted mainly in the formation of the starting dppm derivatives **1a** and **1b**.

On the other hand, the reaction of **1a** and **1b** with ClAuPPh_3 in a 1/2 molar ratio in CH_2Cl_2 in the presence of KOH gave complexes of the type $[\text{FeL}((\text{PPh}_2)_2\text{C}(\text{AuPPh}_3)_2(\text{CNPh})_3)]^{n+}$ (**4a**: $\text{L} = \text{I}$, $n = 1$; **4b**: $\text{L} = \text{CNPh}$, $n = 2$) (see Scheme 1). Those are the first examples of replacement of both of the CH_2 protons of the dppm ligand by metallic moieties. In agreement with the proposed structures, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showed two triplets for compound **4b**, and two doublets of triplets (P^A and P^B) and a pseudotriplet (P^C) for compound **4a**. The possibility of a gold-gold interaction which is usually found in complexes with two "AuPPh₃" groups bonded to one carbon atom [10], could not be confirmed, because we have so far been unable to obtain crystals suitable for an X-ray structural determination.

* Formed in situ from ClAuPPh_3 , TlPF_6 and that, in thf as solvent.

Exploration of the possibility of obtaining new heterometallic complexes by treating **2a** and **2b** with a variety of metallic species containing labile ligands, and by extension of the reaction of compounds **1a** and **1b** to those with other transition metal complexes of general formula XML_n (X = halogen, M = metal, L = neutral ligand) are in progress.

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