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

Preliminary communication

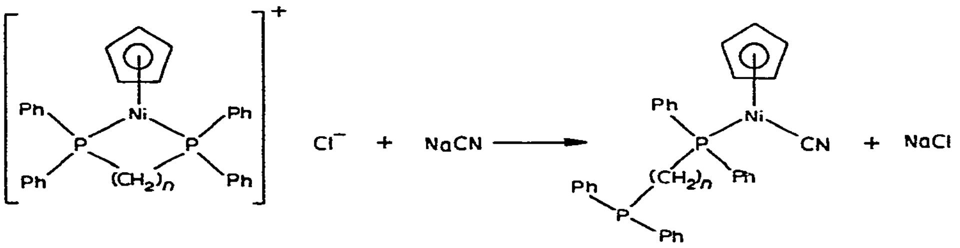
π-Cyclopentadienyls of nickel(II)
IX. Reaction of $[\pi\text{-}C_5H_5NiPPh_2(CH_2)_nPPh_2]^+Cl^-$ (n = 1, 2, 3 and 4) with aqueous NaCN

FUMIE SATO, TADAHIRO UEMURA and MASAO SATO
Department of Chemical Engineering, Tokyo Institute of Technology, Tokyo (Japan)

(Received March 27th, 1972)

We recently described the preparation of cyano-π-cyclopentadienyl tri-n-butylphosphinenickel, $\pi\text{-}C_5H_5NiPBu_3CN$, by treatment of π-cyclopentadienylbis(tri-n-butylphosphine)nickel chloride, $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$, with NaCN in aqueous solution[1].

By analogy, products of the type $\pi\text{-}C_5H_5NiPPh_2(CH_2)_nPPh_2CN$ (I) would be expected from the reaction between $[\pi\text{-}C_5H_5NiPh_2P(CH_2)_nPPh_2]^+Cl^-$ [2] and aqueous NaCN.

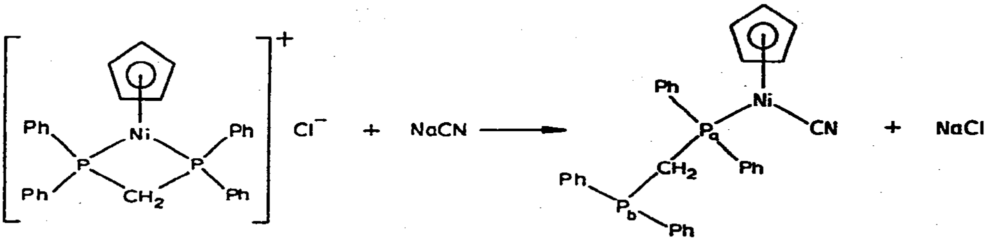


(I)

Such complexes are of special interest because they can be regarded as potential metal-containing ligands.

When an aqueous solution of $[\pi\text{-}C_5H_5NiPh_2PCH_2PPh_2]^+Cl^-$ was treated at room temperature with an excess of aqueous NaCN, instantaneous reaction occurred and a green precipitate was formed. Extraction of this product with dichloromethane, and recrystallization from a mixture of dichloromethane and n-hexane gave green crystals of the molecular formula $\pi\text{-}C_5H_5NiPh_2PCH_2PPh_2CN$ (II), m.p. 140° (Found: C, 69.34; H, 4.68; N, 2.37. $C_{31}H_{27}NNiP_2$ calcd.: C, 69.69; H, 5.09; N, 2.62%.)

From the IR and NMR spectra it was calculated that the product was cyano-π-cyclopentadienylmethylenebis(diphenylphosphine)nickel, *i.e.* complex (II).



(II)

The presence of non-equivalent phosphorus atoms (P_a and P_b) in complex (II) is indicated by the ^{31}P NMR spectrum shown in Fig. 1. The peak at δ +7.7 ppm (measured from PPh_3 external reference) was assigned to the non-coordinated phosphorus atom (P_b), and that at δ −52.2 ppm was assigned to the coordinated atom (P_a), since the coordination chemical shift of ^{31}P NMR for phosphine ligands ($\delta_{complex}$−$\delta_{free\ ligand}$) is known to be usually negative[3]. The proton NMR spectrum of (II) in $CDCl_3$ solution shows bands at τ 2.0–3.0 associated with the phenyl protons of methylenebis(diphenylphosphine), a singlet at τ 4.86 due to the π-cyclopentadienyl protons, and a doublet at τ 6.70 ($J(P_aH)$ 10 cps, $J(P_bH)$ 0) due to the methylene protons of methylenebis(diphenylphosphine).

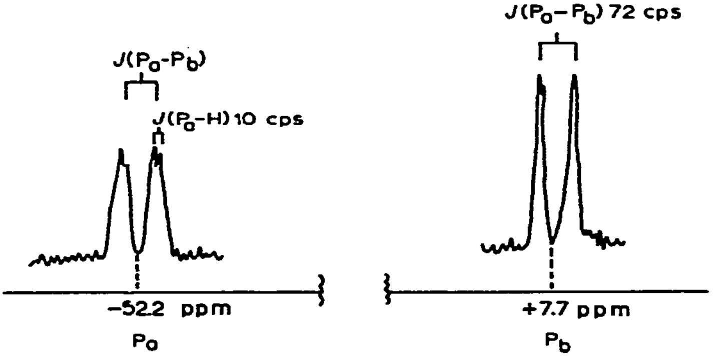


Fig. 1. ^{31}P NMR spectrum of complex (II) in CH_2Cl_2, with PPh_3 as external reference.

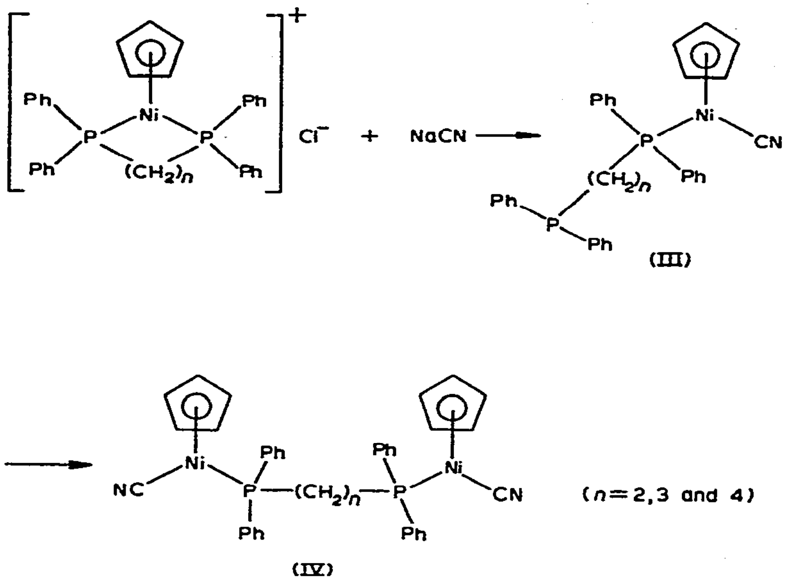
TABLE 1

PROPERTIES AND ANALYTICAL DATA FOR COMPOUNDS (IV)

Compound	*Colour*	*M.p. (°C)*	*Analysis found (calcd.) (%)*			*Proton NMR data* [b]		
			C	*H*	*N*	*τ(π-C₅H₅)*	*τ(PPh₂)*	*τ(methylene protons)*
$n = 2$ [a]	Green	123	71.20 (70.29)	5.46 (5.42)	3.36 (3.28)	4.86s(10)	2.3~2.8(32)	7.13(br)(4)
$n = 3$	Green	162	66.56 (65.78)	5.22 (5.10)	4.25 (3.92)	4.91s(10)	2.2~2.8(20)	6.9~8.1(6)
$n = 4$	Green	190.5	65.34 (66.17)	5.20 (5.27)	4.07 (3.86)	4.82s(10)	2.2~2.7(20)	7.61(br)(4) 8.10(br)(4)

[a] Solvated by two molecules of C_6H_6. [b] Intensity in parentheses.

The reactions of $[\pi\text{-}C_5H_5NiPh_2P(CH_2)_nPPh_2]^+Cl^-$ ($n = 2, 3$ and 4) with aqueous NaCN, on the other hand, gave the alkylenebis(diphenylphosphine) bridged dinuclear organonickel compounds, (IV). The compounds of type (III) are no doubt involved as intermediates, as indicated in scheme 1.



Scheme 1

Some properties and analytical data of the compounds (IV) are listed in Table 1.

REFERENCES

1 M. Sato, F. Sato and T. Yoshida, *J. Organometal. Chem.*, 31 (1971) 415.
2 F. Sato and M. Sato, *J. Organometal. Chem.*, 33 (1971) C73.
3 L.S. Meriwether and J.R. Leto, *J. Amer. Chem. Soc.*, 83 (1961) 3192; S.O. Grim, D.A. Wheatland and W. McFarlane, *J. Amer. Chem. Soc.*, 89 (1967) 5573.