E2-23 Synthesis and structure of a unique gold complex containing a 9-member chelate ring with a large bite angle

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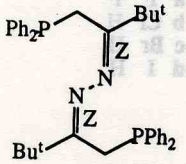
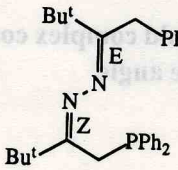
The azine diphosphine (**1**) has the Z,Z-configuration around the C=N bonds, that means the PPh_2 groups are pointing in opposite directions. This Z,Z-azine diphosphine did not chelate through both P atoms to form octahedral or square-

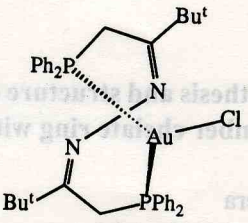
planar complexes, containing 9-membered ring, with group 6 metal carbonyls, Pt or Pd, possibly, because the ligand is not flexible enough to have a relatively small P-M-P angle of about 90° which is required for such complexes. The energy barrier to rotation around the C=N bond is relatively low and the ligand can undergo C=N bond isomerisation to give the *E,Z*-configuration where both PPh_2 groups are in the same side facing each other. Therefore the *E,Z*-azine diphosphine (**2**) forms 9-membered chelate rings. Treatment of (1) with $[AuCl(PPh_3)]$ in CH_2Cl_2 gave (**3**) as white microcrystals in 92% yield. The phosphorus NMR spectrum showed only a singlet at 35.5 ppm for both P atoms suggesting that they are equivalent. X-ray crystal structure was determined and it was found (i) the ligand in the Z,Z-configuration giving a 9-member chelate ring (ii) a trigonal-planar arrangement at the Au(I) centre and (iii) the P-Au-P and P-Au-Cl angles as 139.60° and 110.2°, respectively. The bite angle of 139.6° is significantly larger than the value (120°) expected for a trigonal-planar geometry. The structural requirement of the Au(I) centre was used to prepare the desired 9-member chelate ring complex (**3**) preferentially in very good yield.



(1)



(2)



(3)