## **Accepted Manuscript**

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PII: S0022-328X(13)00212-X

DOI: 10.1016/j.jorganchem.2013.03.027

Reference: JOM 17937

To appear in: Journal of Organometallic Chemistry

Received Date: 12 February 2013

Revised Date: 13 March 2013 Accepted Date: 14 March 2013

Please cite this article as: § . § ztopcu, B. StÇger, K. Mereiter, K.A. Kirchner, Reactivity of Iron Complexes containing Monodentate Aminophosphine Ligands - Formation of Four-Membered Carboxamido-Phospha-Metallacycles, *Journal of Organometallic Chemistry* (2013), doi: 10.1016/j.jorganchem.2013.03.027.

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Reactivity of Iron Complexes containing Monodentate Aminophosphine Ligands -Formation of Four-Membered Carboxamido-Phospha-Metallacycles

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**Abstract** 

Treatment of  $[FeCp(CO)_2CI]$  with 1 equiv of the amidophosphine ligands  $Li[R_2PNR']$  (R = Ph, iPr, R' = iPr, tBu, Cy) afforded complexes of the type  $[FeCp(CO)(\kappa^2(C,P)-(C=O)-NiPr-PPh_2)]$  (1a),  $[FeCp(CO)(\kappa^2(C,P)-(C=O)-NiPr-PPh_2)]$ 

 $NtBu-PPh_2$ ] (1b), and  $[FeCp(CO)(\kappa^2(C,P)-(C=O)-NCy-PtPr_2)]$  (1c) in 40-50% yields. Complex 1a was also

formed when [FeCp(CO)<sub>2</sub>(PPh<sub>2</sub>NH/Pr)]<sup>+</sup> (2) was reacted with 1 equiv of KOtBu. These complexes feature a

four-membered carboxamido-phospha-ferracycle as a result of an intramolecular nucleophilic attack of the

amidophosphine ligand on coordinated CO. Upon treatment of 1a with the electrophile [Me<sub>3</sub>O]BF<sub>4</sub> the

aminocarbene complex  $[FeCp(CO)(\kappa^2(C,P)=C(OMe)-NiPr-PPh_2)]^+$  (3) was obtained bearing an aza-phospha-

carbene moiety. Upon treatment of cis,trans,cis-[Fe(CO)<sub>2</sub>(Ph<sub>2</sub>PNH<sub>i</sub>Pr)<sub>2</sub>(Br)<sub>2</sub>] (4a) and cis,trans,cis-

 $[Fe(CO)_2(Ph_2PNHtBu)_2(Br)_2]$  (4b) with KOtBu the carboxamido-phospha-ferracycles trans- $[Fe(CO)_2(\kappa^2(C,P)-$ 

 $(C=O)-NiPr-PPh_2)(Ph_2PNHiPr)Br$ ] (5a) and  $trans-[Fe(CO)_2(\kappa^2(C,P)-(C=O)-NtBu-PPh_2)(Ph_2PNHtBu)Br$ ] (5b)

were formed in moderate yield. Finally, representative structures were determined by X-ray crystallography.

Keywords: Iron, cyclopentadienyl, carbon monoxide, aminophosphines, nucleophilic attack, ferracycles

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