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PREPARATION AND UV SPECTRA OF SOME OLIGOMER-COMPLEXES COMPOSED OF PLATINUM GROUP METALS AND CONJUGATED POLY-YNE SYSTEMS

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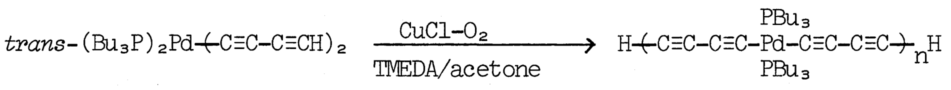
The long straight-line oligomer complexes (1) and (2), composed of metal atoms of the platinum group and conjugated poly-yne systems, and the shorter chain members of the series, (3)~(6), were prepared and their UV spectra were studied.

Although the literature on the polymers containing transition metal atoms is recently increasing, none have been described for the preparation of the polymers having backbones comprised of transition metal-carbon sigma bond. Previously we have reported the formation of the complexes in which two transition metal atoms are linked together through a sigma-bonded conjugated poly-yne system.¹⁾ In expectation of the interesting physical properties associated with a long conjugated structure including dπ(metal)-pπ(acetylenic carbon) interaction, we have now prepared novel straight-line oligomers composed of metal atoms of the platinum group and conjugated poly-yne systems.

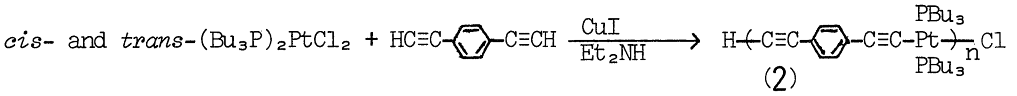
When the palladium complex, *trans*-$(Bu_3P)_2Pd(C{\equiv}C\text{-}C{\equiv}CH)_2$,²⁾ was treated at 25°C for 2 hr with 2 molar quantities of the oxidizing agent solution prepared by the bubbling of oxygen to a mixture of CuCl(300 mg), tetramethylethylenediamine (TMEDA, 405 mg) and acetone (50 ml), an oligomer complex (1) was obtained in a 75% yield after chromatography on an alumina column as an orange yellow powder (eq.1), decomp. at 155°C; soluble in benzene or methylene chloride; i.r. $\nu_{C\equiv C}$ 2200, 2160, 2100 and 1980 cm^{-1}; M_n 5700(VPO in benzene), n=9.5 for (1) in eq.1.



$$trans\text{-}(Bu_3P)_2Pd(C{\equiv}C\text{-}C{\equiv}CH)_2 \xrightarrow[\text{TMEDA/acetone}]{CuCl\text{-}O_2} H(C{\equiv}C\text{-}C{\equiv}C\text{-}\underset{PBu_3}{\overset{PBu_3}{Pd}}\text{-}C{\equiv}C\text{-}C{\equiv}C)_nH \qquad \text{(eq.1)}$$

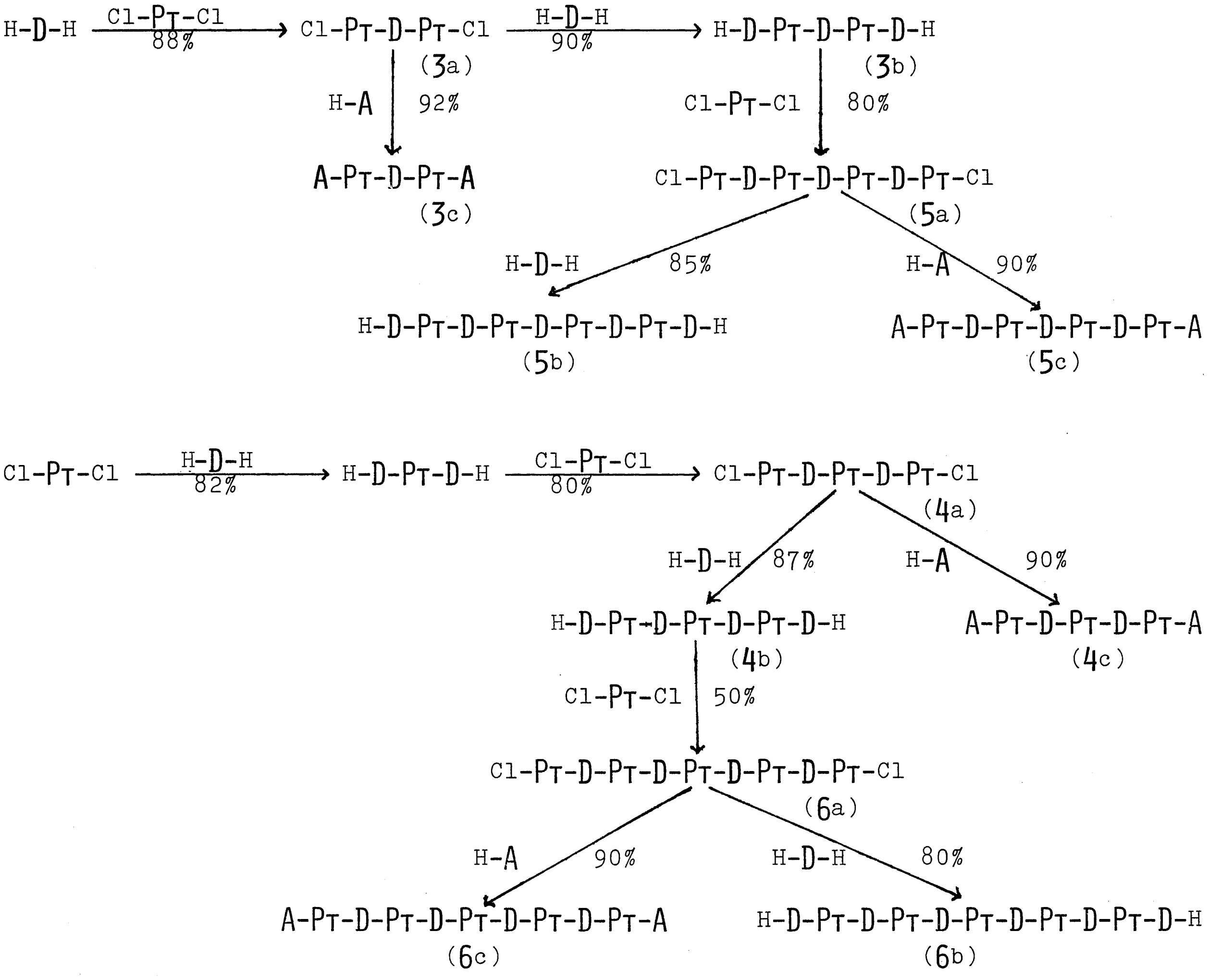
(1)

Treatment of the platinum complex, a mixture of *cis*-and *trans*-$(Bu_3P)_2PtCl_2$, with an equimolar quantity of *para*-diethynylbenzene in the presence of catalytic amounts of CuI in diethylamine (reflux for 15 hr) gave an oligomer complex (2) in a 90% yield after chromatography on an alumina column, as a yellow powder, decomp. above 200°C; soluble in benzene or methylene chloride; i.r. $\nu_{C\equiv C}$ 2100 cm^{-1}; M_n 7300(VPO in methylene chloride), n=10 for (2) in eq.2. The structure of the complex (2) was assumed to be all-*trans* because it has been known that such substitutions as indicated in eq. 2 favor the formation of the *trans*-complexes.



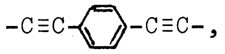
(2) (eq. 2)

In comparison with the UV spectrum of the standard complex (3c) in scheme 1, the absorption band due to the lowest energy UV transition of (2) showed a red shift, but the magnitude of the shift was considerably smaller than that expected for a conjugated long chain. In order to confirm these facts, the complexes (3a,b,c)~(6a,b,c), for which there are strong evidences of all-*trans* structure from the characteristic 1:4:6:4:1 quintet for n.m.r. methyl proton signals of *trans*-PEt_3[3] and the UV spectra[4], were prepared as outlined in scheme 1.



Scheme 1. Stepwise synthesis of the oligomer complexes (3a,b,c)~(6a,b,c)

Pt, A, and D represent $\overset{Et_3P}{\underset{Et_3P}{—Pt—}}$, $-C\equiv CC_6H_5$, and



, respectively.

All reactions were carried out in the presence of piperidine in toluene at 100°C for 5~10 hr.

Table 1. Analytical and spectral data

Compound	Analysis found(calcd.)				MW found[a)] (calcd.)	UV nm $\lambda_{max}^{CH_2Cl_2}$ ($\varepsilon \times 10^{-3}$)[b)]
	C	H	P	Cl		
(1)	62.74 (63.10)	9.54 (9.52)			5700	
(2)	56.44 (56.45)	8.35 (8.07)	8.28 (8.55)		7300	378 (520)
(3a)	38.60 (38.60)	6.29 (6.10)	12.03 (11.71)	6.70 (6.70)	1100 (1057)	348 (51)
(3b)	44.16 (44.01)	6.63 (6.42)	12.30 (11.95)		1037 (1015)	369 (104)
(3c)	50.54 (50.50)	6.42 (6.27)	10.14 (10.42)		1178 (1189)	363 (86.8)
(4a)	41.93 (41.69)	6.38 (6.12)	11.68 (11.52)	4.46 (4.40)	1598 (1613)	365 (103)
(4b)	50.90 (50.92)	6.19 (6.07)	10.72 (10.37)		1817 (1793)	375 (171)
(4c)	49.39 (49.56)	6.30 (6.24)	10.32 (10.65)		1680) (1745)	371 (142)
(5a)	43.22 (43.19)	6.31 (6.13)	11.70 (11.42)	3.40 (3.27)	2124 (2169)	374 (158)
(5b)	50.01 (50.12)	6.13 (6.09)	10.23 (10.55)		2295 (2348)	378 (232)
(5c)	49.32 (49.08)	6.46 (6.22)	10.44 (10.77)		2215 (2300)	376 (199.5)
(6a)	44.01 (44.09)	6.08 (6.14)	11.16 (11.37)	2.67 (2.60)	2660 (2724)	378 (220)
(6b)	49.55((49.63)	6.12 (6.11)	10.38 (10.67)		2800 (2904)	378 (297)
(6c)	48.59 (48.79)	6.46 (6.21)	11.01 (10.85)		2730 (2856)	378 (258)

a) VPO in CH_2Cl_2; (2) in benzene b) the lowest energy band

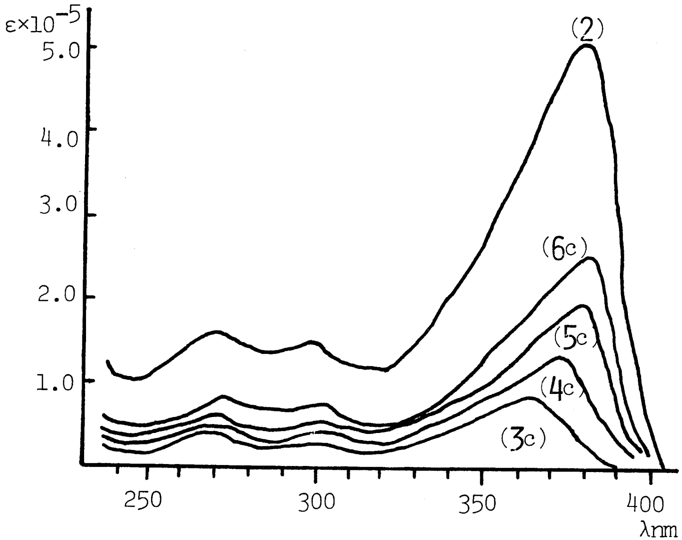


Fig. 1. UV spectra of the oligomer complexes.

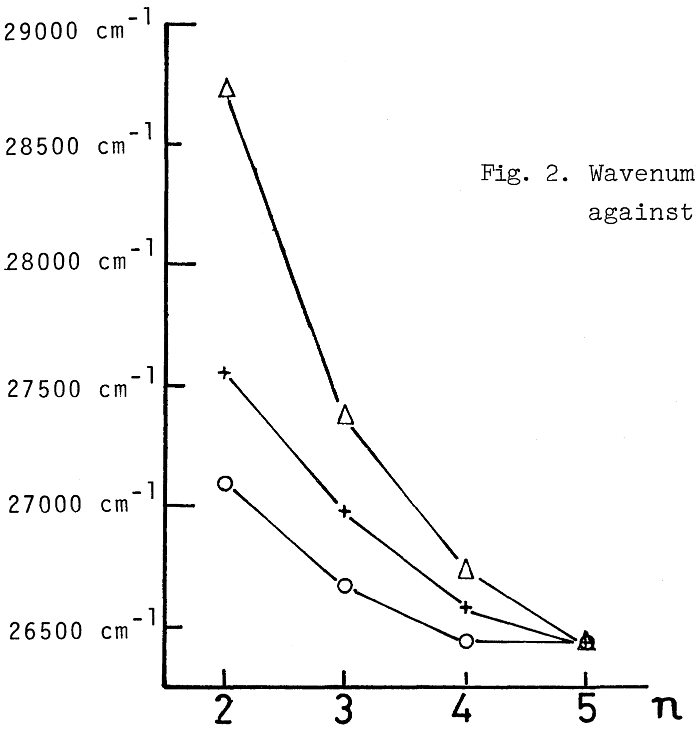


Fig. 2. Wavenumbers of the lowest energy bands against n of $R\text{-}(Pt\text{-}D)_{n-1}Pt\text{-}R$.

Δ : R= Cl
χ : R= $C{\equiv}CC_6H_5$
o : R= $C{\equiv}CC_6H_4C{\equiv}CH$

Comparing the UV spectra for the oligomer complex (2) and the shorter chain members of the series(presented in Fig. 1 and 2), we are led to the conclusion that

1) (2) is established to be all-*trans*[4],
2) as the value of n in $R\text{-}(Pt\text{-}D)_{n-1}Pt\text{-}R$ increases the UV absorption maxima for the lowest energy transition show a red shift, but the magnitude of the shifts rapidly decreases with increasing n value,
3) the three curves in Fig. 2 converge into a value (about 26500 cm^{-1} for the λ_{max} of (6a,b,c), which is the same frequency of λ_{max} of (2)) and the slopes of the curves decrease in the order of the following series of terminal groups : Cl > $-C{\equiv}CC_6H_5$ > $-C{\equiv}CC_6H_4C{\equiv}CH$.

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