

## E2-11: Synthesis and reactivity of some iridium complexes of an azine diphosphine

Sarath D Perera

(Open University, Nawala, Nugegoda)

The azine diphosphine  $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2$ , (LH), (1) has the Z,Z- configuration around the C=N bonds and forms a 9-membered chelate ring with gold(I). The energy barrier to rotation around the C=N bond is relatively low and the ligand can undergo C=N bond isomerisation to give the E,Z-configuration which forms (P-N-P) terdentate complexes with group 6, 8 and 10 metal centres. Therefore, it is of interest to investigate the coordination and organometallic chemistry of this ligand with group 9 metal centres.

Synthesis and reactivity of some iridium complexes are described here. Treatment of the azine diphosphine, LH (1) with  $[\text{IrCl}(\text{CO})_2(\text{p-toluidine})]$  gave the octahedral iridium (III) hydride *mer*- $[\text{IrHCl}(\text{CO})(\text{L})](2)$  [ $\delta_{\text{H}} = -15.40$  ppm] containing 5- and 6-membered chelate rings, where  $\text{L} = [\text{PPh}_2\text{CH}=\text{C}(\text{Bu}^t)\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2]^-$  and it acts as an anionic terdentate (P-N-P) ligand. Dehydrochlorination of (2) with  $\text{NEt}_3$  gave the square-planar iridium(I) complex  $[\text{Ir}(\text{CO})(\text{L})](3)$ . The backbone of (3) was protonated with picric acid to give the picrate salt  $[\text{Ir}(\text{CO})(\text{L})][\text{picrate}](4)$ . The complex (3) underwent oxidative addition reactions with  $\text{H}_2$  to give the iridium (III) dihydride *mer, cis*- $[\text{IrH}_2(\text{CO})(\text{L})](5)$  [ $\delta_{\text{H}}$  at -8.62 and -15.78 ppm], and with MeI to give the methyliridium (III) complex *mer*- $[\text{IrI}(\text{Me})(\text{CO})(\text{L})](6)$  [ $\delta_{\text{H}}(\text{Me}) = 0.14$  ppm]. The complex (3) readily formed 5-coordinate adducts with olefins and acetylenes—thus with *N*-methylmaleimide (Y) it gave  $[\text{Ir}(\text{CO})(\text{L})(\text{Y})](7\text{a})$  [ $\delta_{\text{H}}(\text{NMe}) = 2.85$  ppm]; with ethene it gave  $[\text{Ir}(\text{CO})(\text{L})(\text{CH}_2=\text{CH}_2)](7\text{b})$  [ $\delta_{\text{H}}(\text{CH}_2 = \text{CH}_2)$  at 1.15, 1.83, 2.06 and 2.41 ppm] and with dimethyl acetylenedicarboxylate (Z) it gave  $[\text{Ir}(\text{CO})(\text{L})(\text{Z})](7\text{c})$  [ $\delta_{\text{H}}(\text{OMe})$  at 3.41 and 3.69 ppm]. The reaction of (3) with dioxygen gave the adduct  $[\text{Ir}(\eta^2\text{-O}_2)(\text{CO})(\text{L})](8)$