

STUDIES OF POLY-YNE POLYMERS CONTAINING TRANSITION METALS IN THE MAIN CHAIN

VI. SYNTHESIS OF NICKEL-POLY-YNE POLYMERS BY ALKYNYL LIGAND EXCHANGE USING A COPPER(I) CATALYST

K. SONOGASHIRA, K. OHGA, S. TAKAHASHI, and N. HAGIHARA

The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka, 565 (Japan)

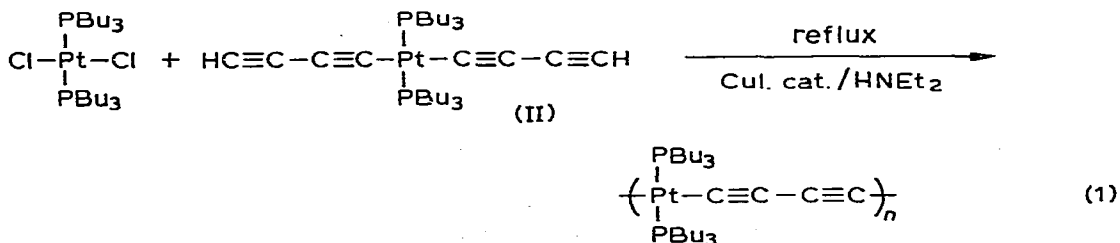
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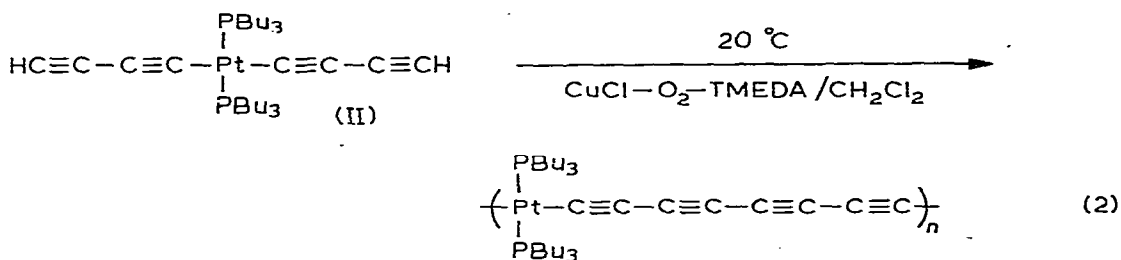
Summary

Reactions of *trans*-bis(tri-*n*-butylphosphine)diethynylnickel(Ia) with 1-alkynes in the presence of an amine complex of a copper(I) salt as a catalyst give quantitatively alkynyl ligand exchange products. By this method, complex(Ia) reacts with appropriate α,ω -diethynyl compounds to afford high molecular weight linear polymers in good yields. This procedure provides a convenient route to such nickel-poly-yne polymers.

Introduction

In view of the interesting properties associated with unidimensional materials, we have studied poly-yne polymers containing transition metals in the main chain backbone for several years and reported the synthesis and solution properties of rod-like conjugated poly-yne platinum polymers [1–4]. These polymers have been synthesized by condensation polymerization of the bis(1,3-butadiynyl)-platinum complex II with the dichloroplatinum complex or by oxidative coupling of II [1,4] as shown in eqs. 1 and 2, respectively. The analogous nickel poly-





mers would be expected to exhibit special physical properties and catalytic activities due to contribution of stronger metal $-\text{C}\equiv\text{C}-$ back bonding and more labile $\text{Ni}-\text{PR}_3$ bonding than found in those of the palladium and platinum analogs. However, these nickel-containing high polymers cannot be synthesized by the above methods because of undesired side reactions of dihalonickel complexes with amine solvents or dialkynynickel complexes with an oxidative coupling reagent [4].

In this paper, we wish to report new synthetic methods for nickel(II) diacetylides of the type *trans*-(PBu_3)₂ $\text{Ni}(\text{C}\equiv\text{CR})_2$ ($\text{R} = -\text{C}\equiv\text{CH}$ (Ib), $-\text{C}_6\text{H}_5$ (Ic)) and nickel-containing poly-yne polymers of the type $(-\text{Ni}(\text{PBu}_3)_2-\text{C}\equiv\text{C}-\text{Y}-\text{C}\equiv\text{C}-\text{M}(\text{PBu}_3)_{3/2}-\text{C}\equiv\text{C}-\text{Y}-\text{C}\equiv\text{C}-)_n$ ($\text{Y} = -, -\text{C}_6\text{H}_4(p)$; $\text{M} = \text{Ni}, \text{Pt}$) by using alkynyl ligand exchange processes catalyzed by CuI-amine complexes.

Experimental

Apparatus. IR spectra were taken of Nujol mulls or films with a Hitachi 295 spectrometer; electronic spectra were recorded in methylene chloride solution with a Shimadzu UV 202 spectrometer. ³¹P NMR spectra were run on a JEOL FX 100 spectrometer and ESCA on a Shimadzu-Du Pont 650 B electron spectrometer employing $\text{Mg}-K_\alpha$ radiation. Thermal analysis was performed with a Shimadzu thermal analyzer DT-30 or TGA-30. Molecular weights of polymers were determined by a Shimadzu-Du Pont liquid chromatograph model 830 as described in a previous paper [3].

Materials. The alkynes, $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$ [5] and *p*- $\text{HC}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{CH}$ [6] and the complexes, *trans*-(PBu_3)₂ MCl_2 ($\text{M} = \text{Pt}$ [9], Pd [10]), *trans*-(PBu_3)₂ $\text{Pt}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{CH})_2$ [9], and (PBu_3)₂ NiBr_2 [11] were prepared by the methods described previously.

trans-(PBu_3)₂ $\text{Ni}(\text{C}\equiv\text{CH})_2$ (Ia). A stirred solution of $\text{HC}\equiv\text{CMgBr}$, prepared from EtMgBr (prepared from 12 g (0.5 g-atom) of magnesium turnings and 60 g (0.55 mol) of EtBr) and gaseous acetylene by the method of Whiting et al. [12], in 500 ml of THF was cooled in ice water. A solution of 100 g (0.16 mol) of (PBu_3)₂ NiBr_2 in 200 ml of THF then was added dropwise. After the addition was completed, the solution was allowed to warm to room temperature and 700 ml of water was added with cooling. Hexane was added and the separated organic layer was dried over anhydrous MgSO_4 and then concentrated to yield dark brown oil. Repeated chromatography of this oil on alumina (Brockmann activity III, hexane eluent) yielded 40 g (50% yield) of a yellow oil (Ia) which solidified in a refrigerator, m.p. $<25^\circ\text{C}$. Anal. Found: C, 65.61; H, 11.26; P, 12.11. $\text{C}_{28}\text{H}_{56}\text{P}_2\text{Ni}$ calcd.: C, 65.50; H, 10.99; P, 12.07%.

trans-(PBU₃)₂Ni(C≡C—C≡CH)₂ (Ib). To a 200 ml three-necked round-bottomed flask equipped with a dry-ice condenser were added 20 ml of HNEt₂, a solution of HC≡C—C≡CH (3 g, 0.06 mol) in 30 ml of ether and 15 mg of CuI at -70°C under a nitrogen atmosphere. A solution of *trans*-(PBU₃)₂Ni(C≡CH)₂ (Ia) (5.1 g, 0.01 mol) in 50 ml of HNEt₂ was added dropwise at 5°C and the resulting mixture was stirred at 25°C for about 0.5 h. After evaporation of the solvent in a rotary evaporator, purification of the residue by short column chromatography on alumina (Brockmann activity III) with hexane and recrystallization from ethanol gave pale yellow crystals of *trans*-(PBU₃)₂Ni(C≡C—C≡CH)₂ (Ib) in 85% yield, m.p. 85–86°C. Anal. Found: C, 68.19; H, 9.81; P, 10.75. C₃₃H₅₆P₂Ni calcd.: C, 68.46; H, 10.05; P, 11.03%.

{*trans*-Ni(PBU₃)₂-C≡C—C≡C—} _n (III). To a solution of Ib (730 mg, 1.3 mmol) and Ia (670 mg, 1.3 mmol) were added CuI (1.9 mg, 0.01 mmol) and PBU₃ (10 μl) under a nitrogen atmosphere. The mixture was refluxed for 6 h and after evaporation of the solvent benzene and ether were added. The two layer were separated and the aqueous layer was extracted twice with benzene. The combined organic layer was washed with water. After evaporation of the solvent, the yellow brownish product was purified by repeated precipitation from CH₂Cl₂ into CH₃OH to afford a brownish yellow polymer of III having a viscosity of 0.19 dL/g (in THF at 25°C). M_w 15.000 (measured by GPC using *a* and *K* values of 1.7 and 6.5 × 10⁻⁹, respectively [3]). Yield, 1.2 g (85%). Anal. Found: C, 64.89; H, 10.48; P, 11.61. (C₂₈H₅₄P₂Ni)_n calcd.: C, 65.76; H, 10.64; P, 12.11%.

{*trans*-Ni(PBU₃)₂-C≡C—C₆H₄(*p*)-C≡C—} _n (IV). The polymer IV was prepared similarly from the reaction between Ia (513 mg, 1 mmol) and *p*-HC≡C—C₆H₄—C≡CH (126 mg, 1 mmol) in HNEt₂ (50 ml) in the presence of CuI (1 mg) and PBU₃ (10 μl). After 6 h, evaporation of the solvent and purification of the residue by chromatography on alumina (Brockmann activity III) with CH₂Cl₂ gave a yellow polymer of IV having [η] of 0.20 dL/g (in THF at 25°C). M_w 13.000. Yield, 590 mg (95%). Anal. Found: C, 68.80; H, 9.67; P, 9.90. (C₃₄H₅₈P₂Ni)_n calcd.: C, 69.51; H, 9.95; P, 10.54%.

{*trans, trans*-Pt(PBU₃)₂-C≡C—C≡C—Ni(PBU₃)₂-C≡C—C≡C—} _{n/2} (V). This polymer was prepared in 95% yield in a manner similar to IV using Ia (513 mg, 1 mmol), *trans*-(PBU₃)₂Pt(C≡C—C≡CH)₂ (II) (698 mg, 1 mmol), CuI (1 mg), PBU₃ (10 μl) and HNEt₂ (50 ml). Anal. Found: C, 57.48; H, 9.06; P, 9.45. (C₅₆H₁₀₈P₄NiPt)_n calcd.: C, 58.03; H, 9.39; P, 10.69%.

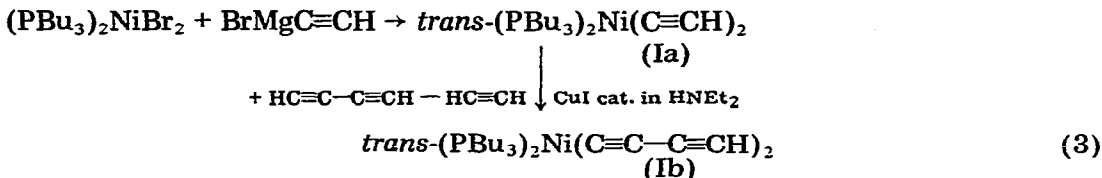
{*trans, trans*-Pt(PBU₃)₂-C≡C—C₆H₄(*p*)-C≡C—Ni(PBU₃)₂-C≡C—C₆H₄(*p*)-C≡C—} _{n/2} (VI). Similarly, this polymer was prepared in 95% yield using Ia (513 mg, 1 mmol) and *trans*-Pt(PBU₃)₂(C≡C—C₆H₄(*p*)-C≡CH)₂. Anal. Found: C, 62.06; H, 8.75; P, 9.10 (C₆₈H₁₁₆P₄NiPt)_n calcd.: C, 62.28; H, 8.92; P, 9.45%.

Results and discussion

Very stable nickel(II) acetylides of the type *trans*-L₂Ni(C≡CR)₂ (R = alkyl or aryl, L = tertiary phosphine) (I) are known and have been prepared by treating L₂NiX₂ (X = halogen) with an alkynyl-metal reagent such as an alkynylmagnesium halide or an alkynyllithium in diethylether or with a sodio-derivative of the acetylene in liquid ammonia [13]. These procedures, which require anhydrous

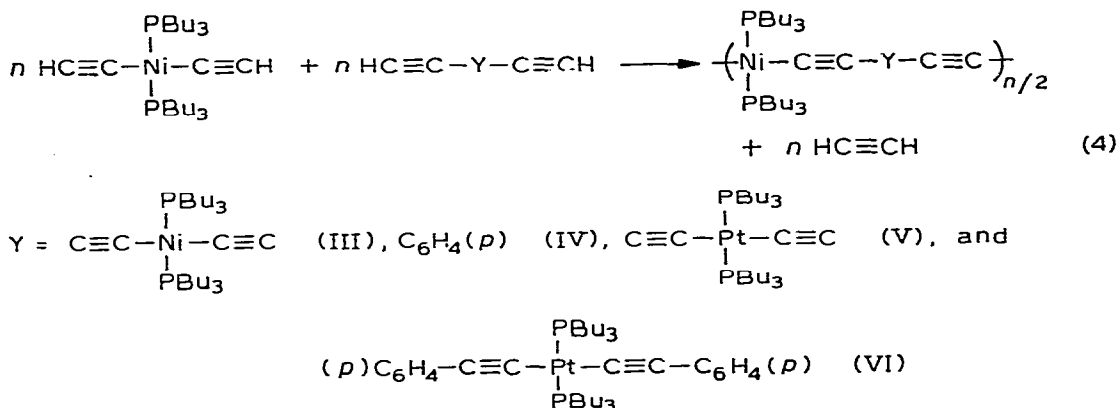
conditions, are troublesome for a large scale synthesis.

We have found a convenient 2-step method for the synthesis of Ib (I, R = $-\text{C}\equiv\text{CH}$, L = PBu_3) as shown in eq. 3. The reaction of $\text{HC}\equiv\text{CMgBr}$ with $(\text{PBu}_3)_2\text{NiBr}_2$ affords a large quantity of Ia (I, R = H, L = PBu_3), which can be stored for a long time in a refrigerator, and serves as starting material for the



preparation of alkynylnickel compounds. Addition of Ia to $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$ in HNEt_2 in the presence of a CuI catalyst gave quantitatively the bis-diyne complex Ib. Since the reaction is very simple and not affected by water in the reaction system, the procedure can be used as a general method to prepare complexes of the type $\text{trans-}(\text{PR}_3)_2\text{Ni}(\text{C}\equiv\text{CR}')_2$ (R = alkyl, aryl; R' = alkyl, aryl). Furthermore, the diethynyl-complex Ia is most suitable as a starting material for acetylide synthesis by alkynyl ligand exchange because the gaseous acetylene which is liberated is easily removed from the reaction system, thus displacing the equilibrium. Although displacement of an acetylene group by a more activated acetylene under drastic conditions is known [14,15], there is no example of its application to the preparation of acetylide complexes.

The fact that complex Ia is stable and readily available as a starting material prompted us to undertake a study of the synthesis of nickel-containing poly-yne polymers by the CuI -amine-catalyzed alkynyl exchange reaction. We found that this process successfully afforded various nickel polymers. Thus, diethynyl-nickel complex Ia reacted with complex Ib, using refluxing diethylamine as a solvent and CuI as a catalyst, to afford poly[$\text{trans-bis}(\text{tri-n-butylphosphine-nickel-1,4-butadiynediyl})$] (III), in a yield of 85%. To prevent the decomposition of the polymer under these reaction conditions, addition of small amounts of PBu_3 is essential. This additive may serve to suppress the phosphine ligand dissociation which causes the decomposition of polymer III.



Similarly, polymers IV, V, and VI were prepared as shown in eq. 4. The poly-

TABLE 1
PHYSICAL PROPERTIES AND SPECTRAL DATA OF THE NICKEL POLY-YNE POLYMERS

Compound	\overline{M}_w^a	$[\eta]^b$ (dl/g)	Decomp. c Point ($^{\circ}\text{C}$)	IR (cm^{-1}) $\nu(\text{C}\equiv\text{C})$	UV d $\lambda_{\text{max}}(\text{nm})$ (log ϵ)	^{31}P NMR e δ (ppm)	ESCA f (eV)
III	13 000	0.19	150	2120m 1980w	414(4.1) 372(4.2) 297(4.0)	-12.69	854.5(Ni 2p 3/2)
IV	10 000	0.20	142	2075m	402(4.5) 368(4.4) 287(4.3)	-13.45	854.8(Ni 2p 3/2)
V	11 000	0.15	190	2125m 1990w	400(4.3) 375(4.2) 290(4.0) 262(sh) (4.3)	-12.96 (P on Ni) -4.02 (P on Pt) $J(\text{Pt}-\text{P})$ 2386.7 Hz	72.8(Pt 4f 7/2) 76.2(Pt 4f 5/2) 854.5(Ni 2p 3/2)
VI	10 000	0.19	159	2100s 2085(sh)m 1950w	383(sh) (4.5) 370(4.5) 291(sh) (4.4) 278(4.4)	-13.4 (P on Ni) -2.91 (P on Pt) $J(\text{Pt}-\text{P})$ 2356.0 Hz	72.7(Pt 4f 7/2) 76.0(Pt 4f 5/2) 854.6(Ni 2p 3/2)

a Measured by GPC. b In THF at 25°C . c From thermal gravimetric analysis in a nitrogen atmosphere at heating rate of $5^{\circ}\text{C}/\text{min}$. d In Nujol. e Measured in CH_2Cl_2 . ^{31}P shift in δ (ppm) from external H_3PO_4 (positive shifts to high field). f X-ray photoelectron binding energies were measured on sticky tape and were referenced to the carbon 1s line (taken to be 285.0 eV) of each sample.

mer sequences were characterized by ^{31}P NMR, ESCA, IR, and electronic spectra. Some physical properties and characteristic spectral data of polymers III, IV, V, and VI, are presented in Table 1.

^{31}P NMR spectroscopy provides information about the oxidation state of a metal and the substituent on the metal, as well as the gross geometry of the metal. ESCA and ^{31}P NMR data of the polymers are consistent with M^{II} oxidation state ($\text{M} = \text{Pt}, \text{Ni}$) and *trans*-configuration. We have examined the electronic spectra of the three polymers $\{trans\text{-M}(\text{PBU}_3)_2\text{-C}\equiv\text{C-C}\equiv\text{C}\}_n$ ($\text{M} = \text{Ni}, \text{Pd}, \text{and Pt}$) and

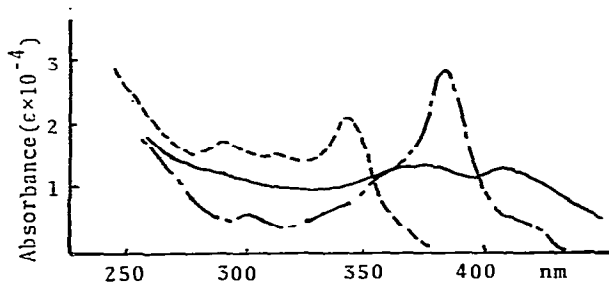


Fig. 1. Electronic spectra of the polymers, $\{trans\text{-M}(\text{PBU}_3)_2\text{-C}\equiv\text{C-C}\equiv\text{C}\}_n$ in CH_2Cl_2 : - - - - $\text{M} = \text{Pt}$; ····· $\text{M} = \text{Pd}$; ——— $\text{M} = \text{Ni}$.

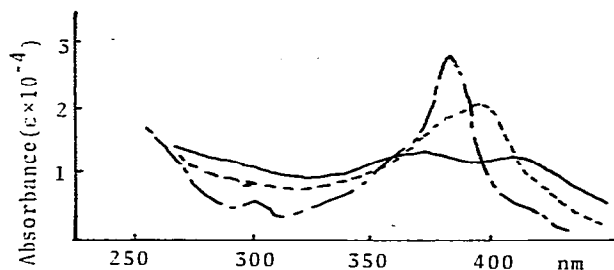


Fig. 2. Electronic spectra of the polymers, $\{trans, trans-M(PBu_3)_2-C\equiv C-C\equiv C-M'(PBu_3)_2-C\equiv C-C\equiv C\}_{n/2}$ in CH_2Cl_2 : ——— $M = M' = Ni$; - - - - - $M = Ni, M' = Pt$; - · - · - $M = M' = Pt$.

assigned the lowest energy bands to the metal to ligand charge-transfer transitions which have λ_{max} values of 342 [10], 382 [10], and 414 nm, respectively (Fig. 1).

The transitions move to lower energy in the series of $Pd < Pt < Ni$, reflecting the increasing metal-to-alkynyl ligand charge-transfer interaction. This is the same order as found in the tetracyanides of Ni^{II} , Pd^{II} , and Pt^{II} , where the charge-transfer absorptions are assigned to metal-to-ligand charge-transfer ($d_{metal} \rightarrow \pi$) [16].

In Fig. 2, the electronic absorption spectrum of the Ni-Pt polymer of the type $\{trans, trans-M(PBu_3)_2-C\equiv C-C\equiv C-M'(PBu_3)_2-C\equiv C-C\equiv C\}_{n/2}$ (V) is compared with those of the Ni-Ni, and the Pt-Pt polymers. The data give no definite evidence about the alternate regularity because of broadening of the absorption band attributed to the nickel-to-alkynyl ligand charge-transfer. On the other hand, the sharp absorptions in the ^{31}P NMR spectrum speak in favor of a fairly good regularity of the alternate arrangement of nickel and platinum metals (Fig. 3).

Polymers III, IV, V, and VI are obtained as yellow or brownish yellow solids and are stable in air. Thermogravimetric analysis (Table 1) exhibits that V shows unusual stability (decomp. point $190^\circ C$) compared with the other nickel-con-

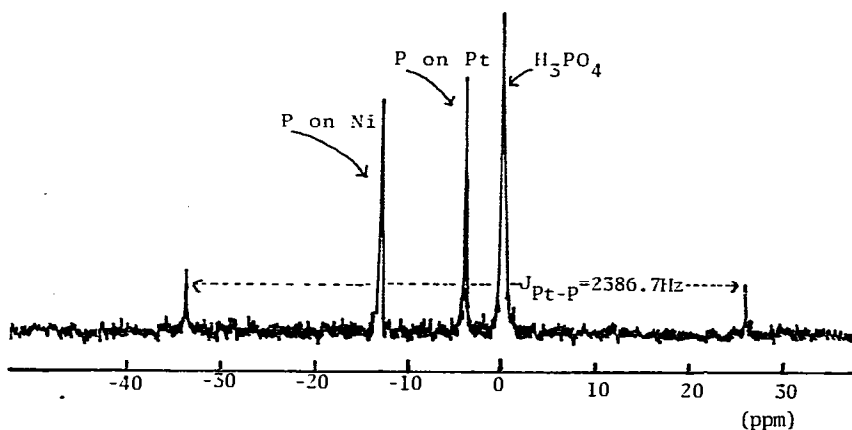


Fig. 3. $^{31}P\{^1H\}$ NMR spectrum of $\{trans, trans-Ni(PBu_3)_2-C\equiv C-C\equiv C-Pt(PBu_3)_2-C\equiv C-C\equiv C\}_{n/2}$.

taining poly-yne polymers III, IV, and VI, which decompose about at 150°C. The unusual stability of polymer V could be attributed to the bulky and stable $\text{Pt}(\text{PBU}_3)_2$ moieties which are arranged in close vicinity to the adjacent and unstable $\text{Ni}(\text{PBU}_3)_2$ groups. The bulky PBU_3 groups on Pt atoms may protect sterically from the thermal dissociation of PBU_3 ligands on Ni atoms which would cause the thermal decomposition of the nickel-containing polymers.

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