Title: **Synthesis and characterization of cyclometallated complexes of imines: 4-ClC6H4CH=NCH2(4'-FC6H4) and 2,3-F2C6H3CH=NCH2(4'-FC6H4). Expanding the scope of cyclopalladations.**

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Date: January 2019

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The treatment of 4-fluorobenzylamine with 4-chlorobenzaldehyde or 2,3-difluorobenzaldehyde in acetone at 80ºC afforded the corresponding imines (**1**), 4-$ClC_6H_4CH=NCH_2(4'-FC_6H_4)$ and $2,3-F_2C_6H_3CH=NCH_2(4'-FC_6H_4)$ respectively, which were isolated in a yield >90%. The same reaction was performed in milder conditions obtaining similar results. The imines (**1**) reacted with a stoichiometric amount of $Pd(OAc)_2$ in acetic acid affording the corresponding acetato-bridged five-membered *ortho*-cyclopalladated dimers (**2**) in 44-69% yield. The reaction was reproduced in different conditions to improve the yield, obtaining the best results at 85ºC for 1h. Compounds **2** were converted by a metathesis reaction with an excess of LiCl and LiBr in acetone into the corresponding chloro- or bromo-bridged dinuclear cyclopalladated compounds. The stoichiometric amount of PPh_3 and dppe was added to the halogen-bridge compounds to obtain the mononuclear compounds *trans*-N,L-[Pd{RHC=$NCH_2(4'-FC_6H_4)$}(X)(L)] [**3-A** (R= 4-ClC_6H_4, X= Br, L= PPh_3); **3-B** (R= 2,3-$F_2C_6H_3$, X = Br, L = PPh_3); **4-A** (R= 4-ClC_6H_4, X= Cl, L= PPh_3); and the dinuclear compounds **5-A** (R= 4-ClC_6H_4, X= Br, L= dppe); **5-B** (R= 2,3-$F_2C_6H_3$, X= Br, L= dppe)] in 50-90% yield. The compounds obtained were characterized by ^1H NMR, ^{31}P NMR spectroscopy –in $CDCl_3$ solution–, elemental analyses, mass spectrometry, and IR spectroscopy.

Some tendencies have been found in this work: i) the *E* isomer of the imine was isolated in all reactions; ii) the *ortho*-fluoro atoms show an interaction with the imine proton; iii) the *endo*-palladacycle is the thermodynamic control isomer; iv) the aromatic protons of the metallated ring are high field shifted in compounds containing phosphines, showing a *trans* arrangement between the phosphines and the nitrogen atom in agreement with the transphobia; v) the methinic proton signal in proton NMR spectra is displaced toward high fields confirming the nitrogen-metal bond.