

Complexes of Nickel(I) with Triphenylphosphine

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WE have prepared complexes of nickel with triphenylphosphine, having the general formula $(PPh_3)_3NiX$ ($X = Cl, Br, \text{ or } I$), by reaction of π -allyl-Ni-X with PPh_3 in the presence of norbornene, at room temperature, in a benzene-diethyl ether mixed solvent (about 80% ether). Both PPh_3 and norbornene are used in about three- to eight-fold excess with respect to the nickel compound. The iodide and bromide were also obtained by boiling a benzene solution of π -allyl-Ni-I or π -allyl-Ni-Br in the presence of an excess of PPh_3 for 2–3 hr. Biallyl is also formed.

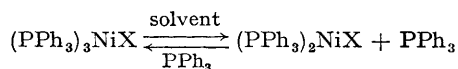
All the above complexes (chloride and bromide, yellow; iodide, brownish-orange) are soluble in benzene, with slight decomposition, but almost insoluble in ether. They can be recrystallized from hot benzene, in which case crystals $(PPh_3)_3NiX \cdot nC_6H_6$ are obtained, ($n = 3$ for the bromide, not yet determined for the others). Crystallization, from a benzene-diethyl ether mixture having more than 50% of ether, gave $(PPh_3)_3NiX$.

The complexes, $(PPh_3)_3NiX$, slowly decompose in the air, but are stable for a long time under nitrogen. In the solid state they are paramagnetic,

the magnetic moment being about 1.9 for the chloride and bromide and 1.98 B.M. for the iodide.

Preliminary X-ray studies, performed in our Institute by Dr. Allegra and his co-workers on single crystals of the bromide, have shown that this complex has a tetrahedral configuration, both for the crystals with and without benzene. The X-ray examination of the other complexes is now in progress.

Cryoscopic determinations of the molecular weight in benzene gave values much lower than the expected ones, which suggests that the complexes are dissociated in solution according to the equation:



A similar phenomenon has recently been observed for the complex $(PPh_3)_3RhCl$.^{1,2} The chemical properties of the complexes $(PPh_3)_3NiX$ are now being examined and will be reported later.

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¹ M. A. Bennett and P. A. Longstaff, *Chem. and Ind.*, 1965, 846.

² J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, 1711.