The Addition of Cyanogen to Nickel(0)-, Palladium(0)-, and Platinum(0)-Phosphine Complexes

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Summary A new oxidative addition reaction of d^{10} transition-metal phosphine complexes (the addition of cyanogen) involves the breaking of a carbon–carbon bond to give dicyano-complexes.

THE addition of a large variety of organic compounds to the phosphine complexes of nickel(0), palladium(0), and platinum(0) has been reported.[1] These addition reactions are of two general types: additions in which the organic molecule does not dissociate so that the formal oxidation state of the metal does not change, and additions in which there is dissociation of the organic molecule resulting in the oxidation ($d^{10} \rightarrow d^8$) of the metal. Examples of this latter type of addition are numerous, but apart from the recently reported[2] addition of nitrosotrifluoromethane to tetrakis(triphenylphosphine)platinum(0) to give nitroso-(trifluoromethyl)bis(triphenylphosphine)platinum(II), have been limited completely to the reactions of chloro-, bromo-, and iodo-carbons in which the carbon–halogen bond is readily cleaved to give the halogen–organometal(II) phosphine complex.

We report a new reaction of this type, the oxidative addition of cyanogen. Heating tetrakis(triphenylphosphine)palladium(0) with a solution of an excess of cyanogen in benzene at 100° for 3 hr. gave dicyanobis(triphenylphosphine)palladium(II)[3]† (60% yield, m.p. >300° (d), $\nu_{\text{Pd-CN}}$ 2150 cm.$^{-1}$). Similar treatment of tetrakis(triphenylphosphine)platinum(0) gave dicyanobis(triphenylphosphine)platinum(II)[4] [44% yield, m.p. >300(d), $\nu_{\text{Pt-CN}}$ 2150 cm.$^{-1}$]. Tetrakis(propyl diphenylphosphinite)nickel(0) was much more reactive. The addition of cyanogen was rapid at room temperature and gave dicyanobis(propyl diphenylphosphinite)nickel(II) (m.p. 135—137°, $\nu_{\text{Ni-CN}}$ 2110 cm.$^{-1}$) in 61% yield.

We believe that these reactions are unique in that they are the first examples of an oxidative addition reaction that involves the breaking of a carbon–carbon bond.

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† All of the compounds described gave satisfactory elemental analyses.

[1] For a review of these addition reactions see R. Ugo, *Co-ordination Chem. Rev.*, 1968, **3**, 319.

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[3] H. Itatani and J. C. Bailar, jun., *J. Amer. Oil Chemists' Soc.*, 1967, **44**, 147.

[4] J. C. Bailar, jun., and H. Itatani, *J. Amer. Chem. Soc.*, 1967, **89**, 1592.