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A convenient route to 1,3,5-trisubstituted benzenes via rhodium catalyzed polymerization of arylacetylenes

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Abstract

 $[(1,2,5,6-\eta)-1,5-Cyclooctadiene](1,3-propanediamine-N,N')$ rhodium(1+)chloride. $[(COD)RhCl(H_2NCH_2CH_2CH_2NH_2)]Cl,$ 11, and the water soluble complexes $(COD)RhCl(Ph_2PC_6H_4-3-SO_3Na)$ 10. trans-[Rh(CO)(Ph₂PC₆H₄-3-CO₂H)(μ - $(Ph_2PC_6H_4-2-CO-O)-Rh(CO)(\overline{NHMe=CHCMe=N})$ NCMe=CHCMe=N)]₂ 12. 13a. $(Ph_2PC_6H_4-2-CO-O)-Rh(CO)(indazole)$ 13b and trans- $[Rh(CO)(Ph_2PC_6H_4-2-CHO)(\mu-CO)(Ph_2PC_6H_4-2-CHO)(Ph_2PC_6H_4$ NCMe-CHCMe-N) 2 14 were shown to catalyze the polymerization of PhC=CH 1 and the substituted arylacetylenes 2-8 at 25°C in a stereoregular manner. The cis-oriented poly (arylacetylenes), so formed, were found to depolymerize selectively at 200-225°C to the corresponding 1,3,5-triarylbenzene derivatives.

Key words: arylacetylenes; polymerization; rhodium; trisubstituted benzenes

Introduction

The ever growing need for polymers with unusual mechanical, optical and electrically conducting properties raised much interest in the synthesis and in the structural features of poly(phenylacetylene) (see, e.g., refs. 1, 2). The transformation of phenylacetylene 1 to polymers has been accomplished with the aid of Ziegler-Natta and a variety of other transition metal catalysts. However, in most cases the polymers consisted either of mixtures of isomers or of stereoirregularly linked phenylethylene units [3]. Only a few papers describe the formation of isomerically pure poly(phenylacetylene) (e.g., refs. 2, 4). In

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this study we report the preparation of stereoregular poly (arylacetylenes) that undergo thermal cleavage selectively to 1,3,5-trisubstituted benzenes (eqn. 1).

 $nArC = CH \rightarrow polymer \rightarrow n/3(1,3,5-Ar_3C_6H_3)$ (1)

Experimental

[(1,2,5,6-η-1,5-Cyclooctadiene](1,3-propanediamine-N,N')rhodium(1+) chloride **11**

To a stirred solution of 99 mg (0.2 mmol) of $[(COD)Rh(\mu-CO)]_2$ in dry benzene was injected under N₂ 33 μ l (0.4 mmol) of 1,3-propanediamine. After 20 min the precipitate was filtered, washed with benzene and dried. Yield 114 mg (89%) of analytically pure **11** as yellow crystals; m.p. (dec.) 165°C; IR (Nujol): 3438, 3175 (N-H), 1347, 1318 cm⁻¹ (1,5-C₈H₁₂) (cf., ref. 5). Analysis: Found: C, 41.15; H, 6.90; N, 8.56%. C₁₁H₂₂C1N₂Rh requires: C, 41.20; H, 6.92; N, 8.74%.

General procedure for the preparation of complexes 12-14

In analogy to the procedure reported by Usón et al. for some other pyrazolato-bridged dirhodium-phosphine complexes [6] a solution of 0.1 mmol sodium pyrazolate, 3,5-dimethylpyrazolate or indazolate in 5 ml of 90% aq. MeOH was added dropwise to a suspension of 247 mg (0.05 mmol) of [(COD)Rh(μ -Cl)]₂ in 15 ml of the same solvent. The yellow precipitate was filtered, dried and dissolved in 15 ml of CH₂Cl₂. A stream of CO was bubbled through this solution for 15 min. Addition of 0.1 mmol of the appropriate tertiary phosphine [2-(diphenylphosphino)benzoic acid, 3-(diphenylphosphino)benzoic acid, (2formylphenyl)diphenylphosphine [7]] caused rapid evolution of CO. When the evolution of the gas ceased the solvent was evaporated under reduced pressure and the residue washed thoroughly with hexane to give the expected rhodium complexes in 80–90% yield.

Compound **12**: m.p. (dec.) 199°C (from $CH_2Cl_2-Et_2O$); IR (Nujol): 1965 (RhC=O) 1716 cm⁻¹ (C=O); 200 MHz ¹H NMR (CDCl₃) 2.384 (s, 12, CH₃), 6.827 (m, 2, CH₃CCH), 7.150–7.850 (m, 28, ArH). Analysis: Found: C, 56.21; H, 4.19; N, 5.35%. $C_{50}H_{44}N_4O_6P_2Rh_2$ requires: C, 56.41; H, 4.17; N, 5.26%.

Compound **13a**: m.p. (dec.) 154° C (from CH_2Cl_2 -pentane); IR (Nujol): 1958 (RhC=O), 1602 cm⁻¹ (OC=O; 400 MHz ¹H NMR (CDCl₃): 2.295 (s, 3, CH₃), 2.368 (s, 3, CH₃), 6.860 (m, 1, CH₃CCH), 7.335-8.223 (m, 14, ArH), 11.836 (br s, 1, NH). Analysis: Found: C, 56.34; H, 4.06; N, 5.10%. $C_{25}H_{22}N_2O_3PRh$ requires: C, 56.41; H, 4.17; N, 5.26%.

Compound **13b**: m.p. (dec.) $171^{\circ}C$ (from CH₂Cl₂-pentane); IR (CHCl₃): 1965 (RhC=O), 1616 cm⁻¹ (OC=O); 400 MHz ¹H NMR (CDCl₃): 6.881-7.785 (m, 18, ArH), 8.391 (m, 1, NCH), 12.493 (br s, 1, NH). Analysis: Found: C, 58.29; H, 3.33, N, 4.89%. $C_{27}H_{20}N_2O_3PRh$ requires: C, 58.50, H, 3.64; N, 5.05%.

Compound 14: m.p. (dec.) 163° C (from THF-pentane); IR (CHCl₃): 1977 (RhC=O), 1685 cm^{-1} (C=O); 400 MHz ¹H NMR (CDCl₃): 2.327 (s, 12, CH₃), 7.073 (m, 2, CH₂CCH), 7.287-7.864 (m, 28, ArH), 10.817 (s, 2, CHO). Analysis: Found: C, 57.95; H, 4.15; N, 5.38%. C₅₀H₄₄N₄O₄P₂Rh₂ requires: C, 58.15; H, 4.29; N, 5.43%.

Further structural data on complexes 12–14, including X-ray diffraction analyses, will be published in a separate paper.

General procedure for polymerization of arylacetylenes

In a typical experiment 5 mg $(1.56 \times 10^{-2} \text{ mmol})$ of complex 11 was added to a degassed solution of 306 mg (3 mmol) of PhC=CH 1 in 55 ml of EtOH. The mixture was stirred under argon for 4 h. The resulting orange polymer was filtered, washed thoroughly with degassed EtOH, dried and stored under exclusion of air. Yield of analytically pure polymer 291 mg (95%); IR (CHCl₃): 1492, 1445, 1383, 917, 888, 843, 741 cm⁻¹ (cf. ref. 3); 400 MHz ¹H NMR (CDCl₃): 5.824 (s, 1), 6.634 (d, 2, J=8.4 Hz), 6.932 (m, 3) (cf. ref. 2); 75 MHz ¹³C NMR (CDCl₃): 126.6, 127.4, 127.7, 131.7, 139.2, 142.7 (cf. ref. 3). The polymer was free of 1,3,5-triphenylbenzene, **15a**, as well as of isomeric macromolecules that usually accompanied polyphenylacetylene prepared by other procedures [2]. Some synthetic, physical and analytical data for

TABLE 1

Starting alkyne	Reaction time (h)	Yield of EtOH- insoluble polymer (%)	M.p. (dec.) (°C)	Average of Z values of isolated polymers (Å) ^b	Approximate average mol. weight of isolated polymers
1	1	> 95	200-203	162	6 600
2	2	91	223-225	199	12 700
3	20	85	210-215	245	12 900
4	1	91	172-176	263	12 200
5	2	87	197-201	439	23 900
6	1.5	89	185-188	526	38100
7	4	84	205-208	535	25 700
8	2	92	156-158	559	25 900
9	20	80	225-232	d	đ

Synthetic and physical data for poly(arylacetylenes) prepared from alkynes 1-9 in the presence of catalyst 11°

^aReaction conditions as described in the Experimental section.

^bAverage of at least four measurements.

°The calculations are based on an approximation that each Z unit is ca. 2.5 Å.

^dNot determined because of low solubility in organic solvents.

TABLE 2

400 MHz $^1\!H$ NMR spectra $^{a,\,b}$ and elemental analyses of the various poly(arylacetylenes) derived from 1-9

Compound	¹ H NMR spectra and analytical data				
1°	NMR: 5.824 (s, 1), 6.634 (d, 2, J=8.4 Hz), 6.932 (m, 3). Analysis: Found: C,				
-	93,83; H, 5.80%. $(C_8H_6)_n$ requires: C, 94.08; H, 5.92%.				
2	NMR: 1.600 (s, 9), 5.805 (s, 1), 6.540 (m, 2), 6.965 (m, 2). Analysis: Found: C,				
	91.29; H, 8.66%. $(C_{12}H_{14})_n$ requires: C, 91.08; H, 8.91%.				
3	NMR: 3.577 (s, 3), 5.763 (s, 1), 6.466 (d, 2, $J=8.3$ Hz), 6.629 (d, 2, $J=8.3$ Hz).				
	Analysis: Found: C, 81.33; H, 6.10% (C ₂ H ₈ O), requires: C, 81.82; H, 6.06%.				
4	NMR: 2.135 (s, 3), 5.812 (s, 1), 6.534 (d, 2, $J=8.2$ Hz), 6.754 (d, 2, $J=8.3$ Hz).				
	Analysis: Found: C. 92.79: H. 6.81%. (C.H.), requires: C. 93.10: H. 6.90%.				
5	NMR: 5.967 (s, 1), 6.707 (d, 2, $J=8.1$ Hz), 7.126 (d, $J=8.1$ Hz). Analysis:				
	Found: C. 70.62; H. 3.73%. (C ₂ H ₅ Cl), requires: C. 70.35; H. 3.69%.				
6	NMR: 5.963 (s, 1), 6.542 (d, 2, $J=8.1$ Hz), 6.942 (d, $J=8.1$ Hz), Analysis:				
-	Found: C. 52.93; H. 2.95%, $(C_{0}H_{-}Br)_{-}$ requires: C. 53.03; H. 2.76%.				
7	NMR: 5.973 (s. 1), 6.795–6.871 (m. 4), Analysis: Found: C. 79.88 H. 4.27%.				
•	(C.H.F.) requires: C 79.98: H 4 20%				
9	$(0,1,5,1)_n$ (0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,				
0	$\mathbf{M}_{\mathbf{M}}_{\mathbf{M}}_{\mathbf{M}}_{\mathbf{M}}}}}}}}}}$				
_	Found: $(0, 92.78; H, 6.62\%, (0.9H_8)_n$ requires: $(0, 93.06; H, 6.94\%)$.				
9	Analysis: Found: C, 64.99; H, 3.55; N, 9.65%. $(C_8H_5NO_2)_n$ requires: C, 65.30; H, 3.42; N, 9.52%.				

^aIn CDCl₃.

^bThe numbers in parentheses that follow the multiplicities represent the *relative* integrations for the protons.

°Cf. ref. 4.

TABLE 3

Synthetic and physical data for 1,3,5-triarylbenzenes obtained by depolymerization of poly(arylacetylenes) [(XC_6H_4)C=CH]^{*}_n

x	Depolym. temp. (°C)	Product	Yield ^b (%)	M.p.° (°C)	Reference for preparation of authentic sample
н	200	15a	34	174-175	[9]
4-CMe ₃	225	15b	28	294-295	[9]
4-OMe	220	15c	17	142-143	[9]
4-Cl	220	15e	20	236-238	[10]
4-Br	220	15f	23	262-263	[9]
4-F	220	15g	15	235-236	[11]
2-Me	200	16	21	124-126	đ

^aDepolymerization time: 2 h.

^bIsolated and purified product.

[°]After recrystallization from EtOH [except for 1,3,5-tris(4-bromophenyl)benzene which was recrystallized from MeOH].

^d200 MHz ¹H NMR (CDCl₃): 2.384 (s, 9), 7.235–2.340 (m, 15). Analysis: Found: c, 93.43; H, 6.76%. $C_{27}H_{24}$ requires: C, 93.10; H, 6.90%.

poly(arylacetylenes) derived from alkynes 1-9 are summarized in Tables 1 and 2.

Molecular weight determination of the poly(arylacetylenes)

The molecular weights of the polymers (8-12 mg) in degassed toluene (3 ml) were determined by light scattering by the method described by Cummins and Pusey [8]. The measurements were taken on a Malvin 4700/SM Photon Correlation Spectrometer (Malvin Precision Devices and Systems Ltd.) which consists of a 633 nm argon-neon laser (Spectra Physics M-128) with an output power of ca. 35 mW, a photomultiplier combined with electronic pulse amplification and standardization devices, and a Malvin K7032 72-channel digital correlator. The sample cell was thermostatted with an LKB 7600 precision bath at 28.7 °C. The available scattering angle was 90°. Data analysis was obtained with the aid of the Malvin software package which utilizes cumulant analysis. The initial slope corresponding to the linear line that would occur from a monosized particle gave the so-called Z average size.

Approximate molecular weights were calculated from the molecular weight of the monomers which are assumed to extend in the polymer to ca. 2.5 Å. The results for the various polymers from 1-8 are summarized in Table 1.

General procedure for transformation of the poly(arylacetylenes) to 1,3,5trisubstituted benzenes

Under an argon atmosphere, the rhodium-free dried polymer was inserted in a thermostat operating at the temperature described in Table 3. After 2 h the resulting triarylbenzene was separated from the polymeric material by chromatography on silica 60 using hexane (containing 0–7% ether in accordance with the polarity of the product) as eluent. The various triarylbenzenes were identified either by comparison with authentic samples or by their NMR, mass spectra and elemental analyses. The results are summarized in Table 3.

Results and discussion

In the preceeding paper [12] we have shown that, in contrast to several other rhodium complexes that catalyze the dimerization and trimerization of PhC=CH, 1, sodium [chloro(1,2,5,6- η)-1,5-cyclooctadiene)][3-diphenyl-phosphino)benzenesulfonato-P]rhodate(1-) monohydrate (COD)RhCl-(dmp)·H₂O 10 [13], promote the stereoregular conversion of the alkyne mainly (or entirely) into *cis*-oriented poly(phenylacetylene) which has already been described by other authors (e.g. ref. 2). The yield and isomeric purity of the polymers were found to depend strongly on the nature of the medium and on the reaction temperature. Thus, e.g., at 25°C 1 was converted in EtOH to the polymer in almost quantitative yield within less than 30 min. In other carbinols (1-butanol, 1-pentanol) as well as in a biphasic system of

water and toluene, the reaction lasted 10–20 h. Upon elevation of the temperature considerable amounts of 1,3,5-triphenylbenzene **15a** were formed and part of the polymer lost its original structure (e.g., **1** in PhMe/H₂O gave 28% of **15a** after 4 h at 92°C).

Since Furlini et al. [2] reported that rhodium complexes with a cyclic diene ligand (*cis,cis*-1,5-cyclooctadiene, 2,5-norbornadiene) gave particularly highly stereoregularly oriented poly (phenylacetylene), we screened a variety of additional COD complexes. We found that $[(1,2,5,6-\eta)-1,5$ -cyclooctadiene](1,3-propanediamine-N,N')rhodium(1+) chloride, $[(COD)Rh(H_2N-CH_2CH_2CH_2NH_2)]Cl$, **11** gives the highest yield (95-98%) of *cis*-poly (phenylacetylene) molecules of almost identical size (96% in the range of Z=160-164 Å). Other alcohol soluble rhodium complexes, such as **12-14**, which do not contain a diene ligand, were found, however, to be just as efficient and selective catalysts as **1**. Yet it should be noted that small variations in the ligands can have a great effect on the polymerization. Thus, e.g., substitution of the 3,5-pyrazole in **13a** (or the indazole moiety in **13b**) by 1*H*-pyrrole[2,3-*b*]pyridine, or removal of the methyl groups in **14**, renders the catalysts almost inactive under our experimental conditions.



The high stereoregularity of the poly(phenylacetylene) formed by the above catalysts was deduced from the sharp NMR singlet of the olefinic protons at 5.824 ppm (which integrates at the ratio 1:2 with the doublet at 6.634 ppm and 1:3 with the signal at 6.932 ppm), from the lack of other ¹H NMR signals and from the characteristic ¹³C NMR and IR spectra that match those reported for *cis*-poly(phenylacetylene) [2]. The observation that the polymer



Fig. 1. cis-cisoidal Poly (arylacetylene).

undergoes thermal (non-catalytic) depolymerization to give 15a (see below) strongly suggests that the polymer exists (or is transformed by heating) to a significant extent into the *cis*-cisoidal helical conformation (Fig. 1).

Extension of the catalytic transformation of 1 to various substituted arylacetylenes (4-Me₃CC₆H₄C=CH 2, 4-MeOC₆H₄C=CH 3, 4-MeC₆H₄C=CH 4, 4-ClC₆H₄C=CH 5, 4-BrC₆H₄C=CH 6, 4-FC₆H₄C=CH 7, 2-MeC₆H₄C=CH 8 and 4-O₂NC₆H₄C=CH 9) resulted in the formation of similar stereoregular polymers. Some experimental and physical data for these poly (arylacetylenes) are summarized in Tables 1 and 2. The Z average values of the polymers which were obtained by laser light scattering measurements of toluene solutions of the polymers [8] (the polymers deteriorated in CH₂Cl₂ and CHCl₃), indicate that the distribution of the molecular weights of each of the polymers lie within an extremely small range. The electronic and steric structures of the starting alkyne was, however, found to have a significant effect on the size of the polymer. The unsubstituted acetylene 1 formed the shortest polymer, and the sterically hindered 2-MeC₆H₄C=CH 8 the longest. Alkynes with electron donating groups furnished shorter macromolecules than acetylenes with electron attracting substituents (see Table 1).

Although similar ¹H NMR spectra of the various poly(arylacetylenes) were recorded, the small but distinguished effect of the substituents on the chemical shift of the vinylic protons is remarkable. The shielding caused by the electron donating groups and the deshielding induced by the electron attracting substituents at the *para* position (see Table 2) can be explained by the proximity of these substituents to the vinylic hydrogen atoms in the helical *cis-cisoid* polymer.





Upon heating of the metal free poly(arylacetylenes) at 200-225 °C they depolymerized and gave the corresponding 1,3,5-triarylbenzenes 15-16. Poly(4-nitrophenylacetylene) could not be transformed to 1.3.5-tris(4-nitrophenyl)benzene because it exploded under the pyrolytic conditions. The triarylbenzene could easily be separated from the residual polymer (which does lose its stereoregular structure) by filtration through silica gel with hexane (containing 0-7% Et₂O) as eluent. Experiments with mixtures of two or several different poly(arylacetylenes) yielded only the respective symmetrically substituted benzenes. The fact that no mixed trisubstituted benzenes were formed indicates that the depolymerization furnishes directly the substituted benzenes rather than 'monomeric' arylethylene units that subsequently cyclotrimerize. It is assumed that C-C bond cleavage of the cis-cisoidal polymer (Fig. 1) is associated with the C-C bond formation between two other closely located carbon atoms that consequently leads to aromatic ring closure. Naturally, the thermolysis causes destruction of some of the cis-cisoidal oriented units and the formation of differently oriented polymers that cannot give substituted benzenes.

Although the yields of the triarylbenzenes are only moderate (see Table 3), the efficiency of the stereoregular polymerization and the simplicity of the depolymerization makes this synthesis an attractive route to symmetrically substituted benzenes. It should be recalled that the current methods for such compounds (see, e.g., refs. 9, 10, 14) are quite tedious processes and seldom high-yielding.

Finally, it is notable that in spite of the fact that the depolymerization of the poly (arylacetylenes) at 200–225 °C takes place in the absence of a catalyst, and the addition of complexes **10–14** during the pyrolysis has no effect on the rate of formation of the 1,3,5-triarylbenzenes, it is likely that some alkyne oligomer intermediates formed during the polymerization do undergo catalytic fission to form substituted benzenes. Support for this assumption is provided by the fact that the poly (phenylacetylene) prepared by Furlini et al. [2] was accompanied by a small amount of **15a**, and by a series of experiments in which **1**, **4** and **5** were treated with **10** either for prolonged periods (e.g. in *n*-BuOH for 7 days at 25°C) or for shorter periods at 92–110°C (in *n*-BuOH for 20 h or in a PhMe/H₂O system for 10 h) in which 6–28% of the symmetrically, and hardly any of the non-symmetrically substituted benzenes were obtained.

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