Metathesis of Phosphorus-containing Olefins catalysed by a Cyclometallated Aryloxo(chloro)neopentylidene–Tungsten Complex

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A cyclometallated *O,O'*-diphenyl aryloxy(chloro)neopentylidene–tungsten complex $\overline{W(OAr)}(OAr)(CHCMe_3)Cl(OEt_2)$ **1** is able to carry out metathesis of phosphorous containing olefins; diallylphenyl phosphane is metathetized intramolecularly to give the corresponding phospholene derivative **2** and allyldiphenyl phosphane gives the corresponding bisphosphane **3**.

In principle, metathesis of functionalized olefins is a powerful reaction in organic synthesis. However, the number of examples is still extremely limited, probably owing to a lack of suitable catalysts. Metathesis of olefinic ethers,[1] esters,[2] amines[3,4] and also thioethers[5–7] has been achieved with various catalytic systems derived from Mo, W, Re or Ru. Yet, to our knowledge, metathesis of phosphorus containing olefins has never been investigated. We have recently synthesized a novel and highly active cyclometallated aryloxide tungsten neopentylidene catalyst $\overline{W(OAr)}(OAr)(CHCMe_3)Cl(OEt_2)$ **1**[8] which enables the metathesis of olefinic esters, sulfides or carbohydrates.[6–9]

In this d^0 complex with very bulky substituents, one of the two bulky *O,O'*-diphenyl(phenoxo) ligands is orthometallated. Given the exceptional activity of this complex in the metathesis of olefins bearing polar groups,[8] or even strongly coordinating groups such as thioethers[7] or carbohydrates,[9] it was logical to study the activity of this catalyst towards the metathesis of a series of allylic phosphanes.

When allyldiphenyl phosphane or diallylphenyl phosphane are contacted with **1** in chlorobenzene at 80 °C ethylene begins to evolve. Overall, diallylphenyl phosphane and allyldiphenyl phosphane produce 0.5 and 1.0 mol of ethylene per mol of starting phosphane, respectively. Chromatographic analysis of the medium showed the production of a single product **2** and **3**, respectively. Each product has been isolated and identified by GC–MS, ^1H, ^{13}C, and ^{31}P NMR spectroscopy.†

Product **2** is obtained from diallylphenyl phosphane metathesis and is formed as the two isomers *syn* and *anti* depending on the respective positions of the two rings.‡ Interestingly, no evidence of oligomers arising from ADMET or ROMP of dihydrophospholene was observed under our experimental conditions. Product **3** obtained from diphenylallyl phosphane is the 1,4-bis(diphenylphosphino)but-2-ene (*Z* and *E*): *M* 424, it is characterized by NMR spectroscopy.§ The formation of these two products is easily explained by the reactions depicted in Scheme 1.

By studying the kinetics of ethylene evolution, it is possible to evaluate the respective reactivity of each substrate and the position of the thermodynamic equilibrium for the two reactions (Fig. 1).

Apparently the two substrates show very different kinetic behaviour. In the case of diallyl phosphane, 95% conversion is achieved in 5 h compared with only 10% for the monoallyl phosphane. Intramolecular metathesis cyclisation leading to the dihydrophosphole derivative is much faster (and has probably a higher thermodynamic equilibrium) than bimolecular metathesis leading to a diphosphane. A probable catalytic cycle is described in Scheme 2 for the monoallyl phosphane. It shows that initiation from the neopentylidene complex should be the same for the two phosphanes studied.

The differences in the kinetic rates are interpreted in the following way: for the diallyl phosphane an intramolecular cyclisation occurs, while for the monoallyl phosphane it is necessary to coordinate another olefinic molecule to the metallocarbene (see Scheme 2).

The reason why the phosphorous atom does not completely inhibit the reaction, as any phosphane would be expected to do (as shown by addition of tributylphosphane which only slows down the metathesis reaction), is not clear. However, it is strongly suggested from other studies that we have carried out with thioethers of various steric hindrance at the vicinity of the sulfur atom,[6] that steric factors are important. The *O,O'*-diphenyl phenoxy ligands are extremely bulky and the metallation of the phenyl substituent makes the geometry of the

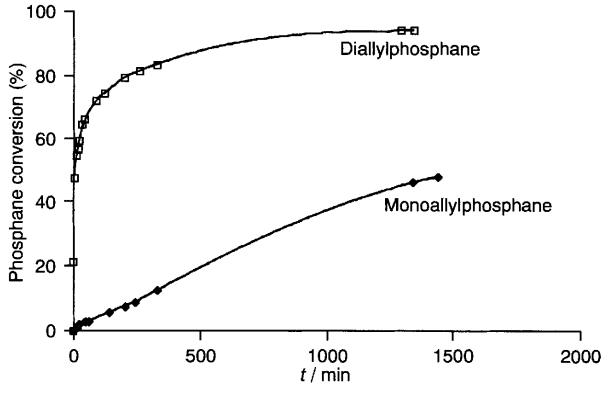
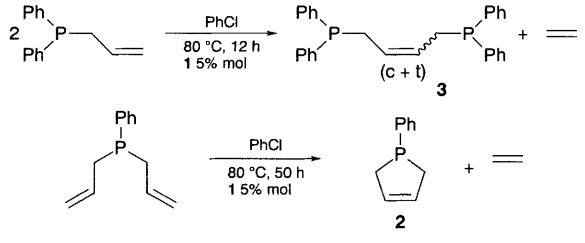
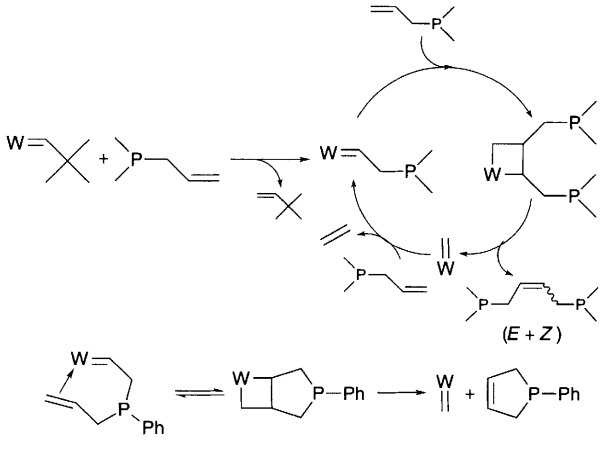


Fig. 1 Phosphane conversion (determined by the yield of ethylene) *vs.* time for the monoallyldiphenyl phosphane and the diallylphenyl phosphane



Scheme 1



Scheme 2

coordinated ligand rather rigid thus preventing a possible rotation of one of the two aryloxy ligands. The high activity is also attributed to the geometry of the complex which is octahedral and cannot relax to a pentacoordination geometry after the formation of the metallacyclobutane, due to the rigidity of the cyclometallated structure. This is a supplementary proof of the high activity of this carbene with functionalized olefins.

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Footnotes

† All experiments were carried out using classical Schlenk techniques working under dried and deoxygenated argon. The solvent (chlorobenzene) was distilled over phosphorus pentoxide under nitrogen. Allylic phosphanes (Aldrich) were used without further purification. The conversion rate was determined by measuring the evolution of ethylene with propane as an internal standard.

In a typical experiment a solution of 89 mg ($4.68 \cdot 10^{-4}$ mol) of diallylphosphane in 1 ml chlorobenzene and 1 ml propane were introduced into a 50 ml Schlenk tube previously purged with argon. Whilst stirring and heating at 80 °C, a solution of 20 mg ($2.35 \cdot 10^{-5}$ mol) of **1** in 1 ml chlorobenzene was added. After 12 h of reaction, the solvent was removed by evaporation at room temp. at 1 Torr. The residue was then distilled at 100 °C and condensed at liquid nitrogen (−196 °C). The same procedure was followed for allyldiphenyl phosphane. Products were characterized by ^{1}H, ^{13}C, ^{31}P NMR spectroscopy and GC–MS.

Due to the small amount of product used during the experiments the isolated yields are rather small (*ca.* 20%). However, the preparations can be easily carried out on a larger scale thus improving the yields and allowing the products to be obtained in sufficient quantities.

‡ ^{1}H NMR (solvent: CD_2Cl_2, 25 °C, ref. $SiMe_4$): δ(P-CH_2) 2.44–2.75 (4 H, m); δ(CH vinyl) 5.8–5.85 (2 H, m, $^3J_{P-H}$ 8.1 Hz); δ(phenyl ring) 7.15–7.4 (5 H, m). ^{13}C NMR (solvent: CD_2Cl_2, 25 °C, ref. $SiMe_4$): δ(P-CH_2 *syn*) 34.75 (d, $^1J_{P-C}$ 50.3 Hz); δ(P-CH_2 *anti*) 35.22 (d, $^1J_{P-C}$ 37.1 Hz); δ(C_2 arom. *syn*) 128.6 (d, $^2J_{P-C}$ 11.5 Hz); δ(C_2 arom. *anti*) 129.35 (d, $^2J_{P-C}$ 11.7 Hz); δ(C_4 arom.) 129; δ(C_1 arom. *syn*) 129.1 (d, $^1J_{P-C}$ 18.3 Hz); δ(C_1 arom. *anti*) 131.8 (d, $^1J_{P-C}$ 18.3 Hz); δ(C_3 arom. *syn*) = 130.4 (d, $^3J_{P-C}$ 6.6 Hz); δ(C_3 arom. *anti*) 130.3 (d, $^3J_{P-C}$ 2.7 Hz); δ(CH vinyl) 132.5 (d, $^2J_{P-C}$ 3.3 Hz). ^{31}P NMR: δ −25.6, in agreement with literature data (J. J. Breen, D. K. Myers and L. D. Quin, *Phosphorus*, 1992, **2**, 55). The attributions of the various carbon resonances to the *syn* and *anti* forms were made in agreement with the data of the literature (see for example L. D. Quin, K. C. Caster, J. C. Kisalus and K. A. Mesch, *J. Am. Chem. Soc.*, 1984, **106**, 7021). The high values of the $^1J_{P-C}$ constants are probably related to steric hindrance and are not exceptional (L. D. Quin, in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, ed. J. G. Verkade and L. D. Quin, VCH, 1987, pp. 391–424).

§ 1,4-Bis(diphenylphosphino)but-2-ene (*Z* and *E*): ^{1}H NMR (solvent: benzene, 25 °C, ref. $SiMe_4$): δ(P-CH_2) 2.6–2.7 (4 H, d, $^2J_{P-H}$ 4.4 Hz); δ(CH vinyl) 5.4–5.6 (2 H, m); δ(H aromatic ring) 7.1–7.9 (10 H, m). ^{13}C NMR (solvent: benzene, 25 °C, ref. $SiMe_4$): δ(P-CH_2) 32.3 (d, $^1J_{P-C}$ 17.3 Hz); δ(C_4 arom.) 129.54 (s); δ(C_5 arom.) 130.29 (s); δ(C_6 arom.) 130.9 (s); δ(CH vinyl.) 131.8 (d, $^2J_{P-C}$ 8 Hz); δ(C_1 arom.) 133.7 (d, $^1J_{P-C}$ 12.2 Hz). ^{31}P NMR (solvent: benzene, 25 °C, ref. H_3PO_4 85%): δ −16.3.

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