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Covalent Rigid-Rod Organometallic Polymers with Alternating Transition Metal Clusters and Conjugated Spacers in the Main Chain

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The first rigid-rod cluster-containing σ-alkynyl polymers E−[({Pt_6}−CC−Ar−CC)]$_{x-\{Pt6\}}$−E [(**3**), {Pt_6} = $Pt_6(\mu\text{-}PBu^t{}_2)_4(CO)_4$, E = end group; M_n = 22 000−38 000] have been prepared by step-growth polycondensation of {Pt_6}Cl_2 and 1,4-didodecyl-2,5-diethynylbenzene (HCC−Ar−CCH) under Sonogashira-type conditions. The monodisperse oligomers HCC−Ar−CC−({Pt_6}CC−Ar−CC)$_x$−{Pt_6}−CC−Ar−CCH [(**4**) $x = 0$; (**11**) $x = 2$; (**15**) $x = 4$] were also prepared by stepwise procedures, still based on Cu(I)-catalyzed dehydrohalogenation reactions. A red-shift of the UV−vis absorption centered at ca. 470 nm, on increasing chain length, suggests some degree of electron delocalization along the backbone.

Introduction

The incorporation of transition metals into oligomeric or polymeric frameworks has been subjected to intense scrutiny, and the interest is rapidly growing further after the discovery of new synthetic procedures and of the valuable properties and technological potential of these materials.[1,2] An important class of such derivatives includes the one-dimensional metal-alkynyls or -polyynyls [(−L_nM−CC−R−CC−)$_x$; R = none, −(CC)$_y$−, aromatic or heteroaromatic−diyl rings],[2] where the metal centers are embedded into the main chain of the polymer by virtue of robust M−CC covalent σ-bonds, not involving the π-electrons of the CC triple bond. The third-order nonlinear optical, liquid-crystalline, and electro-optic properties of these materials have been recently reviewed.[2a] Analogous polymers, containing transition metal cluster units [(−L_nM_z−CC−R−CC−)$_x$; $z \geq 3$], are presently unknown;[3,4] indeed, the inclusion of polyhedral metal clusters into a macromolecular organometallic chain is exceedingly rare,[5,6] even though it is considered a remarkable task.[1d] To our knowledge only two examples of soluble polymers have been reported: {$Ru_6(\mu_6\text{-}C)(CO)_{15}(Ph_2P{-}CC{-}PPh_2)$}$_n$[5c] and the polyurethane [−O(CH$_2$)$_m$C$_5$H$_4${$Mo_2Ir_2(CO)_{10}$}C$_5$H$_4$-(CH$_2$)$_m$OC(O)N(H)−R−N(H)C(O)−]$_n$.[5d] The latter appears to be the unique example where the cluster−spacer connection is made with strong covalent M−C bonds, although the spacer itself is clearly nonconjugated. Additionally, the insoluble diisocyanide-bridged polymers {[$Pt_3(\mu\text{-dppm})_3(\mu\text{-}1,4\text{-}CN{-}C_6R_4{-}NC)$][$PF_6$]$_2$}$_n$ (R = H, Me) were found[5e] to dissolve with breakdown of the oligomeric structure, and a few interesting soluble polymers with Pt_3[5f] or M_4 (M = Pd, Pt) linear chains[5g−h] in the repeating units have been reported. It is worth noting the potential relevance of cluster-containing conjugated structures

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10.1021/om0604021 CCC: $33.50

Scheme 1. Preparation of Polymers 3

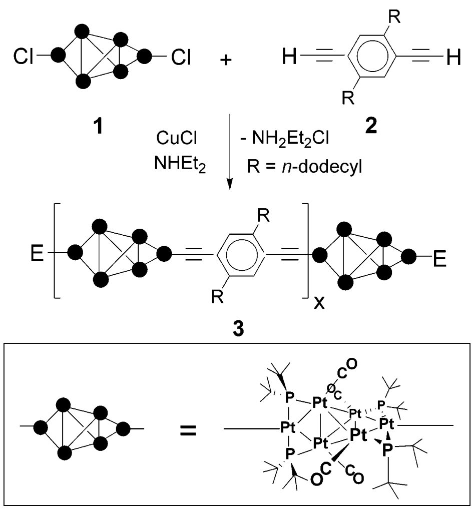

Table 1. Molecular Weights from GPC and NMR Analyses

polymer	M_w[a]	M_n[a]	M_w/M_n[a]	DP$_{GPC(PS)}$[b]	DP$_{NMR}$[c]
3a	64 700	22 500	2.9	9	8
3b	68 156	23 272	2.9	9	8
3c	148 887	37 555	4.0	15	16

[a] Monodispersed polystyrene as GPC standard. [b] DP$_{GPC(PS)}$ = (M_n − M({Pt$_6$}E$_2$)/M({Pt$_6$}CC−Ar−CC) (E = Cl, **3a**, **3c**; CC−Ar−CCH, **3b**). [c] Calculated from NMR spectroscopy.

in the field of molecular electronics, as suggested by recent studies on single-electron tunneling transistors working reliably at room temperature and based on a single molecular metallorganic cluster.[7] On these grounds, in previous communications[8a,b] we reported that the dichloride {Pt$_6$}Cl$_2$ (**1**) [{Pt$_6$} = Pt$_6$(μ-PBu$^t{}_2$)$_4$(CO)$_4$] is a useful synthon for the introduction of the {Pt$_6$} cluster unit in complex structures. Herein we describe the synthesis of the first cluster-containing σ-alkynyl polymers; pure and monodisperse shorter oligomers were also prepared.

Results and Discussion

σ-Alkynyl polymers were prepared via the CuCl-catalyzed coupling between complex **1** and 1,4-didodecyl-2,5-diethynylbenzene [(**2**), HCC−Ar−CCH] (Scheme 1). The course of the polymerization was investigated by taking portions of the reaction mixture and characterizing the polymeric material via GPC and spectroscopic measurements. Indeed, after 16 h of stirring, a first portion of the reaction mixture was taken and evaporated, and the residue was analyzed by IR and NMR (^{1}H, ^{31}P) spectroscopy, showing that the starting materials **1** and **2** were absent. Column chromatography of this residue yielded a single fraction of the σ-alkynyl polymer [E−({Pt$_6$}−CC−Ar−CC)$_x$−{Pt$_6$}−E], **3a** (Scheme 1, E = end group, Ar = 1,4-C$_6$H$_2$-(2,5-C$_{12}$H$_{25}$)$_2$, M_n = 22 500 by GPC, see Table 1). Since (i) no signal for the CCH moiety was observed in the ^{1}H NMR spectrum of **3a**, and (ii) the only two complex and overlapped resonances, observed at 335.5 and 328.0 ppm in its ^{31}P{^{1}H} NMR spectrum, were respectively assigned to the P−Pt−CC and to the terminal P−Pt−Cl groups [δ_P = 335.7 in {Pt$_6$}-(CCPh)$_2$ and 328.9 ppm in **1**],[8b] this sample should mainly contain Pt−Cl terminations (E = Cl).

A further amount of the dialkyne **2** (**2**/**3a** ≅ 2) was added to the mother solution and, after 3 days of stirring, a portion of the solution was separated and treated as described before, yielding polymer **3b**. Noticeably, the GPC measurements showed that the degree of polymerization (DP) is unchanged with respect to **3a** (Table 1), indicating that only the substitution of the Cl end groups with the CC−Ar−CCH moieties occurred. As a consequence, the ^{1}H NMR spectrum of **3b** showed the signal of the CCH moiety at 3.23 ppm, and only one ^{31}P{^{1}H} NMR resonance was observed at 335.5 ppm for the *P*−Pt−CC (both terminal and internal) nuclei. Finally, the reaction mixture was treated with **1** (**1**/**3b** molar ratio ≅ 1) and, after 3 days of stirring, polymer **3c** was recovered as described above [overall yield for **3a**−**c**: >80% with respect to **1**]. The GPC analysis of sample **3c** confirmed a substantial increase of the M_n and M_w values (M_n = 37 555, Table 1), in accord with the step-growth polycondensation character of the polymerization. A residual, small resonance in the ^{31}P{^{1}H} NMR at 328.0 ppm, overlapping the main signal at 335.5 ppm and the absence of a ^{1}H NMR signal at ca. 3.2 ppm, confirmed that, similar to **3a**, polymer **3c** mainly contains Pt−Cl end groups. The IR spectra of **3a**−**c** showed the expected absorptions at 2093 (m, br, $\nu_{C\equiv C}$) and 2010 (s, br, $\nu_{C\equiv O}$) cm^{-1}, and limited to **3b**, a very weak absorption at 3302 cm^{-1} was observed for the terminal CCH moiety. The ^{1}H NMR spectra of **3a**−**c** exhibited, besides the aforementioned peaks, a slightly broadened singlet (7.13 ppm) for the aromatic protons, the *tert*-butyl signal (virtual triplet at 1.51 ppm), and the *n*-dodecyl resonances (2.76−0.87 ppm), with integral ratios that conform to the proposed structures. The chemical shifts of the ^{195}Pt{^{1}H} resonances [δ_{Pt} = −4684 (Pt$_{apical}$), −2980 (Pt$_{tetrahedron}$) ppm] are similar to those reported for {Pt$_6$}(CCR)$_2$ [−4674 (2 Pt), −2996 (4Pt) ppm];[8b] the complex shape of these resonances[9] is diagnostic for the {Pt$_6$} unit symmetrically substituted at the two "apical" positions[8,10] and strictly resembles those previously observed for {Pt$_6$}X$_2$ (X = halogen,[8a,b] CCR,[8b] CHO[10]) and [{Pt$_6$}(CO)$_2$]$^{2+}$,[8c] for many of which the structure was elucidated by X-ray analysis.

The DP values were calculated also from NMR spectroscopy, namely, from the ratios between (i) the ^{31}P{^{1}H} NMR resonances of the P−Pt−CC and P−Pt−Cl nuclei (for **3a** and **3c**) and (ii) the ^{1}H NMR resonances of the CCH (3.23 ppm) and ArCH$_2$ (2.79 ppm) groups (for **3b**); importantly, they were found to be very close to the ones from GPC measurements.[11] Finally, to assess the electronic conjugation along the {Pt$_6$}/arylalkynyl chains, we prepared the monodisperse shorter oligomers HCC−Ar−CC−({Pt$_6$}CC−Ar−CC)$_x$−{Pt$_6$}−CC−Ar−CCH [(**4**) x = 0; (**11**) x = 2; (**15**) x = 4], with precisely controlled lengths. Complex **4** was prepared as previously described[8b] by the dehydrohalogenation of the dichloride **1** with a 3-fold excess

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[7] Gubin, S. P.; Gulayev, Yu. V.; Khomutov, G. B.; Kislov, V. V.; Kolesov, V. V.; Soldatov, E. S.; Sulaimankulov, K. S.; Trifonov, A. S. *Nanotechnology* **2002**, *13*, 185−194.

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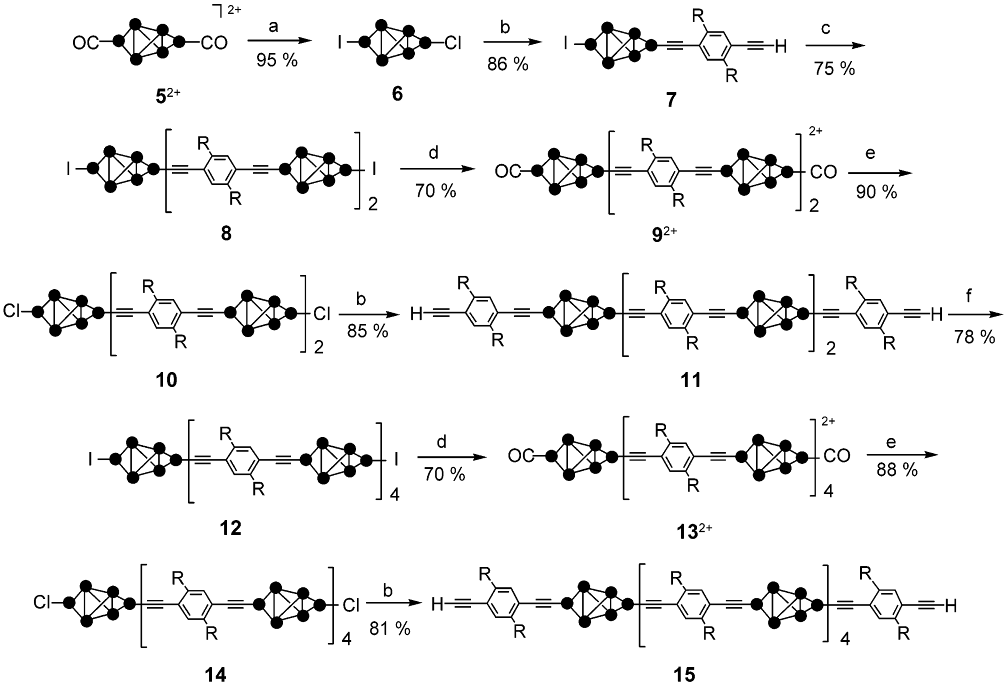
[9] Each Pt$_6$ cluster is constituted by 22 groups of nonequivalent isotopomers (total number of isotopomers: 2^6 = 64), nearly all giving subspectra that cannot be interpreted with simple first-order approximations, and a meaningful accurate simulation of the total spectrum is not accessible with our programs. However, the main features of the complex shape of the signals remain constant and may be taken as a footprint of the hexanuclear {Pt$_6$}X$_2$ structure.[8,10]

[10] Leoni, P.; Marchetti, F.; Marchetti, L.; Pasquali, M.; Quaglierini, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3617−3618.

[11] It is known that overestimated molecular weights are generally obtained by GPC measurements on rigid-rod metal−alkynyl polymers. Nevertheless, Lo Sterzo and co-workers have reported that, in the presence of octyloxy side-chains, the rigid rodlike polymers of general formula [−(Bu$_3$P)$_2$M−CC−Ar−CC−]$_n$ [M = Pd, Pt; Ar = C$_6$H$_2$(OC$_8$H$_{17}$)$_2$][2e] give reliable GPC results.

Scheme 2. Preparation of the Monodisperse Oligomers 11 and 15



a: 1) n-Bu_4NCl / CH_2Cl_2; 2) KI / acetone

b: 1,4-didodecyl-2,5-diethynylbenzene, $NHEt_2$, CuI

c: $\{Pt_6\}Cl_2$ (**1**), $NHEt_2$, CuI

d: $TlPF_6$, CO / THF;

e: n-Bu_4NCl / acetone

f: $\{Pt_6\}ICl$ (**6**), $NHEt_2$, CuI

Table 2. Selected UV−Vis Data for 4, 11, 15, and Polymers 3a−c

compound	λ_{max} (nm)
4	449
11	466
15	470
3a−**c**	476

of the dialkyne **2**, while **11** and **15** were obtained according to the stepwise method shown in Scheme 2.

The key intermediate in this procedure is the unsymmetrical dihalide $\{Pt_6\}ICl$, (**6**), which undergoes selective dehydrohalogenation with terminal alkynes at the chloride ligand, thus allowing a controlled growth of the chain length. Reactive dichlorides can be restored from the intermediate diiodides (**8**/**12**) in two steps (substitution with CO, assisted by Tl^+, followed by reaction with tetra-*n*-butylammonium chloride).

Indeed, the absorption at ca. 450 nm, observed in the UV−vis spectrum of "monomer" **4**, is red-shifted for the "tri-" and "pentamers" **11** and **15**, respectively at 466 and 470 nm, and is further shifted at 476 nm for the polymers **3a**−**c** (Table 2). Similar effects have been observed previously in many oligomeric platinum(II) or palladium(II) polyynes of general formula $[-L_mM-CC-Ar-CC-]_n$ [(M = Pt, Pd)] and have been attributed to an increased delocalization of π-electrons along the polymer backbone, which extends through the metal sites.[2]

In summary, this work describes the step-growth polycondensationof the dichloride $\{Pt_6\}Cl_2$ and the dialkyne HCC−Ar−CCH, giving the first cluster-containing σ-alkynyl polymers, which exhibit (nonoptimized) high molecular weights. Presently, work is in progress in order to (i) synthesize analogous oligo- and polymers with different dialkynyl spacers (both organic and organometallic) and (ii) elucidate the influence of the replacement of single platinum centers with cluster units in the repeating unit of alkynyl polymers of general formula $[(-L_nM_z-CC-R-CC-)_x$, on their interesting and well-established[2] photophysical properties.

Experimental Section

General Data. The reactions were carried out under a nitrogen atmosphere, by using standard Schlenk techniques. $[Pt_6(\mu\text{-}PBu^t{}_2)_4(CO)_6](CF_3SO_3)_2$ (**5**),[10] $Pt_6(\mu\text{-}PBu^t{}_2)_4(CO)_4Cl_2$ (**1**),[8] and 1,4-didodecyl-2,5-diethynylbenzene (**2**)[12] were prepared as previously described. Solvents were dried by conventional methods and distilled under nitrogen prior to use. NMR spectra were acquired using a Varian Gemini 200 BB spectrometer (200 MHz for ^1H) at room temperature (about 293 K) on $CDCl_3$ solutions; frequencies are referenced to the residual resonances of the deuterated solvent (H, ^{13}C), 85% H_3PO_4 (^{31}P), and H_2PtCl_6 (^{195}Pt). The symbol $^{\#}$ is used to label ^1H, ^{13}C, and ^{31}P peaks with ^{195}Pt satellites. UV−vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. IR spectra were (Nujol mulls, KBr) were recorded on a Perkin-Elmer FT-IR 1725X spectrophotometer. Molecular weights were determined (relative to PS standard) on a Waters 2487 equipped with a set of PL gel columns ($CHCl_3$ as the eluent, flow rate 1 mL min^{-1}).

Preparation of Polymer 3. A $NHEt_2/CH_2Cl_2$ (150/50 mL) solution of **1** (500 mg, 0.258 mmol) was treated with 1,4-didodecyl-2,5-diethynylbenzene (120 mg, 0.258 mmol) and CuCl (1 mg, 5.2 μmol). After stirring for 16 h at room temperature, 10 mL of the mixture was taken (fraction A) and all the volatiles were removed in vacuo. The resulting residue was washed with H_2O/acetone (1:1) and eluted with CH_2Cl_2 on a silica gel chromatographic column, yielding a red solid (**3a**, 25 mg). The reaction mixture was treated with 1,4-didodecyl-2,5-diethynylbenzene (25.2 mg, 54.5 μmol) and stirred for 60 h at room temperature. A portion of the mixture was taken (10 mL, fraction B) and handled as detailed for fraction A, yielding **3b** (red, 26 mg). Finally, the dichloride **1** (49.9 mg, 25.8 μmol) was added to the reaction mixture. After 3 days stirring, all

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[12] Kloppenburg, L.; Jones, D.; Bunz, U. H. F. *Macromolecules* **1999**, *32*, 4194.

the volatiles were removed in vacuo, and the residue was washed with H_2O/acetone (1:1) and passed over a silica gel chromatographic column (CH_2Cl_2 as the eluent), yielding a red solid (**3c**, 535 mg).

3a. Anal. Calcd for $C_{596}H_{1064}Cl_2O_{36}P_{36}Pt_{54}$, Cl{[$Pt_6(P^tBu_2)_4(CO)_4$]-$CCC_6H_2(C_{12}H_{25})_2CC$}$_8$[$Pt_6(P^tBu_2)_4$-$(CO)_4$]Cl:[13] C, 34.9; H, 5.22. Found: C, 35.1; H, 5.18. ^{1}H NMR: δ 7.13 (s, CH), 2.79 (br s, $ArCH_2$), 1.65 (br, CH_2 dodecyl), 1.51 (vt, $^3J_{HP}+^5J_{HP} = 6.0$ Hz, P^{t}Bu), 1.27 (br s, CH_2 dodecyl), 0.87 (t, CH_3 dodecyl, $^3J_{HH} = 6.4$ Hz). ^{13}C{^{1}H} NMR: δ 216.6 (CO), 139.4 (*C*CH2, Ar), 131.0 (*C*H, Ar), 125.4 (*C*−C≡C, Ar), 123.0 (*C*CPt), 103.0 (C*C*Pt), 43.7 (P*C*), 34.1, 32.0 (dodecyl), 31.6 (CH_3, ^{t}Bu), 30.4, 29.8, 29.4, 22.7, 14.2 (dodecyl). ^{31}P{^{1}H} NMR: δ 335.5 (P−Pt−CC, m), 328.0 (weak m, P−Pt−Cl). ^{195}Pt{^{1}H} NMR: δ −4684.5 (m, 1 Pt), −2979.8 (m, 2 Pt). IR (CH_2Cl_2): 2093 (C≡C), 2010 (CO) cm^{-1}.

3b. Anal. Calcd for $C_{664}H_{1170}Cl_2O_{36}P_{36}Pt_{54}$, $HCCC_6H_2(C_{12}H_{25})_2$-CC{[$Pt_6(P^tBu_2)_4(CO)_4$]$CCC_6H_2(C_{12}H_{25})_2$-CC}$_8$[$Pt_6(P^tBu_2)_4(CO)_4$]-$CCC_6H_2(C_{12}H_{25})_2CCH$:[4] C, 37.3; H, 5.52. Found: C, 37.5; H, 5.54. The ^{1}H NMR spectrum is similar to that of **3a**, except for the presence of a weak singlet at 3.23 ppm (s, CCH). The ^{13}C and ^{195}Pt NMR spectra are virtually identical to those of **3a**. ^{31}P{^{1}H} NMR: δ 335.5 (m, P−Pt−CC). IR (CH_2Cl_2): 3302 (C≡CH), 2093 (C≡C), 2010 (CO) cm^{-1}.

3c. Anal. Calcd for $C_{1086}H_{1932}Cl_2O_{64}P_{64}Pt_{96}$, Cl{[$Pt_6(P^tBu_2)_4$-$(CO)_4$]$CCC_6H_2(C_{12}H_{25})_2CC$}$_{15}$[$Pt_6(P^tBu_2)_4(CO)_4$]Cl:[4] C, 35.4; H, 5.29. Found: C, 35.2; H, 5.32. The ^{1}H, ^{13}C, ^{31}P, and ^{195}Pt NMR and IR spectra are virtually identical to those of **3a**.

Preparation of $Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4(CC{-}Ar{-}CCH)_2$ (4). 1,4-Didodecyl-2,5-diethynylbenzene (86 mg, 0.186 mmol) and CuI (0.28 mg, 0.0015 mmol) were added to a diethylamine (50 mL) solution of complex **1** (120 mg, 0.062 mmol). After 24 h the solvent was evaporated and the red oil residue was chromatographed on silica gel. The unreacted dialkyne was eluted with CH_3CN, while the subsequent elution with Et_2O provided a red solution of **4**. Solvent removal followed by drying under vacuum afforded **4** as a red oil (152 mg, 88%). Anal. Calcd for $C_{104}H_{178}O_4P_4Pt_6$: C, 44.8; H, 6.44. Found: C, 44.5; H, 6.6. ^{1}H NMR: δ 7.12 (s, Ar, 2 H), 7.18 (s, Ar, 2 H), 3.23 (s, CCH, 2 H), 2.79 (br m, $ArCH_2$, 4 H), 2.70 (br m, $ArCH_2$, 4 H), 1.64 (br, CH_2 dodecyl, 16 H), 1.50 (vt, $^3J_{HP}+^5J_{HP} = 7$ Hz, 72 H), 1.26 (br s, CH_2 dodecyl, 64 H), 0.89 ppm (t, CH_3 dodecyl, 12 H). ^{13}C{^{1}H} NMR: δ 216.6 (CO), 142.2, 140.4, 132.6, 131.6, 129.6 (Ar) 122.1 (*C*CPt), 117.6 (Ar), 108.4, (C*C*Pt), 83.4 (HC*C*), 80.1 (*C*CH), 43.9 (C, ^{t}Bu), 34.2, 32.3, 32.2 (dodecyl), 31.6 (CH_3, ^{t}Bu), 30.9, 30.7, 29.9, 29.8, 29.6, 22.9, 14.2 ppm (dodecyl). ^{31}P{^{1}H} NMR: δ 334.0$^\#$ ppm (s). ^{195}Pt{^{1}H} NMR: δ −2986 (m, 4 Pt), −4693 ppm (m, 2 Pt). IR (CH_2Cl_2): 3300 ($\nu_{C\equiv CH}$), 2090 ($\nu_{C\equiv C}$), 2010 cm^{-1} (ν_{CO}).

Preparation of $Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4ICl$ (6). n-Bu_4NCl (62.5 mg, 0.225 mmol) was added to a red solution of complex **5** (500 mg, 0.225 mmol) in CH_2Cl_2 (10 mL). After a few minutes all the volatiles were removed in vacuo and the resulting red residue was dissolved in acetone/H_2O (20:1) and treated with KI (50 mg, 0.301 mmol). Complex **6** precipitated out as an orange solid and was filtered and vacuum-dried (433 mg, 95%). Anal. Calcd for $C_{36}H_{72}$-$ClIO_4P_4Pt_6$: C, 21.3; H, 3.6. Found: C, 21.4; H, 3.8. ^{1}H NMR: δ 1.52 ppm (vt, $3J_{HP} + ^5J_{HP} = 7.5$ Hz). ^{13}C{^{1}H} NMR: δ 206.0 (s, CO), 203.8 (s, CO), 45.2, 44.7 (s, C, ^{t}Bu), 32.4, 31.5 ppm (s, CH_3). ^{31}P{^{1}H} NMR: δ 333.2$^\#$ (s), 328.7$^\#$ ppm (s). ^{195}Pt{^{1}H} NMR: δ −3356 (m, 2 Pt), −3453 (m, 2 Pt), −4149 (m, 1 Pt), −4941 ppm (m, 1 Pt). IR (CH_2Cl_2): 2016 cm^{-1} (ν_{CO}).

Preparation of $I[Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4](CC{-}Ar{-}CCH)$ (7). 1,4-Didodecyl-2,5-diethynylbenzene (140 mg, 0.30 mmol) and CuI (0.38 mg, 0.002 mmol) were added to a diethylamine (75 mL) solution of complex **6** (405 mg, 0.20 mmol). After 24 h the solvent was evaporated and the orange residue was extracted with Et_2O to give, after chromatography (silica gel, eluent CH_2Cl_2/*n*-hexane, 1:5), 420 mg of **7** (86%). Anal. Calcd for $C_{70}H_{125}IO_4P_4Pt_6$: C, 34.3; H, 5.1. Found: C, 34.4; H, 5.0. ^{1}H NMR: δ 7.21 (s, Ar, 1 H), 7.15 (s, Ar, 1 H), 3.26 (s, CCH, 1 H) 2.76 (br m, $ArCH_2$, 2 H), 2.67 (br m, $ArCH_2$, 2 H), 1.65 (br, CH_2 dodecyl, 8 H), 1.50 (vt, $^3J_{HP}+^5J_{HP} = 7$ Hz, 36 H), 1.47 (vt, $^3J_{HP}+^5J_{HP} = 7$ Hz, 36 H), 1.25, 1.23 (s, br, CH_2 dodecyl, 32 H), 0.86 ppm (t, CH_3 dodecyl, 6 H). ^{13}C{^{1}H} NMR: δ 215.6, 207.6 (CO), 142.4, 140.6, 132.7, 131,7, 129.6 (Ar) 122.3 (*C*CPt), 117.7 (Ar), 102.3 (C*C*Pt), 83.9 (*C*CH), 80.6 (C*C*H), 45.4, 44.2 (C, ^{t}Bu), 34.4, 34.2 (dodecyl), 32.5 (CH_3, ^{t}Bu), 32.4 (dodecyl), 31.8 (CH_3, ^{t}Bu), 31.1, 30.8, 30.1, 29.9, 29.8, 23.1, 14.3 ppm (dodecyl). ^{31}P{^{1}H} NMR: δ 336.1$^\#$ (s), 330.7$^\#$ ppm (s). ^{195}Pt{^{1}H} NMR: δ −3030 (m, 2 Pt), −3326 (m, 2 Pt), −4711 (m, 1 Pt), −4896 ppm (m, 1 Pt). IR (CH_2Cl_2): 3302 ($\nu_{C\equiv CH}$), 2091 ($\nu_{C\equiv C}$), 2014 cm^{-1} (ν_{CO}).

Preparation of I{$[Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4](CC{-}Ar{-}CC)$}$_2$$[Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4]I$ (8). Complex **7** (400 mg, 0.163 mmol) and CuI (0.31 mg, 1.6 × 10^{-3} mmol) were added to a diethylamine (75 mL) solution of complex **1** (155 mg, 0.080 mmol). After 24 h stirring at room temperature, all the volatiles were removed in vacuo and the resulting red residue was extracted with Et_2O and chromatographed on silica gel (eluent CH_2Cl_2/*n*-hexane, 1:2), yielding 406 mg of **8** (75%). Anal. Calcd for $C_{176}H_{320}I_2O_{12}P_{12}Pt_{18}$: C, 31.2; H, 4.77. Found: C, 31.1; H, 4.9. ^{1}H NMR: δ 7.14 (br s, Ar, 4 H), 2.77 (br m, $ArCH_2$, 8 H), 1.65 (br, CH_2 dodecyl, 16 H), 1.52 (vt, $^3J_{HP}+^5J_{HP} = 7$ Hz, 216 H), 1.27 (br s, CH_2 dodecyl, 64 H), 0.88 ppm (t, CH_3 dodecyl, 12 H). ^{13}C{^{1}H} NMR: δ 217.1, 215.8, 207.5 (CO), 139.9, 131.3, 125.8, 125.5 (Ar) 123.0 (*C*CPt), 104.6, 103.7 (C*C*Pt), 45.3, 44.0 (C, ^{t}Bu), 34.4 (dodecyl), 32.4 (CH_3, ^{t}Bu), 32.3 (dodecyl), 31.7 (CH_3, ^{t}Bu), 31.0, 30.2, 30.1, 30.0, 29.8, 23.1, 14.3 ppm (dodecyl). ^{31}P{^{1}H} NMR: δ 336.2$^\#$ (s, 4 P), 333.5$^\#$ (s, 4 P), 330.2$^\#$ ppm (s, 4 P). ^{195}Pt{^{1}H} NMR: δ −2979 (m, 4 Pt), −3052 (m, 4 Pt), −3322 (m, 4 Pt), −4685 (m, 2 Pt), −4697 (m, 2 Pt), −4899 ppm (m, 2 Pt). IR (CH_2Cl_2): 2096 ($\nu_{C\equiv C}$), 2012 cm^{-1} (ν_{CO}).

Preparation of [OC{$[Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4](CC{-}Ar{-}CC)$}$_2$$[Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4]CO$] $(PF_6)_2$ (9). $TlPF_6$ (120 mg, 0.343 mmol) was added to a THF (100 mL) solution of complex **8** (400 mg, 0.059 mmol). The flask was filled with CO (1 atm) and the reaction mixture stirred for 24 h at room temperature. The solvent was evaporated and the residue was washed with hexane and then dissolved in acetone. Filtration of the resulting red solution followed by solvent removal afforded complex **9** as a red solid (285 mg, 70%). Anal. Calcd for $C_{178}H_{320}F_{12}O_{14}P_{14}Pt_{18}$: C, 31.2; H, 4.70. Found: C, 31.1; H, 4.6. ^{1}H NMR: δ 7.19 (br s, Ar, 4 H), 2.79 (m, br, $ArCH_2$, 8 H), 1.66 (br, CH_2 dodecyl, 16 H), 1.51 (vt, $^3J_{HP}+^5J_{HP} = 7$ Hz, 216 H), 1.28 (br s, CH_2 dodecyl, 64 H), 0.89 ppm (t, CH_3 dodecyl, 12 H). ^{13}C{^{1}H} NMR: δ 218.7, 216.9, 204.5 (CO), 139.8, 131.4, 126.6, 124.4 (Ar) 122.9 (*C*CPt), 105.0 (C*C*Pt), 46.1, 45.6, 44.0 (C, ^{t}Bu), 34.4 (dodecyl), 31.9 (CH_3, ^{t}Bu), 30.7, 30.1, 30.1, 29.7, 23.0, 14.5 ppm (dodecyl). ^{31}P{^{1}H} NMR: δ 357.1$^\#$ (s, 4 P), 354.5$^\#$ (s, 4 P), 333.5$^\#$ (s, 4 P), −142.6 ppm (sept, $J_{PF} = 705$ Hz). ^{195}Pt{^{1}H} NMR: δ −2985 (m, 8 Pt), − 3074 (m, 4 Pt), 4494 (m, 2 Pt), −4689 (m, 2 Pt), −4991 ppm (m, 2 Pt). IR (CH_2Cl_2): 2126 (vw) ($\nu_{C\equiv C}$), 2078 (s), 2057 (m), 2045 (s), 2031 (m), 2018 (vs), 2011 (s) cm^{-1} (ν_{CO}).

Preparation of Cl{$[Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4](CC{-}Ar{-}CC)$}$_2$$[Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4]Cl$ (10). NH_4Cl (9.6 mg, 0.18 mmol) was added to a red solution of complex **9** (285 mg, 0.042 mmol) in acetone (10 mL). Addition of H_2O (5 mL) caused the precipitation of a red solid, which was filtered and chromatographed on silica gel (eluent CH_2Cl_2/*n*-hexane, 1:2), yielding 250 mg of **10** (90%). Anal. Calcd for $C_{176}H_{320}Cl_2O_{12}P_{12}Pt_{18}$: C, 32.1; H, 4.90. Found: C, 32.2; H, 4.8. ^{1}H NMR: δ 7.19 (br s, Ar, 4 H), 2.80 (br m, $ArCH_2$, 8 H),

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(13) The average molecular weight agrees with integral ratios of ^{1}H NMR spectra. In the ^{31}P NMR spectra of **3a** and **3c**, the integral ratios between the resonances of the *P*−Pt−CC and *P*−Pt−Cl nuclei have been estimated by comparison with the weighed sum of the spectra of the monomer derivatives {Pt_6}X_2 (X = Cl, CC[(1,4-*n*-$C_{12}H_{25}$)$_2$-2,5-C_6H_2]CCH). ^{1}H and ^{31}P NMR spectra for quantitative evaluations were acquired with a 60 s delay between each transient.

1.64 (br, CH_2 dodecyl, 16 H), 1.52 (vt, $^{3}J_{HP}+^{5}J_{HP} = 7$ Hz, 216 H), 1.28 (br s, CH_2 dodecyl, 64 H), 0.89 ppm (t, CH_3 dodecyl, 12 H). $^{13}C\{^{1}H\}$ NMR: δ 216.9, 215.8, 204.7 (CO), 139.7, 131.3, 125.8, 125.4 (Ar), 123.4, 123.0 (*C*CPt), 119 (Ar), 103.8, 102.9 (C*C*Pt), 44.9, 44.2, 44.0 (C, ^{t}Bu), 34.4, 32.3 (dodecyl), 31.9 (CH_3, ^{t}Bu), 30.7, 30.2, 30.1, 23.0, 14.3 ppm (dodecyl). $^{31}P\{^{1}H\}$ NMR: δ 336.1$^{\#}$ (s, 4 P), 333.0$^{\#}$ (s, 4 P), 325.7$^{\#}$ ppm (s, 4 P). $^{195}Pt\{^{1}H\}$ NMR: δ −2980 (m, 4 Pt), −3033 (m, 4 Pt), −3426 (m, 4 Pt), −4120 (m, 2 Pt), −4686 (m, 2 Pt), −4700 ppm (m, 2 Pt). IR (CH_2Cl_2): 2097 ($\nu_{C\equiv C}$), 2013 cm^{-1} (ν_{CO}).

Preparation of HCC−Ar−CC−{[$Pt_6(\mu\text{-}PBu^{t}_2)_4(CO)_4$](CC−Ar−CC)}$_2$[$Pt_6(\mu\text{-}PBu^{t}_2)_4(CO)_4$]−CC−Ar−CCH (11). 1,4-Didodecyl-2,5-diethynylbenzene (55 mg, 0.119 mmol) and CuI (0.38 mg, 0.002 mmol) were added to a diethylamine (75 mL) solution of complex **10** (250 mg, 0.038 mmol). After 24 h the solvent was evaporated and the red residue was extracted with Et_2O to give, after chromatography (silica gel, eluent CH_2Cl_2/*n*-hexane, 1:2), 240 mg of **11** (85%). Anal. Calcd for $C_{244}H_{426}O_{12}P_{12}Pt_{18}$: C, 39.4; H, 5,78. Found: C, 39.3; H, 5.9. ^{1}H NMR: δ 7.21 (s, Ar, 2 H), 7.19 (s, Ar, 6 H), 3.24 (s, CCH, 2 H), 2.80 (br m, ArCH_2, 16 H), 1.66 (br, CH_2 dodecyl, 32 H), 1.52 (vt, $^{3}J_{HP}+^{5}J_{HP} = 7$ Hz, 216 H), 1.29 (s, br, CH_2 dodecyl, 128 H), 0.89 ppm (t, CH_3 dodecyl, 24 H). $^{13}C\{^{1}H\}$ NMR: δ 217.0, 216.5 (CO), 142.1, 140.4, 139.7, 132.6, 131.7, 131.3, 129.7, 125.6 (Ar) 123.2 (*C*CPt), 122.1, 117.6 (Ar), 108.1, 103.7 (C*C*Pt), 83.9 (*C*CH), 80.1 (C*C*H), 44.0 (C, ^{t}Bu), 34.4, 32.3 (dodecyl), 31.9 (CH_3, ^{t}Bu), 30.7, 30.1, 30.0, 29.9, 29.7, 23.0, 14.5 ppm (dodecyl). $^{31}P\{^{1}H\}$ NMR: δ 339.3$^{\#}$ (s, 4 P), 333.0$^{\#}$ ppm (s, 8 P). $^{195}Pt\{^{1}H\}$ NMR: δ −2983 (m, 12 Pt), −4683 ppm (m, 6 Pt). IR (CH_2Cl_2): 3300 ($\nu_{C\equiv CH}$), 2091 ($\nu_{C\equiv C}$), 2010 cm^{-1} (ν_{CO}).

Preparation of I{[$Pt_6(\mu\text{-}PBu^{t}_2)_4(CO)_4$](CC−Ar−CC)}$_4$[$Pt_6(\mu\text{-}PBu^{t}_2)_4(CO)_4$]I (12). Complex **5** (201 mg, 0.027 mmol) and CuI (0.10 mg, 5.4×10^{-4} mmol) were added to a diethylamine (60 mL) solution of complex **6** (126 mg, 0.062 mmol). After 24 h stirring at room temperature, all the volatiles were removed in vacuo and the resulting red residue was extracted with Et_2O and chromatographed on silica gel (eluent CH_2Cl_2/*n*-hexane, 1:2), yielding 240 mg of **12** (78%). Anal. Calcd for $C_{316}H_{568}I_2O_{20}P_{20}Pt_{30}$: C, 33.25; H, 5.02. Found: C, 33.2; H, 5.1. ^{1}H NMR: δ 7.18 (s, br, Ar, 8 H), 2.80 (br m, ArCH_2, 16 H), 1.65 (br, CH_2 dodecyl, 32 H), 1.51 (vt, $^{3}J_{HP}+^{5}J_{HP} = 7$ Hz, 360 H), 1.28 (br s, CH_2 dodecyl, 128 H), 0.89 ppm (t, CH_3 dodecyl, 24 H). $^{13}C\{^{1}H\}$ NMR: δ 216.9, 215.6, 207.2 (CO), 139.7, 131.4, 125.6 (Ar) 123.1 (*C*CPt), 119.2 (Ar), 103.8 (C*C*Pt), 45.3, 44.2 (C, ^{t}Bu), 34.4, 32.6, 32.3 (dodecyl), 31.9 (CH_3, ^{t}Bu), 30.7, 30.1, 30.0, 29.7, 23.0, 14.5 ppm (dodecyl). $^{31}P\{^{1}H\}$ NMR: δ 335.9$^{\#}$ (s, 4 P), 333.0$^{\#}$ (s, 12 P), 329.7$^{\#}$ ppm (s, 4 P). $^{195}Pt\{^{1}H\}$ NMR: δ −2983 (m, 16 Pt), −3322 (m, 4 Pt), −4686 (m, 8 Pt), −4901 ppm (m, 2 Pt). IR (CH_2Cl_2): 2095 ($\nu_{C\equiv C}$), 2011 cm^{-1} (ν_{CO}).

Preparation of [OC{[$Pt_6(\mu\text{-}PBu^{t}_2)_4(CO)_4$](CC−Ar−CC)}$_4$[$Pt_6(\mu\text{-}PBu^{t}_2)_4(CO)_4$]CO]($PF_6$)$_2$ (13). $TlPF_6$ (70 mg, 0.200 mmol) was added to a THF (80 mL) solution of complex **12** (240 mg, 0.021 mmol). The flask was filled with CO (1 atm) and the reaction mixture stirred for 24 h at room temperature. The solvent was evaporated and the residue was washed with hexane and then dissolved in acetone. Filtration of the resulting red solution followed by solvent removal afforded complex **13** (170 mg, 70%). Anal. Calcd for $C_{318}H_{568}F_{12}O_{22}P_{22}Pt_{30}$: C, 33.2; H, 4.98. Found: C, 33.1; H, 4.9. ^{1}H NMR: δ 7.18 (br s, Ar, 8 H), 2.79 (br m, ArCH_2, 16 H), 1.66 (br, CH_2, dodecyl, 32 H), 1.51 (vt, $^{3}J_{HP}+^{5}J_{HP} = 7$ Hz, 360 H), 1.28 (br s, CH_2 dodecyl, 128 H), 0.89 ppm (t, CH_3 dodecyl, 24 H). $^{13}C\{^{1}H\}$ NMR: δ 218.7, 216.9, 216.7, 204.4 (CO), 139.7, 131.3, 126.6, 125.6, 124.4 (Ar) 123.1 122.7, 120.8 (*C*CPt), 119.1, 118.7 (Ar), 104.5, 103.8 (C*C*Pt), 46.1, 45.6, 44.0 (C, ^{t}Bu), 34.4, 32.2 (dodecyl), 31.9 (CH_3, ^{t}Bu), 30.7, 30.1, 30.0, 29.7, 23.0, 14.5 ppm (dodecyl). $^{31}P\{^{1}H\}$ NMR: δ 357.5.1$^{\#}$ (s, 4 P), 353.8$^{\#}$ (s, 4 P), 332.9$^{\#}$ (s, 12 P), −142.4 ppm (sept, $J_{PF} = 705$ Hz). $^{195}Pt\{^{1}H\}$ NMR: δ −2979 (m, 16 Pt), −3068 (m, 4 Pt), −4493 (m, 2 Pt), −4686 (m, 6 Pt), −4994 ppm (m, 2 Pt). IR (CH_2Cl_2): 2126 (vw) ($\nu_{C\equiv C}$), 2095 (sh), 2078 (w), 2056 (w), 2046 (w), 2031 (sh), 2011 (br, vs) cm^{-1} (ν_{CO}).

Preparation of Cl{[$Pt_6(\mu\text{-}PBu^{t}_2)_4(CO)_4$](CC−Ar−CC)}$_4$[$Pt_6(\mu\text{-}PBu^{t}_2)_4(CO)_4$]Cl (14). NH_4Cl (7 mg, 0.13 mmol) was added to a red solution of complex **13** (150 mg, 0.013 mmol) in acetone (10 mL). Addition of H_2O (5 mL) caused the precipitation of a red solid, which was filtered and chromatographed on silica gel (eluent CH_2Cl_2/*n*-hexane, 1:2), yielding 128 mg of **14** (88%). Anal. Calcd for $C_{316}H_{568}Cl_2O_{20}P_{20}Pt_{30}$: C, 33.8; H, 5.10. Found: C, 33.7; H, 5.2. ^{1}H NMR: δ 7.18 (br s, Ar, 8 H), 2.79 (br m, ArCH_2, 16 H), 1.64 (br, CH_2 dodecyl, 32 H), 1.51 (vt, $^{3}J_{HP}+^{5}J_{HP} = 7$ Hz, 360 H), 1.27 (br s, CH_2 dodecyl, 128 H), 0.89 ppm (t, CH_3 dodecyl, 24 H). $^{13}C\{^{1}H\}$ NMR: δ 216.9, 215.8, 204.7 (CO), 139.7, 131.3, 125.6 (Ar) 123.1 (*C*CPt), 119.2 (Ar), 103.7 (C*C*Pt), 44.9, 44.0 (C, ^{t}Bu), 34.4, 32.3 (dodecyl), 31.9 (CH_3, ^{t}Bu), 30.7, 30.1, 30.0, 29.7, 23.0, 14.5 ppm (dodecyl). $^{31}P\{^{1}H\}$ NMR: δ 336.1$^{\#}$ (s, 4 P), 333.0$^{\#}$ (s, 12 P), 325.7$^{\#}$ ppm (s, 4 P). $^{195}Pt\{^{1}H\}$ NMR: δ −2979 (m, 12 Pt), −3039 (m, 4 Pt), −3426 (m, 4 Pt), −4119 (m, 2 Pt), −4684 ppm (m, 8 Pt). IR (CH_2Cl_2): 2096 ($\nu_{C\equiv C}$), 2012 cm^{-1} (ν_{CO}).

Preparation of HCC−Ar−CC {[$Pt_6(\mu\text{-}PBu^{t}_2)_4(CO)_4$](CC−Ar−CC)}$_4$[$Pt_6(\mu\text{-}PBu^{t}_2)_4(CO)_4$]CC−Ar−CCH (15). 1,4-Didodecyl-2,5-diethynylbenzene (13 mg, 0.028 mmol) and CuI (0.03 mg, 1.8×10^{-4} mmol) were added to a diethylamine (50 mL) solution of complex **14** (101 mg, 0.009 mmol). After 24 h the solvent was evaporated and the red residue was extracted with Et_2O to give, after chromatography (silica gel, eluent CH_2Cl_2/*n*-hexane, 1:2), 88 mg of **15** (81%). Anal. Calcd for $C_{384}H_{674}O_{20}P_{20}Pt_{30}$: C, 38.2; H, 5.62. Found: C, 38.1; H, 5.7 ^{1}H NMR: δ 7.20 (s, Ar, 2 H), 7.18 (s, Ar, 10 H), 3.23 (s, CCH, 2 H) 2.79 (br m, ArCH_2, 24 H), 1.66 (br, CH_2 dodecyl, 48 H), 1.51 (vt, $^{3}J_{HP}+^{5}J_{HP} = 7$ Hz, 360 H), 1.28 (br s, CH_2 dodecyl, 192 H), 0.89 ppm (t, CH_3 dodecyl, 36 H). $^{13}C\{^{1}H\}$ NMR: δ 216.9, 216.5 (CO), 142.1, 140.4, 139.7, 132.6, 131.7, 131.3, 129.7, 125.6 (Ar) 123.1 (*C*CPt), 119.1, 117.7 (Ar), 103.7 (C*C*Pt), 83.9 (*C*CH), 80.1 (C*C*H), 44.0 (C, ^{t}Bu), 34.4, 32.3 (dodecyl), 31.9 (CH_3, ^{t}Bu), 30.7, 30.1, 30.2, 29.7, 23.0, 14.5 ppm (dodecyl). $^{31}P\{^{1}H\}$ NMR: δ 333.9.1$^{\#}$ (s, 4 P), 333.0$^{\#}$ ppm (s, 16 P). $^{195}Pt\{^{1}H\}$ NMR: δ −2979 (m, 20 Pt), −4684 ppm (m, 10 Pt). IR (CH_2Cl_2): 3299 ($\nu_{C\equiv CH}$), 2092 ($\nu_{C\equiv C}$), 2010 cm^{-1} (ν_{CO}).

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