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Organometallic Chemistry of Homoleptic Carbonylmetal Cations. 1. Stereospecific Tetramerization of 2-Propynol and Polymerization of Arylacetylenes by Means of $[Pt(CO)_4][Sb_2F_{11}]_2$

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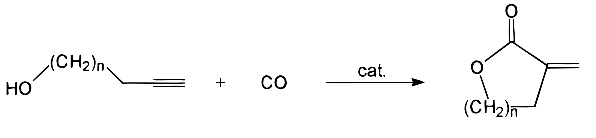
Neat 2-propynol was treated with 7×10^{-3} mol % of solid $[Pt(CO)_4][Sb_2F_{11}]_2$ (**1**) in a carbon monoxide atmosphere to afford 2,5-dimethyl-2,5-bis(2-propynoxy)-1,4-dioxane (**2**) in high yield. The bis-alkyne derivative was converted into its bis(hexacarbonyldicobalt)complex **3** by reaction with 2 equiv of $[Co_2(CO)_8]$. Compound **3** was fully characterized by a single-crystal X-ray analysis. In contrast to this, selected arylacetylenes were polymerized by **1** to afford poly(arylacetylenes) with an all-trans transoidal microstructure. With 2.1×10^{-2} up to 2.7×10^{-2} mol % of catalyst average molecular weights (M_w) between 3000 and 4300 were obtained.

Introduction

Recently thermally stable salts with homoleptic carbonylmetal cations such as $[Au(CO)_2]^+$, $[Hg(CO)_2]^{2+}$, $[M(CO)_4]^{2+}$ (M = Pd, Pt), $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os), and $[Ir(CO)_6]^{3+}$ have attracted considerable interest.[1] The existence of such complex cations is not expected with regard to the well-accepted paradigm that metal carbonyl bonding necessitates a considerable back-donation of electron density from metal d orbitals into CO π^* orbitals.[2]

Disregarding a few carbonyl replacement reactions, the chemistry of the novel carbonyl cations remains practically unexplored.

Hence, we launched a program to investigate the organometallic chemistry of these species. It was obvious to first look at carbonylation reactions of unsaturated hydrocarbons in the presence of the now easily available salts $[M(CO)_4][Sb_2F_{11}]_2$ (M = Pd, Pt). For example, the carbonylative cyclization of acetylenic alcohols with carbon monoxide is one of the most straightforward methods of obtaining α-methylenelactones, which has been intensively studied for the five-membered γ-lactones (eq 1).[3]



(1)

cat. = $Pt(PPh_3)_4$ / ArylSH

The preparation of the six-membered δ-lactones has been described from 5-hydroxy-1-pentyne and carbon monoxide in the presence of arenethiols and under the influence of a platinum(0) catalyst.[4]

In this paper we describe our first results on the reactions of selected alkynes in the presence of catalytic amounts of $[Pt(CO)_4][Sb_2F_{11}]_2$ (**1**)[5] under an atmosphere of carbon monoxide.

Experimental Section

All operations were performed with standard Schlenk techniques in a dry and oxygen-free carbon monoxide or nitrogen atmosphere. Solvents were dried by standard methods and freshly distilled under nitrogen. Infrared spectra were recorded on Bruker FT-IR IFS 66 and Bruker FT-IR VECTOR 22 instruments. ^1H and ^{13}C NMR spectra were taken on Bruker AM Avance DRX 500 (^1H, 500.13 MHz; ^{13}C, 125.76 MHz), Bruker AM 300 (^1H, 300.15 MHz; ^{13}C, 75.47 MHz), Bruker AC 250 P (^1H, 250.13 MHz; ^{13}C, 62.90 MHz), and Bruker AC 100 (^1H, 100.13 MHz; ^{13}C, 25.18 MHz) instruments. EI mass spectra (70 eV) and LSIMS mass spectra were obtained with a Micromass Autospec double-focusing mass spectrometer. MALDI-TOF mass spectra were acquired on GSG future MALDI-TOF mass spectrometer with optional delayed extraction in the GSG laboratory in Karlsruhe. Dithranol served as the matrix of choice in all cases. Gel permeation chromatographic investigations were performed in the research group of Professor F. Bandermann, University of Essen, with the following two instruments:

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(1) Reviews: (a) Willner H.; Aubke, F. *Angew. Chem.* **1997**, *109*, 2506; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*. (b) Aubke, F.; Wang, C. *Coord. Chem. Rev.* **1994**, *137*, 483.

(2) For a recent paper on this topic see: Lupinetti, A. J.; Frenking, G.; Strauss, S. H. *Angew. Chem.* **1998**, *110*, 2229; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2113.

(3) (a) Murray, T. F.; Samsel, E. G.; Varma, N.; Norton, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 7520. (b) Murray, T. F.; Norton. J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4107. (c) Murray, T. F.; Varma, V.; Norton, J. R. *J. Org. Chem.* **1978**, *43*, 353. (d) Murray, T. F.; Varma, V.; Norton, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 8085. (e) Norton, J. R.; Shenton, K. E.; Schwartz, J. *Tetrahedron Lett.* **1975**, 51. (f) Tsuji, Y.; Kondo, T.; Watanabe, Y. *J. Mol. Catal.* **1987**, *40*, 295.

(4) Ogawa, A.; Kawabe, K.; Kawakani, J.; Mihara, M.; Hirao, T.; Sonoda, N. *Organometallics*, **1998**, *17*, 3111.

(5) Hwang, G.; Wang, C.; Aubke, F.; Willner, H.; Bodenbinder, M. *Can. J. Chem.* **1993**, *71*, 1532.

10.1021/om990189r CCC: $18.00

(1) Knauer 64 (pump) with a flow-rate of 1 mL/min; Knauer A 0263 injection unit. Detection: Knauer differential refractometer/viscosimeter, Chromatix low-angle stray light laser-photometer KMX-6; temperature 30 °C; pressure 2−5 MPa (max. 10−14 MPa). Columns: (a) Shodex AC-806/S, 0J601, 10 μm, 250/8 mm, 1.2 MPa; limit of exclusion 50000000 g/mol; (b) Shodex AC-804/S, 9B417, 10 μm, 250/8 mm, 0.5 MPa, limit of exclusion 500000 g/mol; (c) Shodex AC-802/S, 9D212, 10 μm, 250/8 mm, 0.5 MPa, limit of exclusion 5000 g/mol; the number of theoretical plates according to the method of tangents is $N = 27000$ (/750 mm). The analysis of the data was accomplished with the program package Analyst 4.0 utilizing the UCAL GPC 1 and NORM GPC 1 programs KNUC and MTRI, respectively.

(2) Waters GPC with a flow-rate of 1 mL/min. Waters WISP-injector, with sample disk for 16 vials. Detection: high-temperature-differential refractometer/single-capillary viscosimeter; temperature 30−135 °C (max. 150 °C). The device was operated with toluene (13.4 MPa pressure) and 1,2,4-trichlorobenzene (24.0 MPa pressure). Columns: (a) PSS 10^6 A, 1515193, 10 μm, 300/7.8 mm, 1.8 MPa; limit of exclusion 10000000 g/mol; (b) PSS 10^5 A, 1515192, 10 μm, 300/7.8 mm, 1.8 MPa; limit of exclusion 4000000 g/mol; (c) PSS 10^3 A, 1515191, 10 μm, 300/7.8 mm, 1.8 MPa; limit of exclusion 70000 g/mol; the theoretical number of plates according to the method of tangents is $N = 37000$ (/900 mm). The analysis of the data was achieved with the program package Analyst 4.0 employing the UCAL GPC 4 and NORM GPC 4 programs WAUC and MTRI, respectively.

Elemental analyses were performed at the microanalytical laboratory of the University of Bielefeld.

Materials. Compounds $[Pt(CO)_4][Sb_2F_{11}]_2$[5] (**1**), phenylacetylene-d_1,[6] and *p*-chlorophenylacetylene[7] were prepared as described. 2-Propynol, phenylacetylene, *p*-tolylacetylene, C_6D_6, and $[Co_2(CO)_8]$ were purchased commercially.

Preparation of Compounds. 2,5-Dimethyl-2,5-bis(2-propynoxy)-1,4-dioxane (2). A sample of solid $[Pt(CO)_4]$-$[Sb_2F_{11}]_2$ (0.015 g, 12.4 μmol) was added to neat 2-propyn-1-ol (10.0 g, 178.0 mmol) under an atmosphere of carbon monoxide (1.3 bar), and the mixture was stirred for 6 h at ambient temperature. After removing volatiles in vacuo (~1 × 10^{-5} bar) the solid colorless residue was washed with methanol (2 × 5 mL) to give 8.9 g (89% yield) of **2** as an amorphous solid (mp = 118 °C). IR (KBr, cm^{-1}): ν 3270 s [ν(≡C−H)], 2997 m, 2985 w, 2963 w, 2942 m, 2877 w, 2360 w, 2342 w, 2114 w, 1446 w, 1378 m, 1294 m, 1272 w, 1246 m, 1183 m, 1113 m, 1077 m, 1024 s, 1001 s, 924 w, 901 w, 852 s, 768 m, 673 m, 659 m, 581 w, 572 w, 419 w. ^1H NMR (C_6D_6, 22 °C): δ 0.99 (s, 6H, CH_3), 1.96 (t, $^4J_{HH} = 2.5$ Hz, 2H, C≡CH), 3.33 (d, $^2J_{HH} = 11.5$ Hz, 2H, 3-, 6-H), 3.52 (d, $^2J_{HH} = 11.5$ Hz, 2H, 3-, 6-H), 3.92 (d, $^4J_{HH} = 2.5$ Hz, 4H, CH_2C≡C). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 20.3 (s, CH_3), 49.0 (s, *C*H_2C≡C), 66.0 (s, 3-, 6-C), 73.4 (s, C≡*C*H), 81.4 (s, CH_2*C*≡C), 92.2 (s, 2-, 5-C). MS (LSIMS, *m*-nitrobenzyl alcohol matrix): $m/z = 225$ $(M + H)^+$, 169 $(M + H - C_3H_5O)^+$, 113 $(M + H - 2\ C_3H_5O)^+$. Anal. Calcd for $C_{12}H_{16}O_4$ (224.36): C, 64.27; H, 7.20. Found: C, 64.02; H, 7.33.

$Co_2(CO)_6$[HC≡CCH_2OC(CH_3)CH_2OC(CH_3){OCH_2C≡CH-[$Co_2(CO)_6$]}CH_2O] (3). A solution of $[Co_2(CO)_8]$ (3.01 g, 8.8 mmol) in 50 mL of toluene was added dropwise to the chilled solution (−5 °C) of **2** (0.99 g, 4.4 mmol) in 30 mL of toluene. The mixture was stirred for 3 h at 20 °C, and then it was filtered. The red filter-cake was washed with toluene (3 × 10 mL) and dried in vacuo (~1 × 10^{-5} bar) for 1 h. Recrystallization from benzene afforded red crystalline **3** (3.34 g, 95%). IR (KBr, cm^{-1}): ν 3102 w, 3000 w, 2986 w, 2920 w, 2852 w, 2092 s [ν(CO)], 2067 s [ν(CO)], 2042 s [ν(CO)], 2028 vs [ν(CO)], 2011 vs [ν(CO)], 2000 vs [ν(CO)], 1652 w, 1558 w, 1538 w, 1455 w, 1381 w, 1345 w, 1293 w, 1245 w, 1194 w, 1140 w, 1084 s, 1049 m 989 w, 900 w, 874 w, 850 w, 704 w, 614 w, 569 w, 521 w, 497 m, 460 w, 450 w, 434 w, 415 w, 404 w. ^1H NMR (C_6D_6, 22 °C): δ 1.11 (s, 6H, CH_3), 3.52 (d, $^2J_{HH} = 11.2$ Hz, 2H, 3-, 6-H), 3.65 (d, $^2J_{HH} = 11.2$ Hz, 2H, 3-, 6-H), 4.40 (s, 4H, CH_2C≡C), 5.48 (s, 2H, C≡CH). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 20.3 (s, CH_3), 61.4 (s, *C*H_2C≡C), 66.1 (s, 3-, 6-H), 71.7 (s, C≡*C*H), 93.1 (s, CH_2*C*≡CH), 95.0 (s, 2-, 5-C), 200.0 (s, CO). MS (LSIMS, *m*-nitrobenzyl alcohol matrix): $m/z = 797$ $(M + H)^+$, 713 $(M + H - 3\ CO)^+$, 657 $(M + H - 5\ CO)^+$, 629 $(M + H - 6\ CO)^+$, 601 $(M + H - 7\ CO)^+$, 573 $(M + H - 8\ CO)^+$, 545 $(M + H - 9\ CO)^+$. Anal. Calcd for $C_{24}H_{16}Co_4O_{16}$ (796.08): C, 36.21; H, 2.03. Found: C, 35.72; H, 2.10.

Preparation of Phenylacetylene-d_5. A three-necked flask, equipped with a dropping funnel, a reflux condenser, and a stirring bar, was charged with benzene-d_6 (15.00 g, 180.0 mmol) and anhydrous aluminum trichloride (16.00 g, 120.0 mmol). The mixture was cooled by means of an ice bath, and acetyl chloride (9.42 g, 120.0 mmol) was added dropwise to the stirred solution within 15 min. Then the reaction mixture was heated at 50 °C for 5 h. After cooling to room temperature the mixture was cautiously poured onto 100 mL of ice, and precipitated aluminum hydroxide was dissolved in a minimum amount of concentrated hydrochloric acid. The organic layer was separated before the aqueous layer was extracted with 1,2-dichloroethane (2 × 50 mL). The combined organic phases were carefully washed with water, 2% NaOH, and again with water. Drying the solution with K_2CO_3 was followed by distillation. Acetophenone-d_5 (9.99 g, 60%) was collected as a fraction at bp 94 °C and 20 mbar. ^1H NMR ($CDCl_3$, 22 °C): δ 2.46 (s, CH_3).

A sample of finely powdered phosphorus pentachloride (13.32 g, 64.0 mmol) was added to chilled acetophenone-d_5 (8.00 g, 64.0 mmol), and the slurry was heated for 4 h to 100 °C with hydrogen chloride evolution. After cooling to room temperature the mixture was carefully poured onto crushed ice. The organic phase was separated, neutralized with aqueous KOH solution, and dried over anhydrous Na_2SO_4. The crude product was distilled to afford 5.94 g (65%) of α-chlorostyrene-d_5 (bp 64 °C, 20 mbar). ^1H NMR ($CDCl_3$, 22 °C): δ 5.58 (d, $^2J_{HH} = 1.6$ Hz, 1H, cis-HC=C), 5.82 (d, $^2J_{HH} = 1.6$ Hz, 1H, trans-HC=C).

A sample of α-chlorostyrene-d_5 (4.60 g, 32.0 mmol) was combined with 65 mL of a 25% ethanolic KOH solution, and the mixture was heated 2 h under reflux. After cooling to room temperature, the reaction mixture was poured onto ice and subsequently neutralized by means of half-concentrated HCl. It was extracted with diethyl ether (3 × 30 mL), and the combined extracts were dried with Na_2SO_4. After removal of the solvent the residue was distilled to afford 2.86 g (84%) of phenylacetylene-d_5 (bp 140−142 °C). ^1H NMR ($CDCl_3$, 22 °C): δ 3.12 (s, HC≡C). The product was stored over molecular sieve (4 Å) and freshly distilled before use.

Polymerization of Phenylacetylene. A slurry of $[Pt(CO)_4]$-$[Sb_2F_{11}]_2$ (**1**) (2.0 mg, 1.65 μmol) in 5 mL of *n*-pentane was reacted with 2.50 g (24.0 mmol) of phenylacetylene under a CO atmosphere of 1.1 bar at 30 °C. After 2 and 4 h the reaction mixture was transferred into another vessel containing an additional 2.0 mg (1.65 μmol) of **1**. After a total of 6 h of stirring all volatile components were removed in vacuo, affording 2.08 g of a dark-brown solid (mp 190 °C, 83% conversion). Methanol (10 mL) was added to the residue, and the slurry was heated to reflux for 15 min. Decanting the supernatant solution from the polymer and drying at 10^{-5} bar for 6 h at 20 °C afforded 1.89 g of ochre amorphous polyphenylacetylene (mp > 200 °C). IR (KBr, cm^{-1}): ν 3077 w, 3055 m, 3023 m, 1946 w, 1879 w, 1801 w, 1684 m, 1597 m, 1492 s, 1444 s, 1263 w, 1180 w, 1156 w, 1072 m, 1028 m, 910 m, 879 w, 839 m, 756 s, 697 s, 660 w cm^{-1}. ^1H NMR ($CDCl_3$, 22 °C): δ 6.60−7.70 (m, C_6H_5), 7.78 (s,

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[6] Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994**, *13*, 4616.

[7] Vaughn, T. H.; Nieuwland, J. A. *J. Am. Chem. Soc.* **1934**, *56*, 1207.

PhC═C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22 °C): δ 125.2−130.1 (m, *o,m,p*-C-phenyl), 132.1 (m, PhC═*C*H), 141.1−142.3 (m, *i*-C−phenyl and Ph*C*═CH−). GPC analysis: M_n 1874, M_w 3674; M_w/M_n 1.96.

Polymerization of Phenylacetylene-*d*$_1$. A sample of phenylacetylene-*d*$_1$ (2.50 g, 24.0 mmol) was added to the slurry of 2.0 mg (1.65 μmol) of **1** in 5 mL of *n*-pentane. After stirring at 30 °C for 24 and 48 h, respectively, under an atmosphere of CO, the reaction mixture was transferred into a vessel containing 2.0 mg of **1**. After 72 h volatiles were removed in vacuo to yield a dark-brown solid residue (2.05 g, 82% conversion, mp 185−190 °C). The sample was freed from components of low molecular weight by stirring in boiling methanol (10 mL, 15 min) to give 1.91 g of amorphous ochre poly(phenylacetylene-*d*$_1$) (mp > 200 °C). IR (KBr, cm^{-1}): ν 3076 m, 3054 m, 3022 m, 1944 w, 1876 w, 1803 w, 1748 w, 1684 m, 1598 s, 1575 m, 1491 s, 1443 s, 1262 m, 1073 m, 1028 m, 1001 w, 911 m, 840 w, 805 w, 756 s, 697 s cm^{-1}. ^1H NMR ($CDCl_3$, 22 °C): δ 6.82−7.70 (m, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22 °C): δ 124.6−130.1 (m, *o,m,p*-C-phenyl), 131.9 (m, PhC═*C*D−), 141.1−142.2 (m, *i*-C−phenyl and Ph*C*═CD). GPC analysis: M_n 1100, M_w 3330; M_w/M_n 3.03.

Polymerization of Phenylacetylene-*d*$_5$. A vessel with 1.0 mg (0.83 μmol) of **1** was charged with *n*-pentane (2 mL) and 1.00 g (9.2 mmol) of phenylacetylene-*d*$_5$ and stirred for 2 h at 30 °C under an atmosphere of CO. After 2 h the contents of the flask were transferred to another vessel with 1.0 mg (0.83 μmol) of **1**. The same procedure was repeated after 4 h. After a total reaction time of 6 h volatiles were removed in vacuo to afford 0.60 g (60% conversion) of a dark-brown solid residue (mp 183−185 °C). As described above, the residue was extracted with boiling methanol to afford 0.54 g of poly(phenylacetylene-*d*$_5$) as an amorphous ochre solid (mp > 200 °C). IR (KBr, cm^{-1}): ν 2362 w, 2340 w, 2270 m, 2079 w, 1684 m, 1576 w, 1559 m, 1540 w, 1507 w, 1374 m, 1326 m, 1261 s, 1229 w, 1096 s, 1021 s, 958 w, 908 m, 865 w, 839 m, 819 s, 801 s, 731 m, 658 w, 593 w, 540 s, 518 m. ^1H NMR ($CDCl_3$, 22 °C): δ 7.78 (s, PhC═C*H*−). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22 °C): δ 126.5−129.8 (m, *o,m,p*-C-phenyl), 133.1 (m, PhC═*C*H), 141.0−142.3 (m, *i*-C−phenyl and Ph*C*═CH). GPC analysis: M_n 1183, M_w 2996; M_w/M_n 2.53.

Polymerization of *p*-Tolylacetylene. Similarly, a solution of 2.50 g (22.0 mmol) of *p*-tolylacetylene in 5 mL of *n*-pentane was treated with three portions of 2.0 mg (1.65 μmol) of **1** after 2 and 4 h at 30 °C under a CO atmosphere. After 6 h volatiles were removed in vacuo and the dark-brown solid residue (2.15 g, 86% conversion, mp 110−120 °C) was extracted with hot CH_3OH (10 mL, 15 min). Yield: 1.95 g of mustard-colored poly(*p*-tolylacetylene) (mp 125−130 °C). IR (KBr, cm^{-1}): ν 3021 m, 1901 w, 1683 m, 1606 m, 1510 s, 1449 m, 1377 w, 1267 m, 1183 m, 1111 w, 1037 w, 1019 m, 814 s, 659 m. ^1H NMR ($CDCl_3$, 22 °C): δ 2.11−2.42 (m, CH_3), 6.70−7.59 (m, H−aryl), 7.72 (s, *p*-TolC═C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22 °C): δ 21.1−21.6 (m, CH_3), 124.6−130.0 (aryl−C), 132.0 (m, aryl−C═*C*H), 137.0−138.9 (aryl−C and aryl−*C*═CH). GPC analysis: M_n 974, M_w 4330; M_w/M_n 4.45.

Polymerization of *p*-Chlorophenylacetylene. A solution of 3.00 g (22.0 mmol) of *p*-chlorophenylacetylene in 5 mL of *n*-pentane was added to 2.0 mg (1.65 μmol) of **1**. After 2 and 4 h of stirring at 30 °C under a CO atmosphere the reaction mixture was transferred to another vessel with 2.0 mg of **1**. After a total of 6 h the slurry was freed from volatile components to give 1.74 g of a brown solid residue (58% conversion, mp 184−186 °C). The crude product was extracted with boiling methanol (10 mL, 15 min) to afford 1.58 g of mustard-colored poly(*p*-chlorophenyl)acetylene (mp > 200 °C). IR(KBr, cm^{-1}): ν 3064 w, 3030 w, 2086 w, 1899 w, 1777 w, 1683 w, 1622 m, 1588 m, 1572 m, 1544 m, 1489 s, 1442 s, 1394 m, 1379 m, 1311 m, 1247 m, 1189 m, 1177 m, 1093 s, 1048 m, 1012 s, 958 w, 905 w, 879 w, 827 s, 762 w, 723 m, 659 s, 642 sh, 526 w, 490 w. ^1H NMR($CDCl_3$, 22 °C): δ 7.00−7.61 (m, H−aryl), 7.75 (s, aryl−C═C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22 °C): δ 124.5−129.5 (C−aryl), 132.9 (m, aryl−C═*C*H), 134.4−134.8 (m, CCl), 140.9−142.5 (m, *o*-, *m*-C−aryl and aryl−*C*═CH). GPC analysis: M_n 766, M_w 3068; M_w/M_n 4.01.

Estimation of the Isotopic Effect of the Polymerization of Phenylacetylene-*d*$_0$ and Phenylacetylene-*d*$_1$. A slurry of 1.0 mg (0.83 μmol) of **1** in 2 mL of *n*-pentane was treated with phenylacetylene-*d*$_1$ (1.25 g, 12.0 mmol) under a CO atmosphere of 1.1 bar at 30 °C. After 2 h volatiles were removed in vacuo to afford 0.14 g of a dark-brown solid poly(phenylacetylene-*d*$_1$) (11% conversion).

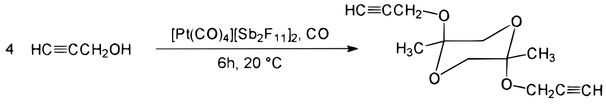
The same reaction was repeated and stopped after 4, 6, or 8 h, respectively, to give 0.24 g (19%), 0.31 g (25%), or 0.39 g of the polymer (31% conversion).

For comparison, 1.0 mg (0.83 μmol) of **1** was reacted with 1.25 g (12.0 mmol) of phenylacetylene-*d*$_0$ under the identical conditions. Workup after 2 h gave 0.41 g of dark-brown crude PPA (33% conversion).

X-ray Crystal Structure Determination of 3. Single crystals of **3** were grown from benzene at 4 °C. A dark red crystal with the approximate dimensions 0.60 × 0.50 × 0.20 mm^3 was measured on a Siemens $P2_1$ diffractometer with Mo Kα radiation at 173 K. Crystal data and refinement details (refined from the diffractometer angles of 20 centered reflections): $a = 9.540(4)$ Å, $b = 13.605(7)$ Å, $c = 11.911(5)$ Å, $\beta = 91.50(4)°$, $V = 1545.4(12)$ Å^3, $Z = 4$, $d_{calcd} = 1.711$ g cm^{-3}, $\mu = 2.180$ mm^{-1}, space group $P2_1/n$, data collection on 4512 unique intensities ($R_{int} = 0.0498$), structure solution by direct methods and anisotropic refinement with full-matrix least-squares methods on F^2 for all non-hydrogen atoms (program used Siemens SHELXTLplus/SHELXL-93), riding groups for hydrogen atoms, 208 parameters, maximum residual electron density 0.5 e/Å^3, R1 = 0.062, R_w = 0.134 based on 2613 reflections with ($I > 2\sigma(I)$) ($w = 1/[\sigma^2(F_o^2) + 0.0647P)^2 + 0.4075P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Results and Discussion

Upon treatment of neat 2-propyn-1-ol with 7 × 10^{-3} mol % of solid $[Pt(CO)_4][Sb_2F_{11}]_2$ (**1**) in an atmosphere of CO (1.3 bar, 20 °C), the liquid turned cloudy with the separation of a colorless precipitate. After about 6 h the content of the flask solidified. The trans-configurated 1,4-dioxane derivative **2** was isolated in 89% yield as the formal tetramer of the alkynol (eq 2).



(2)

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Although no carbonylation products are formed, a positive CO pressure is crucial for the success of the reaction.

The tetramerization of 2-propyn-1-ol is not without precedence. In the early 1980s Keiko et al.[8] and Matnishyan et al.[9] described this reaction in diethyl ether in the presence of a mixture of HgO and $BF_3 \cdot OEt_2$ as a catalyst. This process yielded a cis/trans mixture in only 55% yield.

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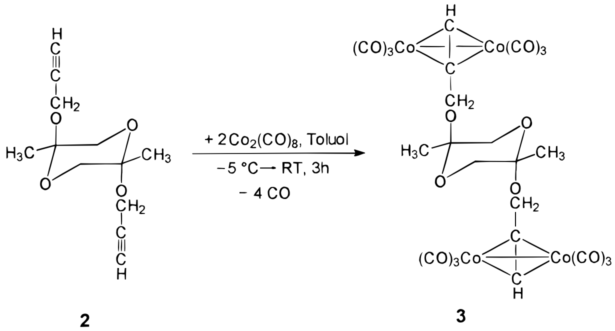
(8) Keiko, N.-A.; Chuvashov, Y. A.; Rulev, A. Y.; Kalikhman, I. D.; Bannikova, O. B.; Voronkov, M. G. *Zh. Org. Khim.* **1982**, *18*, 1152; *Chem. Abstr.* **1982**, *97*, 144277w.

(9) Matnishyan, A. A.; Grigoryan, S. G.; Mkrtchyan, A. A.; Arytyunyan, A. V. *Zh. Org. Khim.* **1983**, *19*, 1549; *Chem. Abstr.* **1983**, *99*, 139869c.

In this context a very recent paper is worth mentioning, which is concerned with the smooth and efficient addition of alcohols to alkynes catalyzed by cationic gold(I) complexes. Thus 2-propynol and methanol afforded *trans*-2,5-dimethoxy-*trans*-2,5-dimethyl-1,4-dioxane under the catalysis of $[Ph_3PAu]^+[SO_4H]^-$.[10]

Alkynols such as $(CH_3)_2CH-C(CH_3)(OH)C\equiv CH$, $CH_3-C\equiv C-CH_2OH$, $CH_3(CH_2)_2-C\equiv C-CH_2OH$, and $HOCH_2-C\equiv C-CH_2OH$ were not affected by compound **1** under comparable conditions. The highly stereoselective formation of **2** is evidenced by ^1H and $^{13}C\{^1H\}$ NMR spectra (see Experimental Section). To unambigiously determine the molecular geometry of **2**, the bis(alkyne) was reacted with 2 equiv of $[Co_2(CO)_8]$ to afford the red bis(tetrahedrane) **3** in 95% yield (eq 3).



(3)

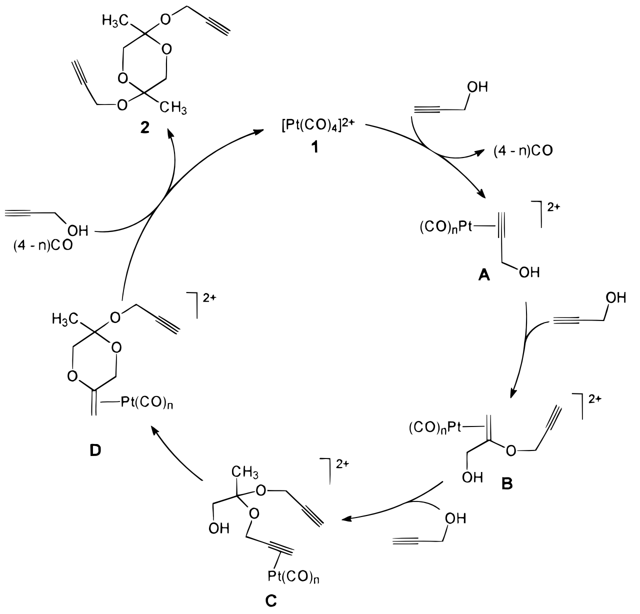
2 **3**

The coordination of the C≡C triple bonds of **2** to the $[Co_2(CO)_6]$ fragments is mainly reflected in the ^1H and $^{13}C\{^1H\}$ NMR absorptions of the 2-propynoxy substituents at the dioxane skeleton. The resonance of the methyne proton of **2** (δ 1.96) is observed at δ 5.48 in complex **3**. Coordination shifts of comparable size are usual in compounds of the type $Co_2(CO)_6(R-C\equiv CH)$.[11] Upon complexation, the protons of the methylene group adjacent to the C≡C bond of **2** (δ 3.92) are encountered in the ^1H NMR spectrum of the complex at δ 4.40. In accordance with other $[(alkyne)Co_2(CO)_6]$ compounds the methyne carbon atom of the triple bond experiences a high-field shift, whereas the quaternary alkyne carbon atom is deshielded by $\Delta\delta$ 11.7 ppm. The resonance of the methylene carbon atom of the side chain of **2** is also markedly deshielded upon complexation [$\Delta\delta^{13}C(CH_2)$ 11.7 ppm]. A singlet at δ 200.0 is registered for the ^{13}C nuclei of the carbonyl ligands of **3**, which is also in good agreement with literature data of comparable systems [e.g., $\delta^{13}C(CO)$ in $[Co_2(CO)_6(HC\equiv CPh)] = 200.0$ ppm].

In principle, the here reported tetramerization of 2-propynol may be effected by cationic, radical or by coordinative oligomerization. Typical cationic oligomerizations and polymerizations of isobutene or cyclic ethers such as THF are caused by Lewis acids. Complex **1**, however, failed to oligomerize these molecules. In a control experiment the attempted tetramerization of 2-propynol by means of SbF_5 also failed.

A radical oligomerization can be discarded because radical scavengers have no influence on the tetramerization. Thus, the described process is most likely complex-catalyzed, and with respect to Teles' findings with complex gold cations,[10] the catalytic cycle in Scheme 1 is proposed.

Scheme 1



Most likely the reaction is initiated by the formation of the transient η^2-alkyne complex **A**. Nucleophilic addition of propynol to the activated C≡C triple bond leads to the η^2-alkene complex **B**, which rapidly adds another molecule of propynol to the coordinated double bond before intramolecular recoordination of a C≡C bond to the platinum atom **C** occurs. The subsequent intramolecular addition of the OH functionality to the activated triple bond of **C** affords η^2-alkene complex **D**. Propynol addition to the coordinated C=C double bond in **D** and subsequent CO displacement regenerate **1** and liberate product **2**.

X-ray Structural Analysis of 3. To elucidate the exact stereochemistry of the 1,4-dioxane **2**, an X-ray structure analysis of its carbonyl cobalt derivative was envisaged. Here we assumed that complexation would occur in the periphery of the molecule without serious perturbation of the stereochemistry of the central heterocycle.

The result of the X-ray diffraction analysis (Table 1; Figure 1) reveals a 1,4-dioxane ring in a chair configuration.

The molecule possesses an inversion center in the center of the dioxane ring. It is remarkable that the methyl groups at C(10) occupy an equatorial position, whereas the substituents with the tetrahedrane units are oriented axially. The geometry within the $[Co_2C_2-RR']$ fragments of **3** is comparable with the situation met in $[Co_2(CO)_6(t\text{-}Bu_2C_2)]$ (**4**), as apparent in the Co−Co bond length of 2.4711(14) Å in **3** and 2.463(1) Å in **4**.[12] The metal−carbon separations within the tetrahedrane skeleton of **3** vary from 1.950(5) to 1.963(5) Å, being significantly shortened as compared with those in **4** [1.992(4)−2.003(4) Å].

The bond lengths Co(1)−C(2) [1.781(6) Å] and Co(2)−C(5) [1.774(6) Å] of the CO ligands perpendicular to the vector Co(1)−Co(2) are slightly shortened when com-

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[10] Teles, J. H.; Brode, S.; Chabanas, M. *Angew. Chem.* **1998**, *110*, 1475; *Angew. Chem., Int. Ed.* **1998**, *37*, 1415.

[11] Aime, S.; Milone, L.; Rosetti, R.; Stanghellini, P. L. *Inorg. Chim. Acta* **1977**, *22*, 135.

[12] Cotton, F. A.; Jamerson, J. D.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 1774.

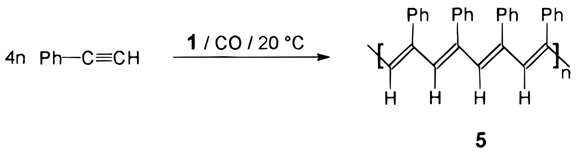
Table 1. Selected Bond Lengths [Å] and Angles [deg] for 3

Co(1)−C(2)	1.781(6)	Co(1)−C(1)	1.812(6)
Co(1)−C(3)	1.815(6)	Co(1)−C(7)	1.952(5)
Co(1)−C(8)	1.958(5)	Co(1)−Co(2)	2.4711(14)
Co(2)−C(5)	1.774(6)	Co(2)−C(6)	1.817(5)
Co(2)−C(4)	1.818(5)	Co(2)−C(8)	1.950(5)
Co(2)−C(7)	1.963(5)	O(7)−C(10)	1.421(5)
O(7)−C(9)	1.422(6)	O(8)−C(10)	1.413(6)
O(8)−C(12)	1.421(6)	C(7)−C(8)	1.328(6)
C(8)−C(9)	1.478(6)	C(10)−C(12)#1	1.509(7)
C(10)−C(11)	1.521(7)	C(12)−C(10)#1	1.509(7)

C(2)−Co(1)−C(1)	100.9(3)	C(2)−Co(1)−C(3)	98.5(3)
C(1)−Co(1)−C(3)	105.8(3)	C(2)−Co(1)−C(7)	100.9(2)
C(1)−Co(1)−C(7)	101.6(3)	C(3)−Co(1)−C(7)	142.5(2)
C(2)−Co(1)−C(8)	99.8(2)	C(1)−Co(1)−C(8)	139.2(3)
C(3)−Co(1)−C(8)	105.4(2)	C(7)−Co(1)−C(8)	39.7(2)
C(2)−Co(1)−Co(2)	148.8(2)	C(1)−Co(1)−Co(2)	98.6(2)
C(3)−Co(1)−Co(2)	99.3(2)	C(7)−Co(1)−Co(2)	51.05(14)
C(5)−Co(2)−C(6)	99.1(3)	C(8)−Co(1)−Co(2)	50.65(13)
C(5)−Co(2)−C(4)	101.1(3)	C(6)−Co(2)−C(4)	107.7(2)
C(5)−Co(2)−C(8)	97.5(2)	C(6)−Co(2)−C(8)	104.0(2)
C(4)−Co(2)−C(8)	139.9(2)	C(5)−Co(2)−C(7)	99.8(2)
C(6)−Co(2)−C(7)	141.0(2)	C(4)−Co(2)−C(7)	101.8(2)
C(8)−Co(2)−C(7)	39.7(2)	C(5)−Co(2)−Co(1)	146.8(2)
C(6)−Co(2)−Co(1)	98.6(2)	C(4)−Co(2)−Co(1)	99.9(2)
C(8)−Co(2)−Co(1)	50.91(14)	C(7)−Co(2)−Co(1)	50.7(2)
O(1)−C(1)−Co(1)	177.1(7)	O(2)−C(2)−Co(1)	177.6(6)
O(3)−C(3)−Co(1)	179.0(5)	O(4)−C(4)−Co(2)	177.2(5)
O(5)−C(5)−Co(2)	178.1(6)	O(6)−C(6)−Co(2)	178.0(5)
C(8)−C(7)−Co(1)	70.4(3)	C(8)−C(7)−Co(2)	69.7(3)
Co(1)−C(7)−Co(2)	78.3(2)	C(7)−C(8)−C(9)	143.8(4)
C(7)−C(8)−Co(2)	70.7(3)	C(9)−C(8)−Co(2)	131.6(3)
C(7)−C(8)−Co(1)	69.9(3)	C(9)−C(8)−Co(1)	134.7(3)
Co(2)−C(8)−Co(1)	78.4(2)		

pared to the remaining Co−C(CO) bond lengths [1.815(6)−1.812(6) Å] in the complex. Bond lengths and bond angles within the 1,4-dioxane ring are as expected and merit no comments.

Polymerization of Arylacetylenes. Polymerization of phenylacetylene (PA) (24.0 mmol) in an *n*-pentane solution was achieved by the addition of three quantities of 2.0 mg (1.65 μmol) (2.1×10^{-2} mol % catalyst) at the beginning of the reaction and after 2 and 4 h of stirring under an atmosphere of carbon monoxide (ca. 1.1 bar). Within 6 h a 83% conversion to a dark-brown precipitate occurred. By treatment of the crude material with hot methanol, oligomers of lower molecular weight were removed to afford a 76% yield of ochre poly(phenylacetylene) (PPA). The polymer obtained by this method with an M_n of 1874 and an M_w/M_n of 1.96 is soluble in chlorinated hydrocarbons such as dichloromethane, chloroform, or chlorobenzene.



(4)

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The polymerization slowed markedly, when phenylacetylene was replaced by PhC≡CD under otherwise analogous conditions. A conversion of 82% was reached after 72 h and the addition of catalyst (2.0 mg, 1.65 μmol) after 24 and 48 h of stirring the *n*-pentane slurry at 30 °C under CO. Extraction of the crude dark-brown poly(phenylacetylene-d_1) with hot methanol led to an ochre powder (76%). By GPC analysis M_n was determined to 1100 and M_w/M_n to 3.03.

In a third run 1.00 g (9.2 mmol) of phenylacetylene-d_5 ($C_6D_5C{\equiv}CH$) in *n*-pentane (2 mL) was treated with three quantities of 1.0 mg (0.83 μmol) of **1** (2.7×10^{-2} mol %) in periods of 2 h. A 54% yield of ochre poly(phenylacetylene-d_5) (PPA-d_5) was obtained after purification of the dark-brown crude product with hot methanol. The ^1H NMR spectrum of PPA-d_5 displayed a singlet at δ 7.78 ppm, indicating the stereoregular head−tail trans-transoidal structure. A PPA with a cis-transoidal microstructure was obtained from the polymerization of PA with rhodium complexes such as $Rh(C{\equiv}CPh)(nbd)(PPh_3)$,[13] $Rh^+(cod)BPh_4^-HSiEt_3$,[14] [Rh(cod)bipy]PF_6,[15] or [Rh(cod)(tmeda)]Cl,[15] whereas with $Pt(C{\equiv}CPh)_2(PPh_3)_2$ as a catalyst a PPA with a trans-transoidal structure was prepared.[15b,16] In agreement with this assignment the ^1H resonance at 7.78 ppm is not present in the ^1H NMR of PPA-d_1. Here a multiplet resonance at δ 6.82−7.70 ppm is attributed to the phenyl hydrogens. In the $^{13}C\{^1H\}$NMR spectra of PPA, PPA-d_1, and PPA-d_5 the vinylic carbon carrying hydrogen or deuterium is observed as a multiplet at δ 132.1, 131.9, and 133.1 ppm. In line with Furlani's[15] assignments, multiplets at δ 141.0−142.3 are due to quaternary carbons, whereas the remaining ring carbon atoms are observed as multiplets at δ 124.6−130.1 ppm.

The IR spectrum of PPA is mainly identical with literature data.[15,17] Intense bands were observed at ν 1492, 697, and 757 cm^{-1}. In particular the weak bands at 920 and 840 cm^{-1} were assigned to trans-configurated polyene strands.[15,17] For cis-configurated polyphenylacetylene bands at ν 740 and 870 cm^{-1} were expected.[15,17] The spectra of the here synthesized PPA are virtually identical with those recorded for the trans-transoidal PPA produced with $Pt(C{\equiv}CPh)_2(PPh_3)_2$ as a catalyst.[15b] These materials have molecular weights in the range 1000−2000 Da.

The WCl_6-initiated polymerization of phenylacetylene in dioxane resulted in an almost all trans-transoidal structure and affords the highest reported molecular weight for a PPA with this microstructure (M_n 900000 Da).[18] On the other hand polymerization of PA catalyzed by Rh(I) complexes of the type [Rh(COD)(*o*-py$(CH_2)_2$P(Ph)$(CH_2)_3$ZR]PF_6, ZR = OEt, OPh, NHPh, NH-*c*-C_6H_{11}, led to cis-transoidal PPA with molecular weight up to 238000 Da.[19a]

With [η^2:η^2-norbornadiene(dbn)$_2$Rh]$^+PF_6^-$ (dbn = 1,5-diazabicyclo-[4.3.0]non-5-ene) the molecular weight of the obtained cis-transoidal PPA is reported to be 1745060 Da.[19b] Analogously, a solution of 2.50 g (22.0 mmol) of *p*-tolylacetylene was treated with three por-

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(13) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Lkariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1994**, *116*, 12131.

(14) Goldberg, Y.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1994**, 1209.

(15) (a) Furlani, A.; Napoletano, C.; Russo, M. V.; Feast, W. J. *Polym. Bull.* **1986**, *16*, 311. (b) Furlani, A.; Licoccia, S.; Russo, M. V. *J. Polym. Sci. Polym. Chem. Ed.* **1986**, *24*, 991. (c) Furlani, A.; Napoletano, C.; Russo, M. V.; Canus, A.; Marsich, N. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 75.

(16) Furlani, A.; Collamati, I.; Sartori, G. *J. Organomet. Chem.*, **1969**, *17*, 463.

(17) Simionescu, C. I.; Percec, V.; Dumitrescu, S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2497.

(18) Masuda, T.; Takahaski, T.; Yamamoto, K.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2603.

(19) (a) Haupt, H.-G.; Ortmann, U. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1209. (b) Schniedermeier, J.; Haupt, H.-G. *J. Organomet. Chem.* **1996**, *506*, 41.

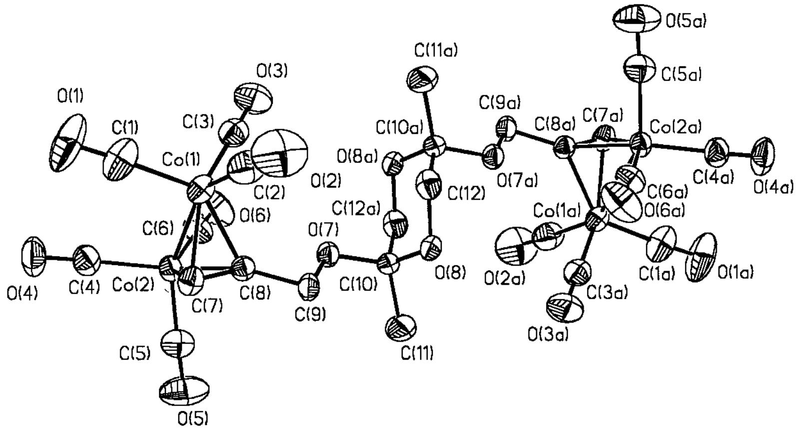

Figure 1. Molecular structure of **3** in the crystal.

tions of 2.0 mg (1.65 μmol) of **1** (2.2×10^{-2} mol % of catalyst). After 6 h 2.15 g (86% conversion) of a dark brown solid (mp 110−120 °C) was obtained. After extraction of this residue with boiling methanol (10 mL, 15 min) 1.95 g of mustard-colored poly(*p*-tolylacetylene) (mp 125−130 °C) with M_n 974 and M_w/M_n 4.45 was isolated. This material was well soluble in chlorinated hydrocarbons and chlorinated arenes. The absence of a resonance at δ 5.85 ppm and a singlet at δ 7.72 ppm is consistent with a trans-microstructure of the polymer.

According to the same procedure 3.00 g (22.0 mmol) of *p*-chlorophenylacetylene were polymerized by a total of 6.0 mg (4.95 μmol) of **1** to afford 1.74 g of a brown solid (58% conversion). Upon purification with boiling methanol, 1.58 g of mustard-colored poly(*p*-chlorophenylacetylene) was obtained (mp > 200 °C). From a GPC analysis M_n was determined to 766 Da and M_w/M_n 4.01. Again the appearance of a signal at δ 7.75 ppm in the ^{1}H NMR spectrum of the product indicates a trans-configuration of the polymer strand.

The polymerization of phenylacetylene has been thoroughly investigated in the past. First investigations date back to 1955, when Natta et al. used catalysts such as $AlEt_3/TiCl_3$, $ZnEt_2/TiCl_3$, or $AlEt_3/Ti(OC_3H_7)_4$.[20] Recent papers on poly(phenylacetylenes) document the continuing interest in these polymers mainly because of their unique properties such as electrical conductivity, photoconductivity, optical nonlinear susceptibility, and magnetic susceptibility.[13,14,20b,21]

Despite numerous papers on phenylacetylene polymerization, the discussion of the mechanism of such a process is controversal.[20a] In many cases, alkyne insertion into the metal−hydrogen or metal−carbon σ bond occurred, constituting the first step in the polymerization of alkynes via a coordination/insertion pathway. Here, however, only cis-configurated C=C bonds were primarily generated. Others invoked metal carbene and metal−vinylidene complexes for the initiation of acetylene polymerization. Depending on the direction of ring opening of the transient metallacyclobutenes, PPA with cis- and trans-microstructures resulted.[22−24]

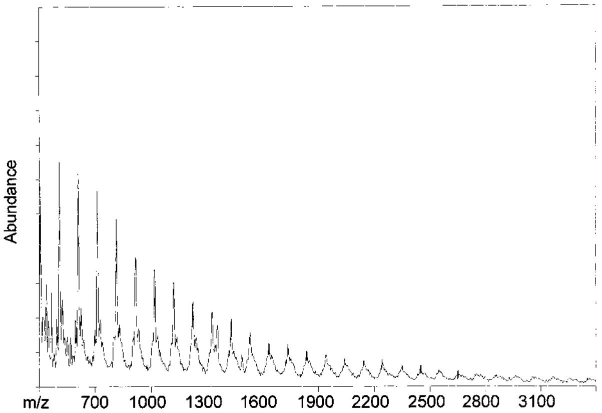

Figure 2. MALDI-TOF spectrum of poly(phenylacetylene).

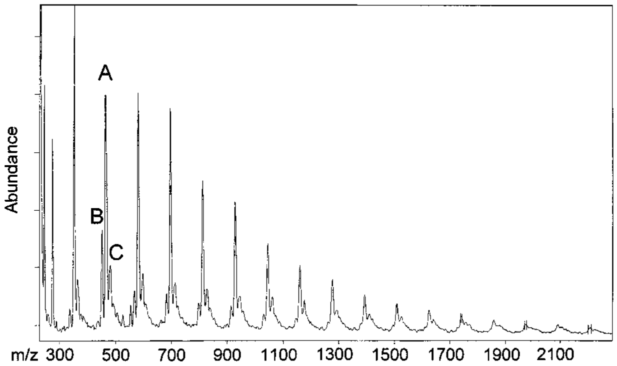

Figure 3. MALDI-TOF spectrum of poly(*p*-tolylacetylene).

To gain further insight into the chemical structure of the polymers, MALDI-TOF mass spectra of poly(phenylacetylene) and poly(*p*-tolylacetylene) generated by catalysis of **1** were recorded.

The MALDI-TOF spectrum (Figure 2) of poly(phenylacetylene) is composed of peaks that correspond to the individual cationized oligomers and polymers. The main peaks are equally spaced at 102 Da apart, representing the particular oligomers which differ by the molecular weight of the repeating phenylacetylene unit. Two series of smaller peaks, which are also equally spaced at 102 Da, are observed at 14 Da higher and lower than each of the main peaks.

Figure 3 shows the MALDI-TOF spectrum of poly(*p*-tolylacetylene) up to 2300 Da. Obviously there is one major series of peaks which are invariably spaced at the molecular weight of a *p*-tolylacetylene monomer, i.e.,

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(20) Reviews: (a) Simionescu, C. I.; Percec, V. *Prog. Polym. Sci.* **1982**, *8*, 133. (b) Wegner, G. *Angew. Chem.* **1981**, *93*, 352; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 361.

(21) La Pointe, A. M.; Brookhart, M. *Organometallics* **1998**, *17*, 1530.

(22) Percec, V. *Polym. Bull.* **1983**, *10*, 1.

(23) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.

(24) Landon, S. J.; Shulman, P. M.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 6739.

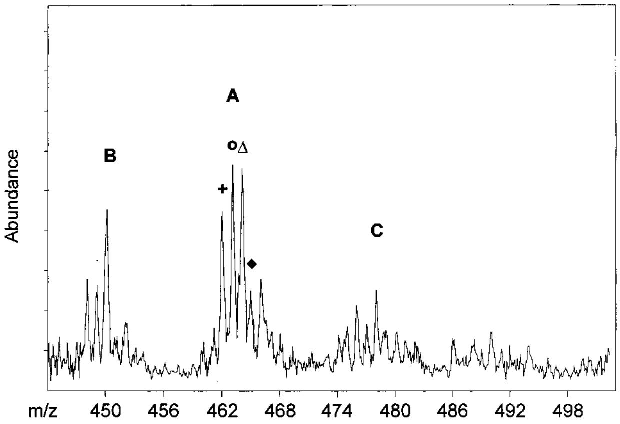


Figure 4. Expanded MALDI-TOF spectrum of poly(*p*-tolylacetylene).

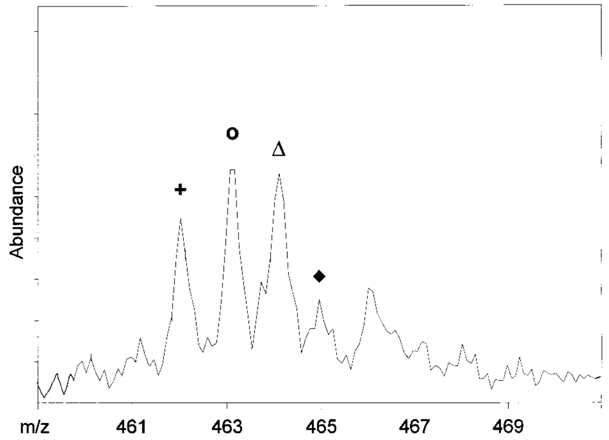
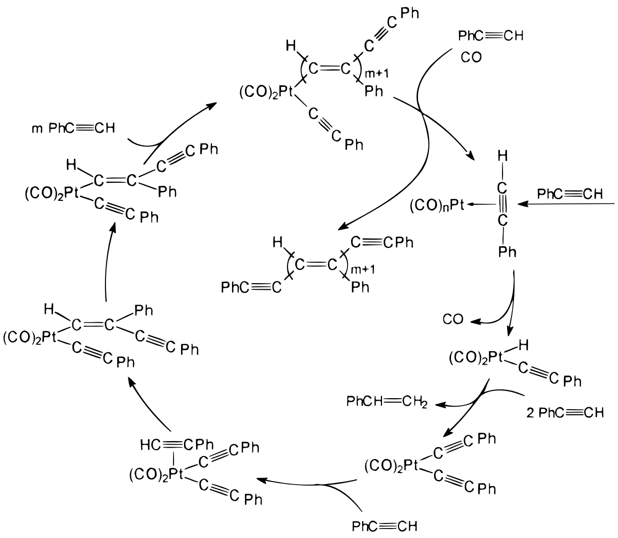


Figure 5. Expanded MALDI-TOF spectrum of poly(*p*-tolylacetylene).

116 Da. Again two minor series of peaks are noticed at 14 Da lower (**B**) and higher (**C**) than each of the main peaks (**A**, Figure 4). The formation of compounds corresponding to the ions marked **B** and **C** during the polymerization of phenylacetylene and *p*-tolylacetylene is most probably due to variation of the end groups based on subordinate mechanisms. The regular spacing of the peaks in intervals of the monomer units confirms the formation of the polymer backbone derived from the NMR data. In addition, a detailed look at the isotopically resolved peaks in Figure 5 yields valuable information about the polymer end groups. Peaks assigned with "+" correspond to the general molecular formula $[n \times M - 2H]^{\bullet +}$. Evidently, the formation of the molecular radical cation competes successfully with the formation of the protonated species $[n \times M - 2H]H^+$ (○). This has been found in several cases, in which the ionization energy of the analyte molecule is very low compared to the IE of the matrix.[25]

Formally, the compounds of formula $[n \times M - 2H]$ correspond to oligomers and polymers with phenylacetylide or *p*-tolylacetylide end groups. Peaks marked "○" refer to the protonated oligomers and polymers with arylacetylide end groups. Unfortunately, it is difficult to decide if the ions $[n \times M]^{\bullet +}$ (△) and $[n \times M + H]^+$ (◆) were formed upon ionization[26] or more likely during the polymerization by a subordinate reaction mechanism.

Scheme 2



n = 2 or 3

The MALDI-TOF mass spectra of PPA and poly(*p*-tolylacetylene) make obvious that the major oligomers and polymers include two PhC≡C moieties as end groups. Moreover, the clearly retarded reactivity of phenylacetylene-d_1 in comparison to phenylacetylene-d_0 ($k_H/k_D \approx 3$) indicates the breaking of a C−H or C−D bond in the rate-determining step as it is given by an oxidative addition process. Considering the fact that the electron affinity of Pt(II) ions is 12.42 eV[27] and that the first ionization potential of phenylacetylene is only 8.82 ± 0.02 eV,[28] it is reasonable to assume a redox process to afford Pt(0) species prior to the polymerization. Thus a complex like $[(CO)_2Pt(C{\equiv}CPh)_2]$ might be the reactive molecule, where the phenylacetylene inserts into the Pt−C bonds (Scheme 2). This situation mirrors the polymerization of phenylacetylene by $[(Ph_3P)_2Pt(C{\equiv}CPh)_2]$ as described by Furlani et al.[15] As the insertion of an η^2-phenylacetylene into a Pt−C bond usually affords cis-configuration of the CC double bond in the polymer strand, a rapid cis/trans isomerization has to follow the insertion step to give the observed microstructure of our polymers. The propagation of the polymer is terminated by the reductive coupling with the remaining phenylacetylide ligand.

A reasonable mechanism for the formation of the reactive intermediate $[(CO)_2Pt(C{\equiv}CPh)_2]$ from a (η^2-phenylacetylene)platinum(0) carbonyl has precedence in phenylacetylene ruthenium chemistry, where a [Ru]-(H)C≡CPh complex reacts with 2 equiv of alkyne to yield $[Ru](C{\equiv}CPh)_2$ and styrene.[29,30]

Acknowledgment. This work was financially supported by the Fonds der Chemischen Industrie, Frankfurt/M., Germany. We are grateful to Prof. H. Willner,

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(25) McCarley, T. C.; McCarley, R. L.; Limbach, P. A. *Anal. Chem.* **1998**, *70*, 4376.

(26) Calba, P. J.; Muller, J. F.; Inouye, M. *Rapid Commun. Mass Spectrom.* **1998**, *12*, 1727.

(27) Nyholm, R. S. *Proc. Chem. Soc.* **1961**, 273.

(28) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276.

(29) Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994**, *13*, 4616.

(30) Rappert, T.; Yamamoto, A. *Organometallics* **1994**, *13*, 4984.

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Supporting Information Available: Tables of X-ray data, atomic coordinates, thermal parameters, and complete bond distances and angles and thermal ellipsoid plots for compound **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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