Alkyne-Coupling Reactions Catalyzed by OsHCl(CO)(P^{i}Pr$_3$)$_2$ in the Presence of Diethylamine

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Summary: Complex OsHCl(CO)(P^{i}Pr$_3$)$_2$, in the presence of diethylamine, catalyzes the dimerization of terminal alkynes HC≡CR (R = Me$_3$C, Cy, Ph, and Me$_3$Si). The reactions initially give butatrienes RCH=C=C=CHR, which are stable under the reaction conditions for R = Me$_3$C and Cy. For R = Ph, the butatrienes polymerize to −[CH(Ph)C≡CCH(Ph)]$_n$−, while for R = Me$_3$Si, the butatriene isomerizes into the enyne Z−Me$_3$SiCH=CH−C≡CSiMe$_3$. The formation of butatrienes takes place via butenynyl intermediates of the type Os(C≡CR){η^3-C(C≡CR)=CHR}(CO)(P^{i}Pr$_3$)$_2$.

Alkyne-coupling reactions catalyzed by transition metals are of considerable current interest because they can afford unsaturated four-carbon compounds, which are versatile intermediates for organic conducting polymers and other carbon-rich allotropes.[1] Although five four-carbon isomers can be obtained, enynes and butatrienes (eq 1), most catalysts give enynes.[2]

(1)
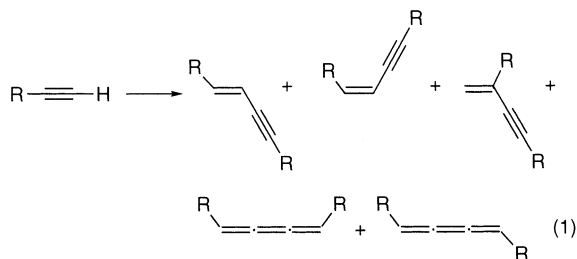
The formation of butatrienes in the dimerization of terminal alkynes is not easy, since the butatriene skeleton is thermodynamically much less stable than the enyne form.[3] As a consequence, only a few catalysts and a few terminal alkynes have produced this type of compound.

The heating of bulky ethynyltetramethylcyclopentadienyl complexes RC≡CH (R = Me$_4$C$_5$Rh(COD), Me$_4$C$_5$Ir(COD), Me$_4$C$_5$Fe(C$_5$Me$_4$H); COD = 1,5-cyclooctadiene) in the presence of catalytic amounts of RuH$_2$(CO)(PPh$_3$)$_3$ affords the corresponding butatrienes RCH=C=C=CHR.[4] At 50−100 °C in benzene, this dihydride also catalyzes the dimerization of *tert*-butylacetylene to (Z)-

1,4-di-*tert*-butylbutatriene with selectivities between 85 and 90% and 25−50 catalytic turnovers per Ru atom.[5] The catalytic turnover increases at higher reaction temperatures, but the selectivity to the butatriene decreases. With the system formed by [Ir(μ-Cl)(COD)]$_2$, P^{n}Pr$_3$, and NEt$_3$, (Z)-1,4-di-*tert*-butylbutatriene has been obtained, after 18 h in cyclohexane at 50 °C. In this case the yield of the dimerization is 73% and the selectivity toward the butatriene is 93%.[6] Other examples include the butatrienes PhCH$_2$CH=C=C=CHCH$_2$Ph and Me$_3$SiCH=C=C=CHSiMe$_3$. The first of them has been obtained in 93% yield and 95% selectivity in the presence of the trihydride RuH$_3$(η^5-C$_5$Me$_5$)(PCy$_3$), by heating of PhCH$_2$C≡CH at 80 °C in tetrahydrofuran during 24 h.[7] The second one is an intermediate in the dimerization of trimethylsilylacetylene to (Z)-Me$_3$SiCH=CHC≡

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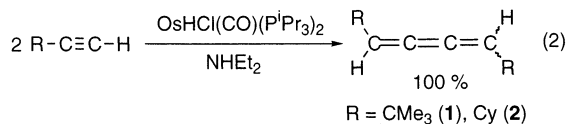‡ Universidad de Cantabria.

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CSiMe₃, catalyzed by a mixture of Ru(COD)(COT) and P^{n}Bu₃ (1:3 ratio, COT = cyclooctatriene).[8]

The five-coordinate hydride-chloro complex OsHCl-(CO)(P^{i}Pr₃)₂[9] has been one of the cornerstones in the development of the modern organometallic osmium chemistry.[10] Furthermore, it has been found to be one of the most important homogeneous catalysts for the reduction of unsaturated organic substrates[11] and for the addition of silanes to alkynes.[12] Now, we have observed that in the presence of diethylamine it also catalyzes alkyne-coupling reactions to afford butatrienes, showing activities and selectivities much higher than those previously reported.

The reactions were carried out in benzene-d_6 or chloroform-d as solvents, at temperatures between 40 and 90 °C using Os:NHEt₂ and Os:alkyne molar ratios of 1:50.[13]

In benzene-d_6 at 90 °C, *tert*-butylacetylene exclusively gives the butatriene **1** (eq 2) in 100% yield, after 20 min. Under the same conditions, cyclohexylacetylene also affords exclusively the butatriene **2** in 100% yield, after 110 min.

$$2\ R-C\equiv C-H \xrightarrow[\text{NHEt}_2]{\text{OsHCl(CO)(P}^i\text{Pr}_3)_2} \overset{R}{\underset{H}{>}}C=C=C=C\overset{H}{\underset{R}{<}} \quad (2)$$

100 %

R = CMe₃ (**1**), Cy (**2**)

The formation of **1** and **2** is strongly supported by the MS and ¹H and ¹³C{¹H} NMR spectra of the obtained products. In the ¹H NMR spectrum of **1** the resonance corresponding to the CH protons appears as a singlet at 5.50 ppm, whereas, in the ¹H NMR spectra of **2**, this resonance is observed as a doublet at 5.50 ppm with a H—H coupling constant of 4.2 Hz. In the ¹³C{¹H} NMR spectra the =C= resonances appear at 160.8 (**1**) or 161.9 (**2**) ppm, whereas the =CH resonances are observed at 118.5 (**1**) or 113.2 (**2**) ppm. These spectroscopic data agree with those previously reported for 1,4-di-*tert*-butylbutatriene.[14] Although the stereochemistry of **1** and **2** is probably *Z*, we cannot assure this, since the

Scheme 1

difference between the reported chemical shifts for the resonances of *Z*- and *E*-1,4-di-*tert*-butylbutatriene is not more than 0.04 ppm.

In chloroform-d at 60 °C, phenylacetylene affords 1,4-diphenylbutatriene (**3**) in about 74% yield, after 90 min, as a 1:6.5 mixture of the *E* and *Z* isomers (Scheme 1). Other alkyne-coupling products are not observed. In the ¹H NMR spectrum of the mixture the =CH hydrogen atoms of the cumulene units display singlets at 6.40 (*E*) and 6.36 (*Z*) ppm. In the ¹³C{¹H} NMR spectrum the =C= resonances are observed at 156.18 (*E*) and 156.33 (*Z*) ppm, whereas the =CH resonances appear at 110.0 (*E*) and 110.1 (*Z*) ppm.

If the above-mentioned mixture is kept at 60 °C for 105 min more, a decrease in the amount of butatrienes is observed, which is accompanied with the formation of a new species. Its ¹³C{¹H} NMR spectrum in benzene-d_6 shows two acetylenic resonances at 85.3 and 84.9 ppm as well as two closely spaced peaks in the aromatic region at 140.0 and 139.3 ppm, in addition to the other expected aromatic resonances, and a C_{sp^3} signal at 46.1 ppm. This spectrum is like that previously reported by Pollack and co-workers for the polymeric material **4** (Scheme 1), which was obtained by heating of *Z*-1,4-diphenylbutatriene in tetrahydrofuran at 120 °C for 48 h.[15] In the ¹H NMR spectrum, the HC_{sp^3} of our material appears as a broad signal between 4.1 and 3.7 ppm, according to a ¹H—¹³C HETCOR NMR spectrum (Figure 1).[16] In benzene-d_6 at 90 °C the formation of **4** is faster. Figure 2 shows the course of the reaction as a function of time under these conditions.

Material **4** was isolated as a yellow solid by addition of methanol to a toluene solution. Its DSC indicates no crystallinity and that it possesses a glass transition temperature of 150 °C. In agreement with Pollack's material, heating **4** above 200 °C produces a pronounced exotherm, which has been attributed to the rearrangement of the nonconjugated **4** to the red conjugated polyacetylenic form **5** (Scheme 1).[15] The change from yellow to red was confirmed by polarized light hot-stage microscopy. GPC analysis of the isolated material in THF, using polystyrene standards, reveals that it is a 43:57 mixture of polymeric (M_w = 17.9 kg mol⁻¹, M_n = 9.1 kg mol⁻¹, PD = 2.0) and oligomeric units (M_w = 0.7 kg mol⁻¹, M_n = 0.4 kg mol⁻¹, PD = 1.6).

It has been previously shown that complex OsHCl-(CO)(P^{i}Pr₃)₂ reacts with phenylacetylene in the presence

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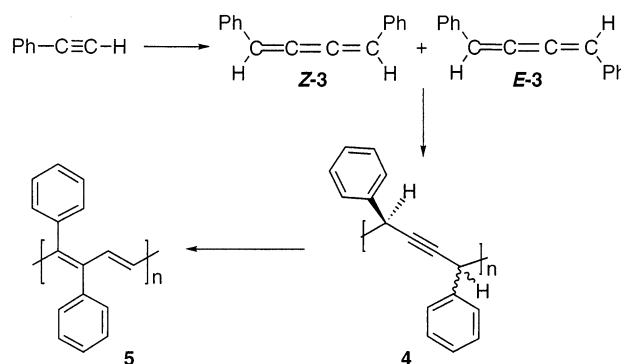
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(13) If an Os:NHEt₂ molar ratio of 1:5 is used, very similar results are obtained. Even with a molar ratio of 1:1 the reactions take place, but under these conditions the rate of the processes is slightly slower. Because the presence of an excess of the amine does not disturb the reaction, we have systematically used an Os:NHEt₂ molar ratio of 1:50.

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(16) Pollack and co-workers have reported 6.35–6.80 ppm as the chemical shift of the CH resonance (ref 15).
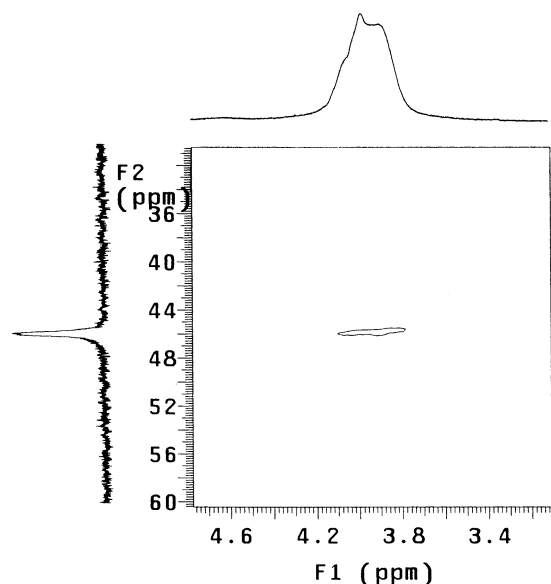
Figure 1. Partial view of the ^{1}H$-^{13}$C HETCOR NMR spectrum of **4**.
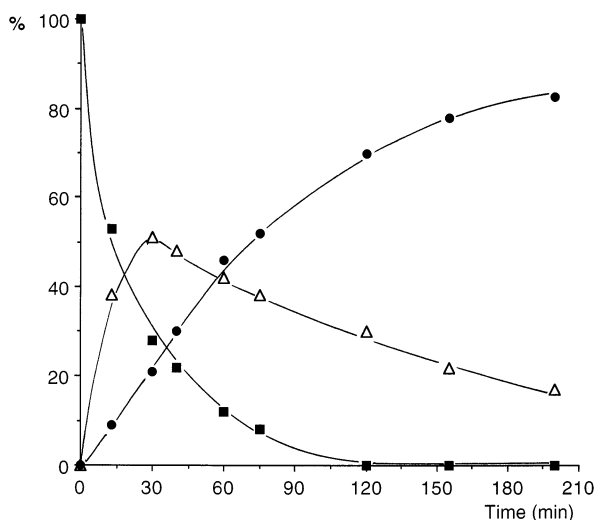
Figure 2. Time vs conversion curve for the coupling of PhC≡CH catalyzed by OsHCl(CO)(P^{i}Pr$_3$)$_2$ in the presence of NHEt$_2$. (■) % of remaining PhC≡CH. (△) % of PhC≡CH converted in butatrienes **3**. (●) % of PhC≡CH converted in polymer **4**.

of strong bases to afford the five-coordinate bisalkynyl derivative Os(C≡CPh)$_2$(CO)(P^{i}Pr$_3$)$_2$.[17] This compound adds a new phenylacetylene molecule to give the diphenylbutenynyl complex Os(C≡CPh){η³-C(C≡CPh)=CH-Ph}(CO)(P^{i}Pr$_3$)$_2$[18] via the π-alkyne intermediate Os(C≡CPh)$_2$(η²-HC≡CPh)(CO)(P^{i}Pr$_3$)$_2$.[17]

For the dimerization of *tert*-butylacetylene to (*Z*)-1,4-di-*tert*-butylbutatriene catalyzed by RuH$_2$(CO)(PPh$_3$)$_2$, Wakatsuki and co-workers[5b] have proposed that the rearrangement of a butenynyl complex, related to Os-(C≡CPh){η³-C(C≡CPh)=CHPh}(CO)(P^{i}Pr$_3$)$_2$, into the corresponding trienyl isomer is the key step for the formation of the butatriene.

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Scheme 2
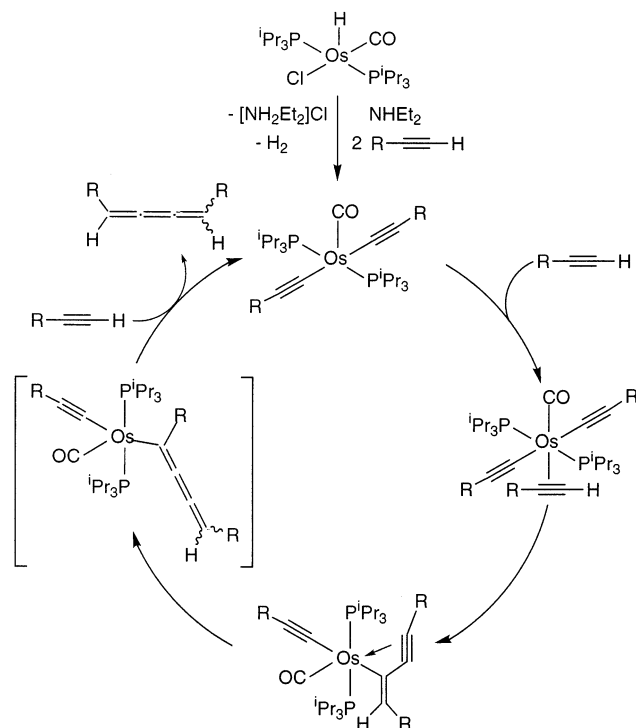
Both precedents prompted us to study the catalytic activity of Os(C≡CPh){η³-C(C≡CPh)=CHPh}(CO)(P^{i}Pr$_3$)$_2$ in alkyne-coupling reactions, to determine the role of the amine. As expected, the results of the experiments carried out with OsHCl(CO)(P^{i}Pr$_3$)$_2$ and NHEt$_2$, Os(C≡CPh){η³-C(C≡CPh)=CHPh}(CO)(P^{i}Pr$_3$)$_2$ and NHEt$_2$, and Os(C≡CPh){η³-C(C≡CPh)=CHPh}(CO)(P^{i}Pr$_3$)$_2$ in the absence of NHEt$_2$ were very similar. Thus, in benzene-d_6 after 1 h at 90 °C, about 90% of phenylacetylene is converted into the butatrienes **3** and the polymer **4**, in a weight ratio close to 1. This indicates that the amine does not play any role during the alkyne-coupling processes and that its function is to generate the active species, the five-coordinate bis(alkynyl) complex Os(C≡CPh)$_2$(CO)(P^{i}Pr$_3$)$_2$. According to this, and in agreement with the Wakatsuki's proposal, the mechanism for the formation of **1**–**3** is that shown in Scheme 2.

In addition, it should be mentioned that the transformation of **3** into **4** catalyzed by Os(C≡CPh){η³-C(C≡CPh)=CHPh}(CO)(P^{i}Pr$_3$)$_2$ is highly sensitive to the presence of water in the reaction mixture. The addition of water produces a notable increase in the transformation rate. Thus, we have observed that in benzene at 90 °C the presence of 5 equiv of water gives rise to the very fast disappearance of phenylacetylene and transformation of **3** into **4**. So, after 20 min under these conditions, 30% of phenylacetylene has been converted in **3** and 70% in **4**.

Complex OsHCl(CO)(P^{i}Pr$_3$)$_2$ in the presence of diethylamine also catalyzes the coupling of trimethylsilylacetylene. However, in this case, the main product of the reaction is (*Z*)-1,4-bis(trimethylsilyl)-1-en-3-yne (**6**). In benzene-d_6, at 90 °C, **6** is obtained in 82% yield after 75 min. In addition, the formation of 5% of 1,4-bis(trimethylsilyl)butatriene (**7**) is also observed. When the reaction was carried out at 40 °C, an increase in the amount of the butatriene **7** occurs (ca. 10%) along

with a decrease of the conversion of alkyne into C_4 products. This is in agreement with the behavior previously reported for the catalytic system generated from $Ru(COD)(COT)$ and P^nBu_3[8] and suggests that the enyne is the result of the catalytic isomerization of the butatriene (eq 3).

(3)
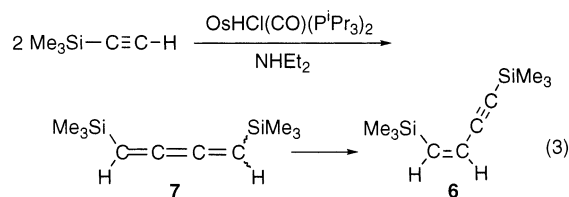
In conclusion, in the presence of diethylamine, complex $OsHCl(CO)(P^iPr_3)_2$ catalyzes the coupling of terminal alkynes $HC≡CR$ (R = Me_3C, Cy, Ph, and Me_3Si). The reaction initially gives butatrienes, which are stable under the reaction conditions for R = Me_3C and Cy. For R = Ph, the butatrienes polymerize, whereas for R = Me_3Si, the butatriene isomerizes into the corresponding Z-enyne. The formation of butatrienes takes place via butenynyl intermediates of the type $Os(C≡CR)\{\eta^3-C(C≡CR)=CHR\}(CO)(P^iPr_3)_2$. This system is the most active and selective of those reported so far.

Experimental Section

All reactions were carried out with rigorous exclusion of air using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. $OsHCl(CO)(P^iPr_3)_2$[9] and $Os(C≡CPh)\{\eta^3-C(C≡CPh)=CHPh\}(CO)(P^iPr_3)_2$[18] were prepared as previously reported. $PhC≡CH$ (Aldrich) was distilled prior to use. The other alkynes were used as received. In the NMR spectra, chemical shifts are referenced to residual solvent peaks. Coupling constants are given in hertz. Mass spectra analyses were performed with a VG Auto Spec instrument. GPC data were obtained using polystyrene standards.

Alkyne-Coupling Reactions Catalyzed by $OsHCl(CO)(P^iPr_3)_2$. In a typical experiment, complex $OsHCl(CO)(P^iPr_3)_2$ (5 mg, 8.7×10^{-3} mmol), diethylamine (45 μL, 0.43 mmol), and the corresponding alkyne (0.43 mmol) in 0.4 mL of benzene-d_6 were sealed in an NMR tube, under argon, and heated at the chosen temperature in an oil bath. The reaction was periodically monitored by ^1H NMR.

Phenylacetylene-Coupling Reactions Catalyzed by $Os(C≡CPh)\{\eta^3-C(C≡CPh)=CHPh\}(CO)(P^iPr_3)_2$. Three different experiments were carried out: (a) The reaction was carried out in 0.4 mL of benzene-d_6, at 90 °C, as described above for complex $OsHCl(CO)(P^iPr_3)_2$ but with complex $Os(C≡CPh)\{\eta^3-C(C≡CPh)=CHPh\}(CO)(P^iPr_3)_2$ (7.3 mg, 8.7×10^{-3} mmol), diethylamine (45 mL, 0.43 mmol), and phenyl-

acetylene (47 mL, 0.43 mmol). (b) The reaction was carried out as in experiment (a) but without diethylamine. (c) The reaction was carried out as in experiment (b) but with water (0.8 μL, 0.04 mmol). In all cases the reaction was periodically monitored by ^1H NMR.

Spectroscopic Data for Dimeric Products. (*E*)- or (*Z*)-1,4-Di-*tert*-butylbutatriene (1). ^1H NMR (C_6D_6, 300 MHz): δ 5.50 (s, 2 H, =CH), 1.06 (s, 18 H, Me). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.43 MHz): δ 160.8 (s, =C=), 118.5 (s, =CH), 35.1 (s, CMe$_3$), 29.7 (s, Me). MS (EI): m/z 164 (M$^+$).

(*E*)- or (*Z*)-1,4-Dicyclohexylbutatriene (2). ^1H NMR (C_6D_6, 300 MHz, plus COSY): δ 5.50 (d, J_{H-H} = 4.2, 2 H, =CH), 2.20 (m, 2 H, CH Cy), 1.80−1.10 (m, 20 H, CH$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.43 MHz): δ 161.9 (s, =C=), 113.2 (s, =CH), 40.9 (s, CH Cy), 32.6, 26.3, 26.0 (all s, CH$_2$). MS (EI): m/z 216 (M$^+$).

(*E*)- and (*Z*)-1,4-Diphenylbutatriene (3). ^1H NMR (C_6D_6, 300 MHz): δ 7.47−6.87 (m, Ph), 6.40 (s, 2 H, =CH, *E* isomer), 6.36 (s, 2 H, =CH, *Z* isomer). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.43 MHz): δ 156.33 (s, =C=, *Z* isomer), 156.18 (s, =C=, *E* isomer), 137.6 (C$_{ipso}$ Ph, *Z* isomer), 137.5 (C$_{ipso}$ Ph, *E* isomer), 129.0, 128.9, 128.3, 128.2, 128.0, 127.7 (Ph), 110.1 (s, =CH, *Z* isomer), 110.0 (s, =CH, *E* isomer). MS (EI): m/z 206 (M$^+$).

(*Z*)-1,4-Bis(trimethylsilyl)-1-en-3-yne (6). ^1H NMR (C_6D_6, 300 MHz): δ 6.23 (d, J_{H-H} = 15, 1 H, =CHSiMe$_3$), 6.00 (d, J_{H-H} = 15, 1 H, =CHC≡), 0.22 (s, 9 H, SiMe$_3$), 0.14 (s, 9 H, SiMe$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.43 MHz): δ 145.8 (s, =CHSiMe$_3$), 125.3 (s, =CHC≡), 105.7 (s, ≡CSiMe$_3$), 98.8 (s, =CHC≡), −0.5 (s, SiMe$_3$), −1.3 (s, SiMe$_3$). MS (EI): m/z 196 (M$^+$).

(*E*)- or (*Z*)-1,4-Bis(trimethylsilyl)butatriene (7). ^1H NMR (C_6D_6, 300 MHz): δ 6.34 (s, 2 H, =CH), 0.11 (s, 18 H, SiMe$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.43 MHz): δ 131.2 (s, =C=), 121.2 (s, =CH), −1.4 (s, SiMe$_3$).

Synthesis of −[CH(Ph)C≡CCH(Ph)]$_n$− (4). A solution of complex $OsHCl(CO)(P^iPr_3)_2$ (15 mg, 0.026 mmol) in 2 mL of toluene was treated with diethylamine (135 μL, 1.3 mmol) and phenylacetylene (142 μL, 1.3 mmol). The dark red solution was stirred at 90 °C overnight. After this time, the resulting brown solution was concentrated to ca. 1 mL, and 10 mL of a solution of 2,6-di-*tert*-butyl-4-methylphenol (0.1%) in methanol was added. A yellow solid was formed, which was filtered, washed with methanol, and vacuum-dried. Yield: 60 mg (45%). ^1H NMR (C_6D_6, 300 MHz): δ 7.3−6.7 (br, 10 H, Ph), 4.1−3.7 (br, 2 H, ≡CCH). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.43 MHz): δ 140.0, 139.3 (C$_{ipso}$, Ph), 129.3, 127.1 (Ph), 84.9 (≡C), 46.1, ≡CCH). GPC molecular weight analysis, bimodal behavior: M_w = 17.9 kg mol^{-1}, M_n = 9.1 kg mol^{-1}, PD = 2.0 and M_w = 0.7 kg mol^{-1}, M_n = 0.4 kg mol^{-1}, PD = 1.6.