

Wittig-type Reaction of Carbon Monoxide with Triphenyl(phenylimino)-phosphorane Co-ordinated to Palladium. Novel Phenyl Isocyanide and Carbonyl Complexes of Palladium

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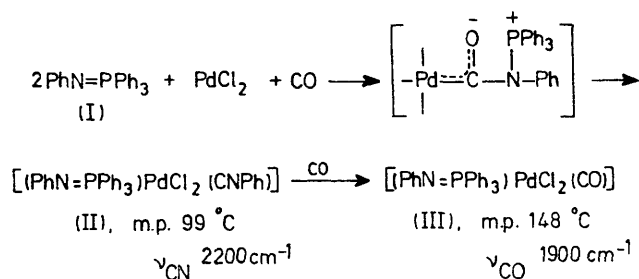
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Summary The reaction of carbon monoxide with triphenyl-(phenylimino)phosphorane proceeds smoothly at room temperature in the co-ordination sphere of Pd^{II} to give a Pd^{II} -phenyl isocyanide complex, which is converted finally into a Pd^{II} -carbonyl complex in the presence of a large excess of carbon monoxide.

ALTHOUGH ylides and carbon monoxide are versatile reagents in organic synthesis, no reaction between them has been recorded. The carbon atom of a metal carbonyl is susceptible to nucleophilic attack and various carbene complexes have been prepared from metal carbonyls.¹ Ylides possess nucleophilic character and react with metal carbonyls.² While no Pd^{II} -carbonyl complex with definite stoichiometry has been characterized, carbonylation by carbon monoxide is generally accepted to occur within the co-ordination sphere of the Pd^{II} -ion.³ We have now investigated the reaction of carbon monoxide with ylides in the presence of Pd^{II} -complexes, and we report a Pd^{II} -assisted Wittig-type reaction of carbon monoxide.

Shaking a toluene solution of the iminophosphorane (I) (2 mol) and the complexes (1 mol) of PdCl_2 with cyclo-octene, cyclohexene, or styrene under CO at room temperature gave quantitatively a mixture of the insoluble yellow Pd^{II} -isocyanide (II) and -carbonyl (III) complexes, the ratio of which depended on the reaction time (1–40 h). Early in the reaction, complex (II) predominated, which was then converted into the carbonyl complex (III). The isocyanide

complex (II) was soluble in chloroform and could be separated from (III). The structure of the ylide-co-ordinated complexes (II) and (III) was based on their spectral data, analysis, and molecular weight.† $\text{Ph}_3\text{P}=\text{O}$, the other product of the Wittig reaction, was also detected [ca. 40% yield from (I)].



The reaction of complex (II) with CO is noteworthy. In solution in toluene (II) reacted with CO with replacement of the co-ordinated PhNC by CO to give (III) and polymeric phenyl isocyanide was obtained from the solution. In the presence of (I) [(I):(II) < 1] the PhNC co-ordinated to Pd^{II} in (II) reacted with (I) under CO to give the insoluble (III) and *NN*-diphenylcarbodi-imide, the presence of which was shown by i.r. absorptions at 2137 and 2104 (sh) cm^{-1} .

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† Since complex (III) is insoluble in common organic solvents, the measurement of its molecular weight has so far been unsuccessful. Reaction of (III) with Ph_3P gave the known $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$ (in 78% yield).

¹ E. O. Fischer, *Angew. Chem.*, 1974, **86**, 651.

² H. Alper and R. A. Partis, *J. Organometallic Chem.*, 1972, **35**, C 40.

³ J. Tsuji, M. Morikawa, and J. Kiji, *J. Amer. Chem. Soc.*, 1964, **86**, 4851.