

## Rhodium complexes of an azine diphosphine

There is an interest in the use of (P-N) ligands to generate new coordination, organometallic or catalytic chemistry. The azine diphosphine

$Z, Z\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2$  (**1**) was prepared by dilithiation of  $\text{MeC}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{Me}$  followed by treatment with  $\text{PPh}_2\text{CL}$ . The energy barrier to rotation around the C=N bond is relatively low. Thus, the ligand (**1**) can undergo C=N bond isomerisation to give the E, Z-form (E, Z-**1**), which can now form (P-P) and (P-N-P) chelates. Since rhodium complexes are good catalysts for hydrogenation, hydroboration and hydroformylation reactions it was decided to study the coordination and organometallic chemistry of (**1**) with Rh. Syntheses of some rhodium complexes are described here. Treatment of the chlorodicarbonylrhodium (I) dimer  $[\text{RhCl}(\text{CO})_2]_2$  with 2 moles of (**1**) in benzene gave

the binuclear metallacycle  $[(\text{CO})\text{CIRh}(\mu^-)_2\text{RhCl}(\text{CO})]$  (**2**) where (**1**) acts as a

bridging ligand through both phosphorus atoms forming a 18-atom ring. The initial molecular weight of **(2)** was 1280 Dalton.

However, this binuclear complex **(2)** was not stable in CHCl<sub>3</sub> and gradually dissociated to the monomeric square-planar complex [Rh(CO)(E,Z-1)]Cl(**3a**) During this conversion, **(1)** has isomerised to its E,Z,-form (E,Z-1) which now acts as a terdentate (P-N-P) ligand forming two fused five and six membered rings. The phosphorus-31 NMR data of **(3a)**

{ $\delta_P$  = 63.6, (