Synthesis of transition metal–poly(yne) polymer possessing chiral acetylene bridges

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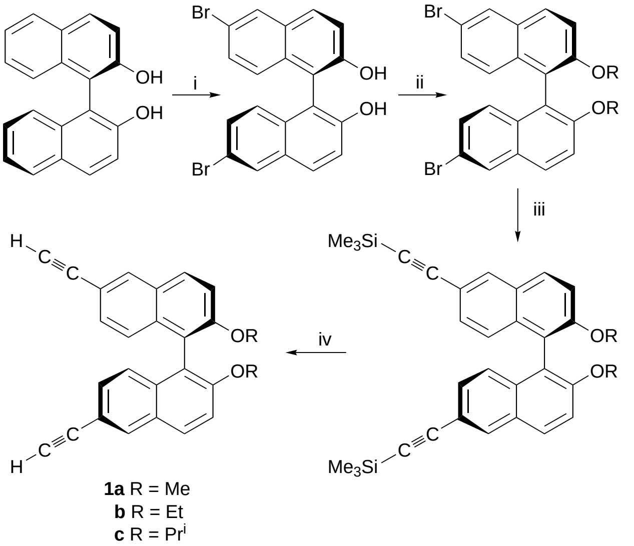
Treatment of C_2-symmetric chiral acetylenes, prepared from (*R*)-1,1′-bi-2-naphthol, with dichlorobis(trialkylphosphine)-platinum or -palladium in the presence of a Cu^I catalyst in amine gave high molecular-weight polynuclear complexes, which show a large negative optical rotation.

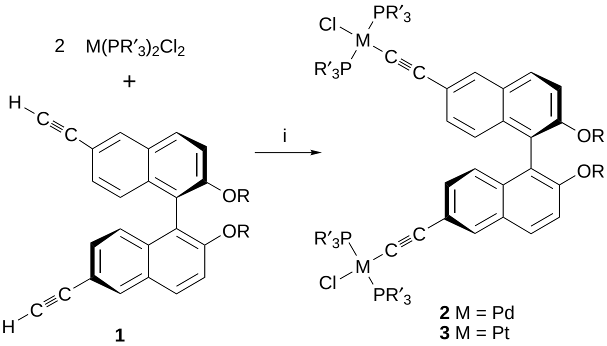
In recent years much attention has been drawn to molecular architecture incorporating coordination chemistry of transition metals.[1] We have been studying the chemistry of transition metal–poly(yne) polymers, in which metal atoms are linked by diynes such as butadiyne or *p*-diethynylbenzene to form rigid rod-like molecules.[2] Recently we showed that our methodology for the synthesis of multinuclear transition metal acetylides in one-dimension can be successfully applied to the synthesis of a three-dimension system giving a platinum–acetylide dendrimer.[3] Now we have expanded our methodology to the synthesis of polymers having a controlled main chain such as a helical structure. Since artificial polymers with a chiral backbone may maintain a stable single-handed helical conformation, they are of interest in view of their potential as new materials.[4] Here we report the first synthesis of a novel optically active poly(yne) polymer possessing a chiral acetylene bridge.

Bridging acetylene ligands **1** were easily prepared from 1,1′-bi-2-naphthol as shown in Scheme 1.[5] When optically active (*R*)-1,1′-bi-2-naphthol (commercially available, > 99% ee determined by HPLC using a chiral column) was used as a starting material, optically active acetylenes [**1a**: $[\alpha]_D$ −69 (*c* 0.05, $CHCl_3$); **1b**: $[\alpha]_D$ −29 (*c* 0.05, $CHCl_3$); **1c**: $[\alpha]_D$ −8 (*c* 0.1, $CHCl_3$)] having C_2 symmetry were obtained. X-Ray crystallographic study of **1b** and **1c** showed that the two naphthyl groups make a dihedral angle of 112.8° in **1b** and 105.3° in **1c**, respectively.‡



Scheme 1 *Reagents and conditions*: i, Br_2, CH_2Cl_2, −78 °C to room temp., 4 h, 91%; ii, RI, K_2CO_3, acetone, reflux, overnight, 85–89%; iii, $Me_3SiC{\equiv}CH$, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, reflux, overnight, 68–78%; iv, K_2CO_3, MeOH, overnight, 85–87%

As a model compound of the polymer we prepared optically active dinuclear complexes possessing a chiral acetylene bridge (Scheme 2). Treatment of **1a** with 2 equiv. of $Pd(PEt_3)_2Cl_2$ in the presence of a CuCl catalyst in Et_2NH at room temperature gave dipalladium complex **2a**. Similarly the reaction of **1b** with $Pd(PEt_3)_2Cl_2$ gave **2b**. Platinum analogs **3** were also prepared in a similar manner but at higher temperature (under piperidine reflux) because proportionation between platinum diacetylides and dichlorides takes place only at high reaction temperature.[2] These complexes were fully characterized by IR and NMR spectroscopy and elemental analysis.§ Yields and optical rotations are summarized in Table 1. The ^1H NMR spectrum of **3a** using the chiral shift reagent $Eu(fod)_3$ showed that no racemization took place during the conversion from chiral 1,1′-bi-2-naphthol.¶



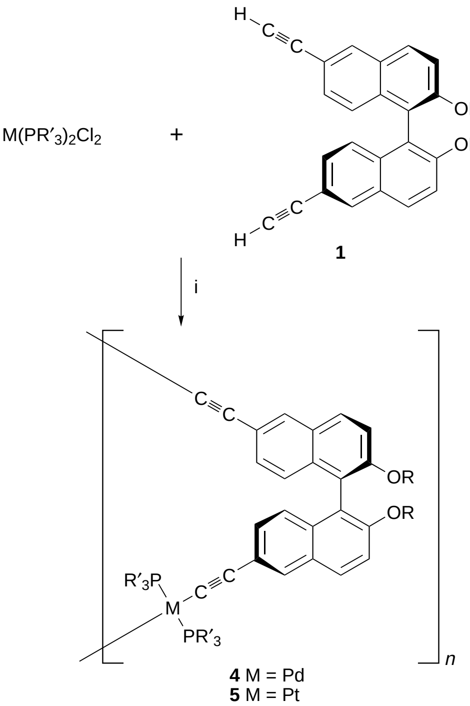
Scheme 2 *Reagents and conditions*: i, CuCl, Et_2NH, room temp., 4 h (M = Pd); CuCl, piperidine, reflux, overnight (M = Pt)

Reactions of chiral acetylene **1** with an equimolar amount of $M(PR'_3)_2Cl_2$ in the presence of a CuI catalyst in Et_2NH result in the formation of polynuclear complexes **4** and **5** having high molecular weight (Scheme 3). Experiments using ^{31}P NMR spectroscopy and GPC indicated the formation of dinuclear complexes **2** or **3** at an early stage, which slowly condense with terminal acetylene to propagate a metal–acetylide main chain. Since the resulting polymers are stable and soluble in common organic solvents, purification was performed by column chromatography on alumina followed by reprecipitation from CH_2Cl_2 into MeOH. The regular structures of **4** and **5** were

Table 1 Yields and optical rotations of dinuclear complexes **2** and **3**

Complex	M	R′	R	Yield (%)	$[\alpha]_D{}^a$
2a	Pd	Et	Me	82	−142
2b	Pd	Et	Et	78	−150
3a	Pt	Et	Me	62	−147
3b	Pt	Et	Et	61	−148
3c	Pt	Bu	Me	76	−103
3d	Pt	Bu	Et	57	−87

[a] In 10^{-1} deg cm^2 g^{-1} (*c* 0.05, $CHCl_3$, 25 °C).



Scheme 3 *Reagents and conditions*: i, CuI, Et_2NH, room temp., 4 h (M = Pd); CuCl, Et_2NH, reflux, overnight (M = Pt)

Table 2 Yields, molecular weights and optical rotations of poly(yne) polymers **4** and **5**

Polymers	M	R′	R	Yield (%)	$M_w/10^{3\,a}$	M_w/M_n	$[\alpha]_D{}^b$
4a	Pd	Et	Me	69	5.4	1.6	−370
4b	Pd	Et	Et	71	12	1.9	−227
4c	Pd	Et	Pr^i	73	11	1.9	−278
4d	Pd	Bu	Me	69	6.1	1.6	−265
4e	Pd	Bu	Et	63	9.8	1.6	−206
4f	Pd	Bu	Pr^i	59	7.4	1.6	−182
5a	Pt	Et	Me	73	12	2.7	−364
5b	Pt	Et	Et	73	30	2.9	−350
5c	Pt	Bu	Me	76	46	3.5	−331
5d	Pt	Bu	Et	92	100	4.0	−262
5e	Pt	Bu	Pr^i	71	22	2.2	−288

[a] Determined by GPC using poly(styrene) standards. [b] In 10^{-1} deg cm^2 g^{-1} [*c* 0.05 (R = Me, Et), *c* 0.10 (R = Pr^i), $CHCl_3$ at 25 °C].

confirmed by spectral analyses. For example, the ^{31}P NMR spectrum of **5d** exhibited one singlet signal at δ 3.27 with satellite signals (J_{Pt-P} = 2365 Hz). Only one set of signals, attributed to the naphthyl group, was observed in the ^1H and ^{13}C NMR spectra of **5d**.‖ Yields, molecular weights and optical rotations for **4** and **5** are shown in Table 2. The M_w values for palladium polymers **4** are in the range of 5400–12 000 regardless of the substituent on acetylene and the nature of the phosphine ligands, and are smaller than those of the platinum analogs **5**. A similar trend was observed in *p*-diethynylbenzene-bridged poly(yne) polymers.[2] In contrast, the M_w values of platinum polymers **5** were influenced to a certain extent by the substituent on the naphthyl group of the acetylene bridges and the nature of the phosphine ligands. Thus, the M_w values of ethoxy analogs **5b** and **5d** are much higher than those of the methoxy and isopropoxy variants. Since there is no significant difference in the structure of the bridging acetylene ligands **1b** and **1c** as determined *via* X-ray analysis, it is not clear why the molecular weights of the resulting polymers depend on the bridging acetylene ligands. Tributylphosphine analogs **5c** and **5d** have higher M_w values than triethylphosphine analogs **5a** and **5b**. It should be noted that all polymers prepared here showed larger specific optical rotations than both acetylene ligands **1** and model compounds **2** and **3**, which may indicate that the main chain of the polymers adopts a one-handed helical conformation and induces the helical chirality of the polymers.

In summary, we prepared novel optically active poly(yne) polymers of palladium and platinum possessing C_2-symmetric chiral acetylene bridges, which provide the first organometallic polymer with an optically active backbone, although some optically active organic acetylene polymers, in which chirality is similarly derived from 1,1′-bi-2-naphthol, have been reported very recently.[5]

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Notes and References

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‡ *Crystal data* for **1b**: $C_{28}H_{22}O_2$, orthorhombic, $P2_12_12_1$, a = 16.576(2), b = 18.193(3), c = 7.319(4) Å, V = 2207(1) Å^3, Z = 4, D_c = 1.175 g cm^{-3}, μ(Mo-Kα) = 0.73 cm^{-1}, $6 < 2\theta < 55°$, $R(R_w)$ = 0.054 (0.056) against 1420 reflections with $I > 2.0\sigma(I)$ out of 2914 unique reflections, GOF = 1.35. For **1c**: $C_{30}H_{26}O_2$, orthorhombic, $P2_12_12_1$, a = 16.359(7), b = 17.898(7), c = 8.025(9) Å, V = 2349(2) Å^3, Z = 4, D_c = 1.183 g cm^{-3}, μ(Mo-Kα) = 0.72 cm^{-1}, $6 < 2\theta < 55°$, $R(R_w)$ = 0.045 (0.046) against 2025 reflections with $I > 3.0\sigma(I)$ out of 3089 unique reflections, GOF = 1.44.

Data were measured on a Rigaku AFC5R diffractometer at −75 °C using the ω–2θ scan technique. The structure was solved by direct methods (SAPI91) and refined by full-matrix least-squares methods using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms are located at calculated positions. CCDC 182/755.

§ *Selected data* for **3b**: ν_{max}(KBr)/cm^{-1} 2115 (C≡C); δ_H($CDCl_3$, $SiMe_4$) 1.06 (t, *J* 7.0, 6 H), 1.20 (dt, J_{P-H} 14.1, J_{H-H} 7.1, 36 H), 2.04–2.11 (m, 24 H), 4.01 (q, *J* 7.0, 4 H), 6.95 (d, *J* 8.8, 2 H), 7.07 (dd, *J* 8.8, 1.5, 2 H), 7.34 (d, *J* 9.0, 2 H), 7.70 (d, *J* 1.5, 2 H), 7.80 (d, *J* 9.0, 2 H); δ_C($CDCl_3$, $SiMe_4$) 8.06, 14.67, 16.53, 65.26, 81.53 (t, J_{Pt-C} 1432, J_{P-C} 14.9), 102.02 (J_{Pt-C} 407), 116.17, 120.73, 123.67, 125.06, 128.28, 129.01, 129.28, 129.59, 132.23, 154.06; δ_P($CDCl_3$, H_3PO_4) 15.35 (J_{Pt-P} 2393.

¶ Only one signal assignable to the protons of the methoxy group appeared in the ^1H NMR spectrum of **3a** using the chiral shift reagent Eu(fod)$_3$, while two signals of the methoxy protons were separately observed in a similar NMR experiment of the corresponding racemic mixture.

‖ *Selected data* for **5d**: ν_{max}(KBr)/cm^{-1} 2114 (C≡C); δ_H($CDCl_3$, $SiMe_4$) 0.90 (t, *J* 7.3, 18 H), 1.02 (t, *J* 6.8, 6 H), 1.43 (sextet, *J* = 7.4, 12 H), 1.60–1.61 (m, 12 H), 2.17–2.20 (m, 12 H), 3.96–4.02 (m, 4 H), 6.97 (d, *J* 9.0, 2 H), 7.11 (d, *J* 9.0, 2 H), 7.33 (d, *J* 9.0, 2 H), 7.73 (s, 2 H), 7.76 (d, *J* 9.0, 2 H); δ_C($CDCl_3$, $SiMe_4$) 13.84, 14.99, 23.86 (vt, *N* 16.7), 24.40 (vt, *N* 6.8), 26.36, 65.31, 107.81 (t, J_{Pt-C} 968, J_{P-C} 14.3), 109.28 (J_{Pt-C} 272), 116.05, 120.86, 124.10, 124.97, 128.13, 128.88, 129.38, 129.67, 132.00, 153.79; δ_P($CDCl_3$, H_3PO_4) 3.27 (J_{Pt-P} 2365).

1 For recent reviews, see: B. Linton and A. D. Hamilton, *Chem. Rev.*, 1997, **97**, 1669; M. M. Conn and J. Rebek, Jr., *Chem. Rev.*, 1997, **97**, 1647; J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; D. B. Amabilino and J. F. Stoddart, *Chem. Rev.*, 1995, **95**, 2725.

2 N. Hagihara, K. Sonogashira and S. Takahashi, *Adv. Polym. Sci.*, 1981, **41**, 149.

3 N. Ohshiro, F. Takei, K. Onitsuka and S. Takahashi, *Chem. Lett.*, 1996, 871.

4 O. Vogl and G. D. Jaycox, *CHEMTECH*, 1986, **16**, 698; G. Wulff, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 21; Y. Okamoto and T. Nakano, *Chem. Rev.*, 1994, **94**, 349; R. J. M. Nolte, *Chem. Soc. Rev.*, 1994, 11.

5 L. Ma, Q.-S. Hu, K. Y. Musick, D. Vitharana, C. Wu, C. M. S. Kwan and L. Pu, *Macromolecules*, 1996, **29**, 5083; L. Ma, Q.-S. Hu, D. Vitharana, C. Wu, C. M. S. Kwan and L. Pu, *Macromolecules*, 1997, **30**, 204; C.-J. Li, W. T. Slaven IV, V. T. John and S. Bannerjee, *Chem. Commun.*, 1997, 1569.

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