Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

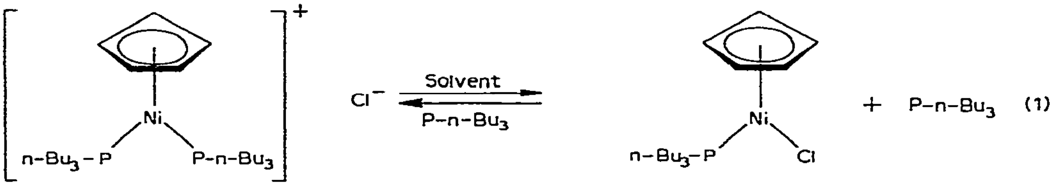
Preliminary communication

π-Cyclopentadienyls of nickel(II)
II★. Properties of the ionic complex π-cyclopentadienylbis(tri-n-butylphosphine)nickel chloride

MASAO SATO, FUMIE SATO and TADAO YOSHIDA
Department of Chemical Engineering, Tokyo Institute of Technology, Tokyo (Japan)

(Received October 26th, 1970)

In the course of the investigation of the properties of the ionic complex $[\pi\text{-}C_5H_5Ni(P\text{-}n\text{-}Bu_3)_2]^+Cl^-$ [1] (I), it was found that the complex (I) dissociated in non-polar solvents such as benzene and n-hexane according to Eq.1.



(I) (II)

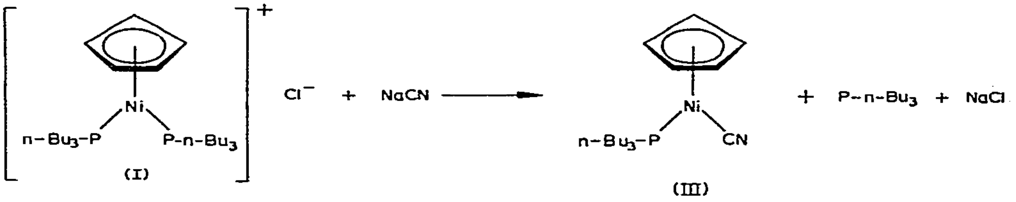
It appears that the dissociation is essentially complete in benzene solution, in which the apparent molecular weight (278) is about half that corresponding to the undissociated species (563). The dissociation also takes place above the melting point of (I) in the absence of solvent.

The green-yellow complex (I) is very soluble in benzene and n-hexane to give red solution, and addition of $P\text{-}n\text{-}Bu_3$ to the red n-hexane solution gives a green-yellow precipitate of (I). (I) melts at 85–87° turning to red, and (I) is converted into (II) when heated about 90° under vacuum. (II) reacts with $P\text{-}n\text{-}Bu_3$ to give (I) quantitatively.

In view of the observed dissociation of (I) complexes of the type $\pi\text{-}C_5H_5Ni{\cdot}P\text{-}n\text{-}Bu_3{\cdot}X$ might be expected to be isolable. The aqueous solution of (I) was treated at room temperature with excess NaCN aqueous solution, instantaneous reaction occurred and a green oily product appeared. Extraction of this product with benzene and recrystallization from a mixture of benzene and n-hexane gave green crystals which had a molecular formula $\pi\text{-}C_5H_5Ni{\cdot}P\text{-}n\text{-}Bu_3{\cdot}CN$ (III), m.p. 94–95° [Found: C, 61.67;

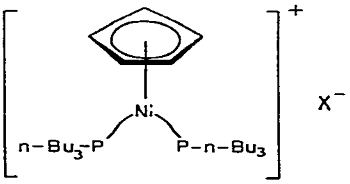
★For Part I see ref.1.

H, 9.34; N, 3.90; mol.wt. 352. $C_{18}H_{32}NNiP$ calcd.: C, 61.50; H, 9.10; N, 3.98%; mol.wt., 351.7]. Based on IR and NMR spectra the product was formulated as cyano-π-cyclopentadienyltri-n-butylphosphine nickel, (III).



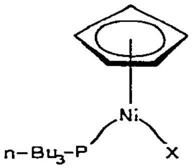
The IR spectrum of (III) resembles that of π-C_5H_5Ni·P-n-Bu_3·Cl except that a new band appears at 2125 cm^{-1} characteristic of C≡N stretching band. The NMR spectrum of (I) in CCl_4 solution shows bands at τ 8.1–9.3 (intensity 28) due to the P-n-Bu_3 protons and a sharp singlet at τ 4.82 (intensity 5) due to the π-C_5H_5 protons.

Similar reactions of (I) with $NaClO_4$, $NaClO_3$, NaN_3, $NaNO_2$ and $NaNO_3$ gave ionic complexes with structures of type (IV), and molecular weight determination in benzene indicated the existence of the covalent complexes of type (V) in the case of ClO_3^-, N_3^- and NO_2^-. We are now attempting to isolate the complexes (V).



(IV)

(X=ClO$_4$, ClO$_3$, N$_3$, NO$_2$, NO$_3$)



(V)

(X=ClO$_3$, N$_3$, NO$_2$)

REFERENCES

1 M. Sato, F. Sato and T. Yoshida, *J. Organometal. Chem.*, in press.