E2-10: Synthesis and chemistry of chiral diphosphines derived from camphor

Sarath D Perera
(*Open University, Nawala, Nugegoda*)

Tertiary phosphines and (P-N) ligands play an important role in homogeneous catalysis. In the literature, the syntheses of the azine diphosphine derived from pinacolone, i.e. Z,Z-$PPh_2CH_2C(Bu^t)$=N-N=$C(Bu^t)CH_2PPh_2$, and its complexes with Cr, Mo and W have been described. Since chiral ligands based on camphor (a cheap chiral source) are used in enantioselective catalysis, it is of interest to synthesize the analogous chiral azine diphosphine(s) and to investigate their coordination chemistry.

Treatment of (1*R*)-(+)-camphor azine $C_{10}H_{16}$=N-N=$C_{10}H_{16}$ with 2 equivalents of BuLi followed by 2 equivalents of PPh_2Cl gave the azine diphosphines Z,Z-3,3'-$P^nPh_2C_{10}H_{15}$=N-N=$C_{10}H_{15}P^xPh_2$, P^nNNP^x, (**1**) and Z,Z-3,3'-$P^xPh_2C_{10}H_{15}$=N-N=$C_{10}H_{15}P^xPh_2$,P^xNNP^x, (**2**) where (x= *exo* and n = *endo*). These azine diphosphines were separated by fractional crystallization and their molecular structures were determined by X-ray crystallography. In hot EtOH, (**2**) isomerised to (**1**) in the presence of NaOEt. Treatment of (**1**) with $[W(CO)_4(nbd)]$ (nbd = norbornadiene) in boiling toluene afforded the tricarbonyl tungsten(0) complexes *fac*-$[W(CO)_3(P^nNNP^x)]$ (**3**) and *mer*-$[E(CO)_3(P^nNNP^x)]$ (**4**) which were separated by thin layer chromatography. Prolonged treatment of (1) with $[W(CO)_6]$ in boiling toluene gave the complex (**4**) and *fac*-$[W(CO)_3(P^nNNP^n)]$ (**5**). Treatment of (**2**) with $[W(CO)_4(nbd)]$ gave the tricarbonyl tungsten(0) complex *fac*-$[W(CO)_3(P^xNNP^x)]$ (**6**) of which the X-ray crystal structure was determined.