Synthesis and characterization of non-bridging mono- and bis-σ-η1-alkynyl derivatives of the phosphido-bridged hexaplatinum core $[Pt_6(\mu\text{-}PBut_2)_4(CO)_4]^{2+}$

Veronica Bonuccelli, Tiziana Funaioli,* Piero Leoni,* Fabio Marchetti, Lorella Marchetti and Marco Pasquali

Several mono- or bis-alkynyl derivatives of general formula $Pt_6(\mu\text{-}PBut_2)_4(CO)_4X(CuC–R)$, $Pt_6(\mu\text{-}PBut_2)_4(CO)_4(CuC–R)_2$ or $Pt_6(\mu\text{-}PBut_2)_4(CO)_4(CuC–R)(CuC–R')$ were obtained under Sonogashira type conditions. The new clusters have been characterized with microanalysis and using IR and multinuclear NMR spectroscopy. The crystal and molecular structures of $Pt_6(\mu\text{-}PBut_2)_4(CO)_4(CuC–R)_2$ (R = H, C_6H_4-4-n-C_5H_{11}) are presented and electrochemical and spectroelectrochemical studies of some representative compounds are also reported.

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Giuseppe Moruzzi 13, I-56124 Pisa, Italy.

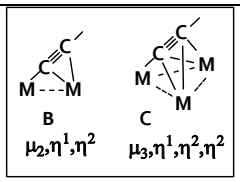
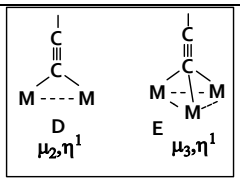
Introduction

Transition metal alkynyl complexes[1] are attracting considerable interest for their versatility as intermediates for organometallic and supramolecular synthesis, and have a great potential as precursors of non-linear optical[2] or luminescent materials,[3] of antitumoral drugs[4] or as metal containing oligo- or polymeric compounds with remarkable redox, magnetic, optical and electronic properties.[5] The about four thousand structures presently deposited with the Cambridge Crystallographic Data Centre[6] show a rich structural diversity. The σ,η^1- terminal bonding mode (**A** in Table 1) is the unique observed in mononuclear complexes and is still frequent in non-metal-metal-bonded dinuclear (72%) and polynuclear (56%) derivatives, especially when the metal centres are compelled by bridging ligands to lie far from each other. As metals approach one another, terminal bonding becomes less frequent and drops off from 55%, in metal-metal-bonded dinuclear complexes, to 22% in polynuclear derivatives having a linear or branched acyclic M_n chain. Actually, terminal alkynyls are notably rare (3%)[7,8] in triangular, square or polyhedral clusters, being limited to cases in which a remarkable steric congestion prevents the simultaneous interaction of the alkynyl ligand with two or more metal centres. Concurrently, different types of bridging modes acquire importance. In these cases, the alkynyl ligand interacts with two or three metal atoms either in a σ-η^1 fashion (modes **D**/**E** in Table1, less frequent)[9] or, more commonly, by the σ,π-coordination modes **B** or **C**,[10] in which one or two π,η^2-metal-alkynyl contributions add to the omnipresent σ bond. It is worth noting that **B**/**D** and **C**/**E** modes can be related by equilibria whose dependence on stereoelectronic effects has been investigated either experimentally and theoretically.[11] Other bonding modes, in which the metal bridges four or more metal centres, are far less represented.[12]

We have already shown[13] that hexanuclear clusters of general formula $[Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4L_nX_{2-n}]^{n+}$, sterically protected by the bulky bridging phosphides, have a thermally and chemically stable $[Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4]^{2+}$ core (hereafter shortly represented by the notation {Pt_6}) and two reactive positions located at the two opposite extremes of the major longitudinal molecular axis. These are useful pre-requisites for the construction of ordered covalent structures containing {Pt_6} subunits connected to each other, or to other cluster units, by bis- or tris-alkynyl spacers.[8b,c,14]

Actually, the addition of alkynyl ligands to the {Pt_6} unit is rather straightforward. For example, the unsymmetrical hexanuclear cluster {Pt_6}ClI, (**1**),[13] and the symmetrical dichloride {Pt_6}Cl_2, (**2**),[8b,c,13-14] react with terminal alkynes under Sonogashira-type conditions (catalyst: 1% CuI *per* terminal alkyne, solvent: NEt_2H or NEt_2H/CH_2Cl_2 mixtures) to give the corresponding {Pt_6}(CC–R)I or {Pt_6}$(CC–R)_2$ clusters, respectively in high yields and good purity, with the alkynyl function(s) invariably bonded in a terminal σ,η^1-fashion.[8b,c,14] Herein we describe the synthesis of several mono-alkynyl or bis-alkynyl derivatives of the {Pt_6} core bearing different functional substituents in the alkynyl ligands and their cyclovoltammetric and IR-spectroelectrochemical profiles.

Table 1. Approximate number of structures of transition metal alkynyl derivatives deposited at May 2015 with the Cambridge Crystallographic Data Centre.

Nuclearity	MM Bonds	A	B + C	D + E	Total
		M–C≡C– A η^1	 B μ_2,η^1,η^2 C $\mu_3,\eta^1,\eta^2,\eta^2$	 D μ_2,η^1 E μ_3,η^1	

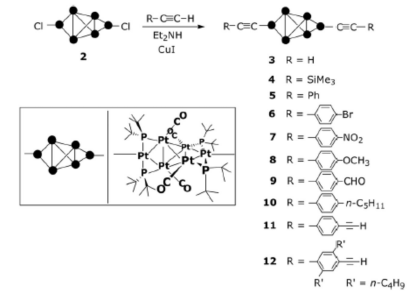
1-Mononuclear	-	1660 (100%)	-	-	1660
2- Dinuclear	No	770 (72%)	240 (22%)	60 (6%)	1070
3- Polynuclear	No	235 (56%)	143 (34%)	42 (10%)	420
Subtotals (1-3)		2665 (85%)	383 (12%)	102 (3%)	3150
4- Dinuclear	Yes (any order)	120 (55%)	80 (36%)	20 (9%)	220
5-Polynuclear [a]	Yes (any order)	31 (22%)	82 (59%)	27 (19%)	140
6-Polynuclear [b]	Yes (any order)	21 (3%)	521 (77%)	138 (20%)	680
Subtotals (4-6)		172 (16%)	683 (66%)	185 (18%)	1040
Totals (1-6)		2837 (68%)	1066 (25%)	287 (7%)	4190

[a] Linear or branched acyclic M_n networks; [b] Cyclic or polyhedral M_n networks

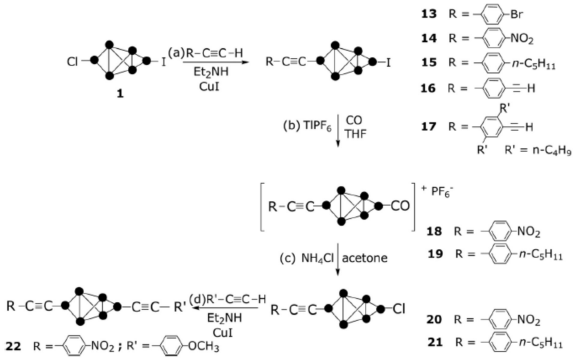
Results and Discussion

As shown in Scheme 1, the symmetrical bis-alkynyl derivatives $\{Pt_6\}(C{\equiv}C{-}R)_2$ [R = H (**3**), $SiMe_3$ (**4**), C_6H_5 (**5**),[8c] C_6H_4-4-X (X = Br (**6**), NO_2 (**7**), OCH_3 (**8**), CHO (**9**), *n*-C_5H_{11} (**10**), C≡CH (**11**)[8c]) and R = C_6H_2-2,5-di-*n*-butyl-4-C≡CH (**12**)] were obtained by dehydrohalogenation from mixtures of the proper terminal alkyne and cluster **2** in 2:1 molar ratio, according to an adaptation of the Sonogashira coupling route.

The synthesis of the corresponding mono-chloro, mono-alkynyl derivatives was first attempted by applying the same procedure to 1:1 mixtures of **2** and the terminal alkyne. However this approach gave the desired products in mixture with the bis-alkynyl derivatives and cluster **2**. The Pt–I bond in the asymmetrically substituted chloro-iodo derivative **1** proved to be much more resistant to dehydrohalogenation, and, therefore, high yields of the pure monosubstituted products $\{Pt_6\}I(C{\equiv}C{-}R)$ [R = C_6H_4-4-X (X = Br (**13**), NO_2 (**14**), *n*-C_5H_{11} (**15**), C≡CH (**16**)) and R = C_6H_2-2,5-di-*n*-butyl-4-C≡CH (**17**)] were obtained by employing **1** in place of cluster **2** as the precursor (Scheme 2).



Scheme 1 Synthesis of symmetrical bis-alkynyl derivatives **3**–**12**.



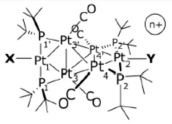
Scheme 2 Synthesis of the mono-alkynyl derivatives **13**–**17** and **18**–**21** and of the unsymmetrical bis-alkynyl clusters **22**–**23**.

The reactive Pt–Cl bond can be restored from the intermediate iodo-alkynyl derivatives in two steps (I^-/CO substitution assisted by Tl^+, followed by reaction with ammonium chloride). By applying this sequence to clusters **14** and **15**, we obtained the corresponding chlorides **20** and **21** in good overall yields (95 and 93% respectively)

Spectra

Significant IR and NMR parameters for clusters **3**-**23**, and for some reference compound, are shown in Table 2. The IR ν_{CO} absorptions for the neutral mono- and dialkynyl derivatives were all found at *ca.* 2010 cm^{-1}, very close to the corresponding absorptions of the dihalides $\{Pt_6\}XX'$ [X = X' = Cl (**2**), Br, I and X = Cl, X' = I (**1**); 2017-2018 cm^{-1}],[13] despite the different donor-acceptor properties of the alkynyl substituents. Although chloro and some alkynyl ligands have similar donor properties and, occasionally, the substitution of the former by the latter has been found to exert a small influence on redox potentials[15] the marginal effect on ν_{CO} of large modifications of the properties of the alkynyl substituents could appear quite surprising. Actually, we recall that the value of ν_{CO} in neutral $\{Pt_6\}XX'$ derivatives is comprised in only **16** (2006-2022) cm^{-1} when the properties of X/X' are varied even more considerably (X/X' = halides, alkynyls, CHO, COOR, CN, SCN, NCO, N_3, OTf, BF_4, OTs, OOCR),[13,14,16] and that significant shifts (to higher wavenumbers) have only been observed on passing to the cationic systems $[\{Pt_6\}XL]^+$ or $[\{Pt_6\}L_2]^{2+}$ (see below), probably due to charge effects. In our opinion this behaviour is justified by the peculiar features of these clusters, i. e., by the limited electronic communication, ascertained by an electrochemical study on $\{Pt_6\}(CC\text{-}Fc)_2$,[8d] between the inner tetrahedral Pt_4 unit, that binds the carbonyl ligands, and the apical platinum centers, coordinated to the X/X' (or L) moieties.

Table 2 Significant IR [ν, cm^{-1}] and NMR [δ, ppm] parameters for clusters **3–23** and for some reference compounds



Cluster	$\delta(Pt_1)$	$\delta(Pt_2)$	$\delta(Pt_3)$	$\delta(Pt_4)$	$\delta(P_1)$	$\delta(P_2)$	$\delta(H)$	ν_{CO}	ν_{CC}	Ref.
X = Y = CO, *n* = 2	−4960	−4960	−3203	−3203	383.7	383.7	1.47vt (8.0)	2089, 2056	—	13
X = CO, Y = Cl, *n* = 1	−5012	−3928	−3112	−3516	360.5	348.4	1.54vt (7.6)	2080, 2059, 2047, 2036, 2025	—	13
X = Y = I, *n* = 0	−4933	−4933	−3352	−3352	333.2	333.2	1.50vt (7.4)	2017	—	13
1 X = I, Y = Cl, *n* = 0	−4938	−4149	−3354	−3452	333.4	328.8	1.52vt (7.5)	2017	—	13
2 X = Y = Cl, *n* = 0	−4153	−4153	−3463	−3463	328.9	328.9	1.51vt (7.2)	2017	—	13
3 X = Y = CC-H, *n* = 0	−4685	−4685	−2291	−2291	334.7	334.7	1.46vt (7.7)	2014	1969	—
4 X = Y = CC-SiMe$_3$, *n* = 0	−4672	−4672	−2975	−2975	333.5	333.5	1.46vt (6.9)	2016	1977	—
5 X = Y = CC-Ph, *n* = 0	−4678	−4678	−2293	−2293	334.9	334.9	1.48vt (7.3)	2011	2106	—
6 X = Y = CC-C_6H_4Br, *n* = 0	−4691	−4691	−3000	−3000	337.1	337.1	1.49vt (7.6)	2012	2107	—
7 X = Y = CC-$C_6H_4NO_2$, *n* = 0	−4678	−4678	−3006	−3006	337.2	337.2	1.51vt (7.5)	2014	2099	—
8 X = Y = CC-$C_6H_4OCH_3$, *n* = 0	−4671	−4671	−3004	−3004	335.4	335.4	1.52vt (7.2)	2010	2107	—
9 X = Y = CC-C_6H_4CHO, *n* = 0	−4664	−4664	−2998	−2998	336.2	336.2	1.48vt (7.1)	2014	2101	—
10 X = Y = CC-C_6H_4-*n*-C_5H_{11}, *n* = 0	−4688	−4688	−2293	−2293	334.9	334.9	1.48vt (7.3)	2012	2106	—
11 X = Y = CC-C_6H_4-CC-H, *n* = 0	−4677	−4677	−3001	−3001	337.2	337.2	1.49vt (7.3)	2011	2100	—
12 X = Y = CC-$C_6H_2R_2$-CC-H, *n* = 0	−4691	−4691	−2987	−2987	334.5	334.5	1.51vt (6.9)	2010	2090	—
13 X = I; Y = CC-C_6H_4Br, *n* = 0	−4891	−4697	−3302	−3046	331.3	336.8	1.49vt (7.6), 1.55vt (7.6)	2014	2108	—
14 X = I; Y = CC-$C_6H_4NO_2$, *n* = 0	−4885	−4709	−3353	−3015	332.5	337.4	1.50vt (7.1)	2011	2102	—
15 X = I; Y = CC-C_6H_4-*n*-C_5H_{11}, *n* = 0	−4899	−4683	−3323	−3040	330.5	336.7	1.52vt (7.4)	2009	2107	—
16 X = I; Y = CC-C_6H_4-CC-H, *n* = 0	−4891	−4697	−3325	−3052	333.3	338.9	1.50vt (7.6)	2010	2099	—
17 X = I; Y = CC-$C_6H_2R_2$-CC-H, *n* = 0	−4895	−4761	−3321	−3028	331.0	336.3	1.49vt (7.3)	2014	2093	—
18 X = CO; Y = CC-$C_6H_4NO_2$, *n* = 0	−4996	−4543	−3092	−3092	364.7	357.0	1.56vt (8.0)	2076, 2064, 2044, 2033, 2016	2105	—
19 X = CO; Y = CC-C_6H_4-*n*-C_5H_{11}, *n* = 0	−4794	−4065	−3495	−3088	357.7	354.8	1.51vt (7.3)	2074, 2052, 2037, 2018, 2010	2086	—
20 X = Cl; Y = CC-$C_6H_4NO_2$, *n* = 0	−4100	−4712	−3430	−3044	330.2	339.5	1.53vt (7.5)	2013	2103	—
21 X = Cl; Y = CC-C_6H_4-*n*-C_5H_{11}, *n* = 0	−4116	−4688	−3426	−3048	326.1	336.7	1.52vt (7.4)	2006	2108	—
22 X = CC-$C_6H_4NO_2$; Y = CC-$C_6H_4OCH_3$, *n* = 0	−4691	−4655	−3003	−3003	335.9	335.0	1.51vt (7.3), 1.53vt (7.2)	2013	2101	—
23 X = CC-C_6H_4-*n*-C_5H_{11}; Y = CC-C_6H_4CHO, *n* = 0	−4672	−4672	−2998	−2998	334.2	335.5	1.50vt (7.2)	2010	2101	—

For the high local symmetry (D_{2d}) of the central core, only one carbonyl absorption (ν_{as}) was observed in the IR spectra of the symmetrical bis-alkynyls (and bis-halides) $\{Pt_6\}X_2$. Apparently, and as already observed for the chloro-iodo derivative **1**, the reduction of symmetry (C_{2v}), occurring when the two ligands in the apical positions are different, has little effect on the spectra of the neutral unsymmetrical bis-alkynyls **22**-**23** or of the halo-mono-alkynyls **13**-**17** or **20**-**21**, which still show a single carbonyl absorption, although slightly broadened, centered close to 2010 cm^{-1}. However, when the two apical substituent are substantially different, as happens in the cationic carbonyl-alkynyl derivatives **18**-**19**, five carbonyl absorptions appear in the region 2080-2010 cm^{-1}. The one at higher wavenumbers (*ca* 2080 cm^{-1}) can unquestionably be assigned to the additional apical carbonyl ligand (the hexacarbonyl dication $\{Pt_6\}(CO)_2^{2+}$ exhibits one absorption at 2089 cm^{-1}, conclusively assigned to the two apical carbonyls,[16b] and one at 2056 cm^{-1} for the inner four CO ligands). Two of the remaining four absorptions (2035-2065 cm^{-1}) can reasonably be assigned to ν_{as} and ν_s of the two inner carbonyls lying closer to the apical carbonyl and the other two (2010-2035 cm^{-1}) to ν_{as} and ν_s of the other two inner carbonyls; similar assignments can be made for the five absorptions found in the chloro-carbonyl cation $\{Pt_6\}Cl(CO)^+$.[17] The ν_{CC} absorptions were found at *ca.* 1970 (complexes **3** and **4**), or 2100 cm^{-1} (complexes **5**-**23**), in the regions observed for the σ,η^1-alkynyl platinum complexes known in literature.[7,8,14,16,18]

The $^{31}P\{^1H\}$ NMR spectra of the symmetrical bis-alkynyl derivatives 3-12 show the expected singlet, due to the four equivalent phosphorus atoms, at *ca.* 335 ppm.[8c-d,13,14,16,17] The central singlet is flanked by satellites due to the coupling with the NMR active ^{195}Pt nuclei (I = ½, isotopic abundance 33.8%) and arising from the subspectra due to the presence of 64 non-equivalent isotopologues.[8c-d,13,17] The main features of the complex shape of the signal remain constant and may be taken as fingerprints of the hexanuclear $\{Pt_6\}XX'$ cluster's structure. The $^{31}P\{^1H\}$ NMR spectra of the unsymmetrical derivatives exhibit two analogous signals of equal intensity; in the halo-alkynyl compounds the singlet due to the two equivalent P atoms close to the alkynyl ligand is found at *ca.* 337 ppm and the other at *ca.* 330 ppm. In the cationic compounds **18** and **19** we noticed a low-field shift of the values of $\delta(P)$ due to the increase of the positive charge [$\delta(P_1)$ = 364.7 and 357.7 ppm and $\delta(P_2)$ = 357.0 and 354.8 ppm, respectively]. $^{195}Pt\{^1H\}$NMR spectra contain the characteristic resonances observed for other apically substituted $\{Pt_6\}XX'$ derivatives,[8c-d,13,17] which were assigned to the two apical centers [−4996 ÷ −4065 ppm] and to the four internal platinum atoms [−3426 ÷ −2291 ppm]. Also in this case, due to equivalence, the symmetrical derivatives show only two multiplets, each split in two in the spectra of the unsymmetrical clusters. The ^1H and the $^{13}C\{^1H\}$ NMR spectra of all the compounds show the expected signals for the *t*-butyls of the $\{Pt_6\}$ core,[8c-d,13,17] together with signals typical of the different alkynyl ligands (see experimental), in full agreement with the supposed structures.

Electrochemistry of 5, 7-10 and 22.

The dication $[\{Pt_6\}(CO)_2]^{2+}$,[16b,17] with two easily displaceable carbonyl ligands bonded to the apical platinum centers, is the precursor of the entire class of dibridged tetrahedral clusters sharing the $\{Pt_6\}$ core prepared in our labs.[8c-d,13,14,16,17] Its CV profile exhibits two reversible monoelectronic reduction waves (−0.27, −0.54 V) that typify the redox fingerprint of this

class of clusters[8d,13,16a,17] and, in addition, also undergoes a partially chemically reversible bielectronic reduction at more negative potentials (−1.72 V).[17] The substitution of the apical carbonyls with halides or pseudohalides shifts cathodically all the redox processes due to the decreasing positive charge. For example, for the monocationic cluster $[\{Pt_6\}(CO)Cl]^+$ and the neutral dihalide **2**, the bielectronic reduction at very low potentials is no longer detectable,[13] the reversible reductions were respectively observed at −0.84, −1.14 V and −1.38, −1.60 V, and an irreversible bielectronic oxidation appears at +1.65 and +1.30 V, respectively. As detailed below, similar cathodic shifts can be observed in the electrochemical analysis of selected examples of the bis-arylalkynyl derivatives prepared in this work. Formal electrode potentials for the redox processes exhibited by $\{Pt_6\}(C{\equiv}C{-}C_6H_4\text{-}4\text{-}R)(C{\equiv}C{-}C_6H_4\text{-}4\text{-}R')$ [R = R' = H (**5**),[8d] NO_2 (**7**), OCH_3 (**8**), CHO (**9**), *n*-C_5H_{11} (**10**) and R = NO_2, R' = OCH_3 (**22**)], and by reference compounds,[13] are summarized in Table 3; the CV profiles of some selected compounds (**5**, **7** and **8)** are shown in Figure 1. All dialkynyl clusters show the expected processes centered on the cluster unit, *i. e.*: two monoelectronic reductions ($E°_3$ from −1.36 to −1.55 and $E°_2$ from −1.49 to −1.69 V *vs* SCE, respectively) and one bielectronic oxidation process ($E°_5$ from +0.93 to +1.18 V). In comparison to the corresponding processes of the dichloro derivative **2**, the oxidation waves ($E°_5$) and at least the first ($E°_3$) cluster-centered reduction (with the exception of the electron-poor **9**) are catodically shifted. On the CV time scale, the two reductions are reversible and the oxidation is irreversible. A further reversible process ($E°_4$, i_c/i_a = 1 at 0.1 V·s^{-1}) at *ca.* −1.20 V, due to the reduction of the nitro group, was observed in the voltammograms of clusters **7** (bielectronic) and **22** (monoelectronic process).

These values are at *ca.* 120 mV more negative potentials compared to the one measured in the same conditions for *p*-nitrophenyl-trimethylsilylethyne ($E° = -1.08$ V), since coordination to the platinum cluster increases the electron density on the arylalkynyl ligand.[19]

As expected, by increasing the electron-donating ability of the *para*-substituent, we observed a cathodic shift of the oxidation potentials (+1.19, for **9** (R = CHO), +1.18 for **7** (R = NO_2),+1.09 for **5** (R = H), +1,06 for **10** (R = C_5H_{11}), +0.95 for **22** (R = OCH_3; R' = NO_2) and +0.93 V for **8** (R = OCH_3)) with a total $\Delta E°$ gap of +260 mV between the more electron poor **9** and the more electron rich **8**.

Large/very large ($\Delta E° > 400$mV),[20] medium/large ($400 > \Delta E° \geq 200$ mV)[21] or medium/very small ($200 > \Delta E° \geq 0$ mV)[22] differences between the oxidation potentials of mononuclear complexes containing *p*-nitro- and *p*-methoxy-phenylethynyl ligands have been observed and have been related to the alkynyl character of the metal centered HOMO.[20a,b,22a] Thus, the HOMO of neutral $\{Pt_6\}XX'$ dialkynyl clusters is probably localized on the apical Pt centers and is significantly delocalized on the alkynyl ligand. It is also worth noting that **22** is oxidated at a potential (+0.95 V) much closer to that of cluster **8** (+20 mV) than to the one of **7** (−230 mV) which implies that the HOMO reasonably lies on the Pt-CC-C_6H_4-4-OCH_3 moiety and is practically insensitive to the presence of the *p*-nitrophenylethynyl ligand on the other side of the molecule. This is a further indirect evidence of the above-mentioned lack of communication between the central Pt_4 tetrahedron and the apical Pt centers, already observed and studied in more detail in the bis-ferrocenyl derivative $\{Pt_6\}(C{\equiv}C{-}Fc)_2$,[8d] and also assessed by a theoretical study on $[\{Pt_6\}(CO)_2]^{2+}$, in which, however, the HOMO was found to be strictly confined on the central Pt_4 unit.[17] As far as the reduction processes are concerned, while compounds **8** and **10**, with two electron-donor methoxy or alkyl groups, show the expected cathodic shift when compared to the unsubstituted cluster **5**, compounds **7** and **22** also show a cathodic shift, *in spite of* the presence of electron-withdrawing nitro groups.

The apparent incongruity arises from the reduction of the nitro groups, occurring at *ca.* −1.20 V, *prior* to the reduction of the cluster unit. This increases the negative charge of the compounds and drives the subsequent reductions to more cathodic potentials. Therefore, two conflicting contributions cancel each other in clusters **7** and **22**, and their values of $E°_2$ and $E°_3$ are accidentally very similar to those of **8**. It is worth noting that the simultaneous reduction of both the nitro groups in **7** further confirms the absence of electronic communication between the two apical ligands, evidently related to the above-mentioned lack of communication between the central tetrahedral unit and the apical platinum centres. As expected, cluster **9**, which contains non reducible electron-withdrawing formyls in place of nitro groups on the alkynyl ligands, exhibits reduction potentials anodically shifted in comparison to either **5** or **7**

Table 3 Formal electrode potentials (V *vs.* SCE) and peak-to-peak separations (mV) for the redox processes exhibited by selected bis-alkynyl derivatives of the $\{Pt_6\}$ unit

	Reduction								Oxidation
	$E°_1$ [a]	ΔE_{p1} [b]	$E°_2$ [a]	ΔE_{p2} [b]	$E°_3$ [a]	ΔE_{p3} [b]	$E°_4$ [a]	ΔE_{p4} [b]	$E°_5$ [a,c]
$[\{Pt_6\}(CO)_2]^{2+}$ (ref. 17)	−1.73	88	−0.54	60	−0.27	58	—	—	—
$[\{Pt_6\}(CO)Cl]^+$ (ref. 16*a*)	—	—	−1.14	88	−0.84	78			+1.65
2[16a]	—	—	−1.60	94	−1.38	60	—	—	+1.30
5	—	—	−1.53	84	−1.42	74	—	—	+1.09
7	—	—	−1.69	110	−1.55	86	−1.21[a,d]	83	+1.18
8	—	—	−1.66	92	−1.52	90	—	—	+0.93
9	—	—	−1.49	85	−1.36	74	—	—	+1.19
10	—	—	−1.57	85	−1.44	85	—	—	+1.06
22	—	—	−1.69	105	−1.53	95	−1.20[a,d]	85	+0.95

[a] Measured in V *vs.* SCE, at 0.1 V s^{-1} in CH_2Cl_2 solution. [b] Measured in mV. [c] Peak potential value for irreversible processes. [d] $E°$ = −1.08 V for *p*-nitrophenyl-trimethylsilylethyne.

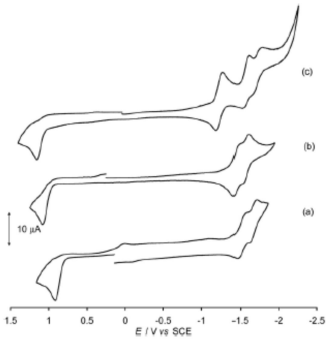


Fig. 1 Cyclic voltammograms recorded at a platinum electrode in CH_2Cl_2 solutions of (a) **8**, (b) **5** and (c) **7**. [^{n}Bu$_4$N]PF$_6$ (0.2 mol dm^{-3}) as supporting electrolyte. Scan rate: 0.1 V s^{-1}.

IR Spectroelectrochemistry

The hexanuclear clusters prepared in this and in our previous studies appear as ideal candidates for IR spectroelectrochemical analyses, due to their rich electrochemistry and to the presence of carbonyl ligands acting as strong IR chromophores. The reduction processes of compounds **5**, **7**-**10** and **22,** reversibile in the ciclovoltammetric time scale, were therefore investigated by this technique in CH_2Cl_2 solutions, using [^{n}Bu$_4$N]PF$_6$ (0.2 M) as the supporting electrolyte. The potential of the working electrode of an OTTLE cell[23] was lowered at the scan rate of 0.5 mV s^{-1} and a sequence of vibrational spectra was collected at constant time intervals during the reduction processes.

All these complexes show one ν_{CO} and one $\nu_{C\equiv C}$ absorption, respectively close to 2010 and 2100 cm^{-1}. As expected, on lowering the applied potential, both absorptions were gradually replaced by new bands at lower frequencies. Well-defined isosbestic points were observed in the case of cluster **10** for the time required for the complete reduction, during which the absorptions at 2012 and 2106 cm^{-1} downshift respectively at 1993 and 2088 cm^{-1} (Table 4), thus suggesting the formation of the monoreduced product **10**$^-$ (Figure 2a).

The stability of the electrogenerated **10**$^-$ on the time scale of the spectroelectrochemistry allowed the quasi-complete recovery of the starting compound **10** in the backward oxidation. The spectral changes observable during the reduction of compound **9** are shown in Figure 2b: well-defined isosbestic point are maintained while the bands at 2101 and 2014 cm^{-1} are gradually replaced by two new peacks at lower frequencies (2080 and 1994 cm^{-1}), but the reduction product **9**$^-$ is less stable than **10**$^-$ and only a small amount of cluster **9** was obtained in the backward oxidation step.

Upon the first monoelectronic reduction, the ν_{CO} (2010 cm^{-1}) and $\nu_{C\equiv C}$ (2107 cm^{-1}) absorptions exhibited by cluster **8** were replaced by new bands at lower frequencies (ν = 1992 and 2093 cm^{-1}, respectively, Figure 3). During this process, well-defined isosbestic points were observed for the time required for the quasi-complete reduction of **8**, suggesting the initial formation of the monoreduced product **8**$^-$**.**

Table 4 IR data of **5**, **7**–**10** and their reduction products

	5	**5**$^-$	**8**	**8**$^-$	**9**	**9**$^-$	**10**	**10**$^-$
ν_{CO}/cm^{-1}	2011	1991	2010	1992	2014	1994	2012	1993
$\nu_{C\equiv C}$/cm^{-1}	2106	2087	2107	2093	2101	2080	2106	2088

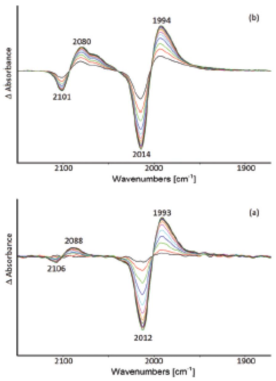


Fig. 2 IR spectral changes recorded in an OTTLE cell during the progressive reduction of (a) **10** and (b) **9** in CH_2Cl_2 solution containing [^{n}Bu$_4$N]PF$_6$ (0.2 M) as supporting electrolyte. A reference spectrum, collected before the application of a reduction potential, is used to calculate the differential absorbance spectra.

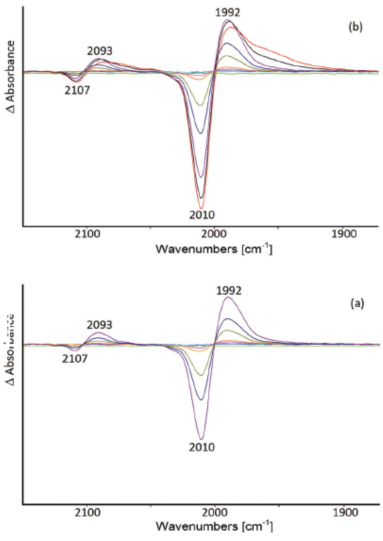


Fig. 3 IR spectral changes recorded in an OTTLE cell during the progressive one-electron reduction of **8** in CH_2Cl_2 solution containing [^{n}Bu$_4$N]PF$_6$ (0.2 M) as supporting electrolyte: (a) before and (b) after the beginning of the decomposition of the reduced cluster. A reference spectrum, collected before the application of a reduction potential, is used to calculate the differential absorbance spectra.

Unfortunately, before the complete consumption of **8** the bands assigned to $\mathbf{8}^{-}$ start to decrease, while a new shoulder starts growing at 1970 cm^{-1}, thus suggesting the formation of unidentified decomposition products. The instability of $\mathbf{8}^{-}$ on the time scale of the spectroelectroche-mistry was confirmed by the trace recovery of the starting compound **8** in the backward oxidation. Similar redox behaviour was found for cluster **5**: its ν_{CO} and $\nu_{C\equiv C}$ absorptions at 2011 and 2106 cm^{-1} are isosbestically replaced upon reduction by those at 1991 and 2087 cm^{-1}, which can be attributed to the reduced species $\mathbf{5}^{-}$, but the starting compound **5** was not restored in the backward oxidation.

The IR spectral changes during the reduction of **7** and **22** are complicated by the presence of the nitro groups, which, as mentioned above, are reduced before the cluster unit. The starting spectrum of **7** shows ν_{CO} (2014), $\nu_{C\equiv C}$ (2099 cm^{-1}) and two ν_{NO2} absorptions at 1585 and 1336 cm^{-1}. Reduction of both nitro groups at −1.21 V increases the negative charge of the compound and the carbonyl band is gradually shifted to 2010 cm^{-1}. (Figure 4) A similar behavior was expected for the $\nu_{C\equiv C}$ absorption at 2099 cm^{-1}, which, however, simply decreases in intensity, without noticeable shift (Figure 4).

This could be due to the decrease of the electron withdrawing aptitude of the nitro groups after their reduction. In fact, a decrease of intensity of the $\nu_{C\equiv C}$ band was observed upon increasing the donor strength of the R groups in the $\{Pt_6\}(C\equiv C–C_6H_4\text{-}4\text{-}R)_2$ series.[24] Other spectral changes observed in this step concern the ν_{NO_2} absorptions at 1586 and 1335 cm^{-1}, that are replaced by a new very weak band at 1360 cm^{-1} (Figure 4).[25] The lack of reversibility of the process in the backward oxidation suggested that the reduction of the nitro groups is complicated by a subsequent reaction to unidentified products in the time scale of the IR experiments.[26] This precluded further studies on the cluster unit reduction.

The unsymmetrical cluster **22**, with one nitro and one methoxy group, mirrors the behavior described above for **7**: after the monoelectronic reduction centered on the nitro group, the $\nu_{C\equiv C}$ band of the precursor at 2101 cm^{-1} decreases, while the carbonyl absorption at 2013 cm^{-1} is shifted to 2011 cm^{-1} and the absorptions at 1586 and 1335 cm^{-1} (ν_{NO2}) are gradually replaced by a new very weak band at ca. 1360 cm^{-1}. The reduced cluster is not stable on the spectroelectrochemical time scale and the restoration of the starting compound **22** is not achieved after the reverse cycle.

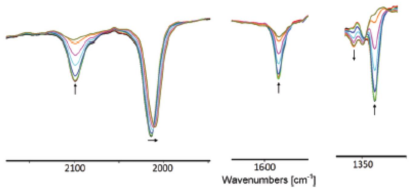


Fig. 4 IR spectral changes recorded in an OTTLE cell during the progressive two-electron reduction of **7** in CH_2Cl_2 solution containing $[^nBu_4N]PF_6$ (0.2 M) as supporting electrolyte. The absorption of the solvent and the supporting electrolyte have been subtracted.

Crystal and Molecular Structures of 3 and 10

Single crystals of **3** and **10** suitable for crystallographic studies were obtained by layering acetone on CH_2Cl_2 solutions of the clusters. ORTEP projections of the molecular structures are shown in Figures 5 and 6 and significant parameters are summarized in Table 5 and Table 6. Cluster **3** shows the symmetry of the tetragonal bisphenoid $\bar{4}2m$ (D_{2d}, in the Schönflies notation) as already found for the bis-pseudohalide derivatives $\{Pt_6\}(X)_2$ [X = CN, SCN, NCO].[16a] The pseudo-tetrahedral core has two short equivalent edges, Pt(2)–Pt(2') and Pt(2'')–Pt(2''') (2.6753 Å) in the Figure 5, and four equivalent long edges (2.8563 Å).

The apical Pt atoms show four equivalent distances from the Pt atoms of the short edges of the bisphenoid, which are intermediate among the two above (2.7352 Å). Due to the length (12 Å about) and to the flexibility of the apical 4-n-pentylphenylethyne ligands, the cluster **10** is induced to crystallize in a C2/*c* space group and the metal core do not shows an exact bisphenoidal symmetry like cluster **3**. The core geometry is, however, very similar to that of cluster **3**, namely made by two short distances, four long ones and the last four others intermediate between them. The mean values of the three Pt–Pt distance types in the cluster **10** are, in fact, 2.6809, 2.8494 and 2.7269 Å, respectively. Such an arrangement was found in $\{Pt_6\}(CC–C_6H_5)_2$.[8c] The molecules of **3** and **10** are completed by four bridging di-t-butylphosphido ligands and a carbonyl group terminally bonded to each inner platinum, as already observed in other clusters belonging to this class.[8b-d,13,14,16,17]

The distance between the apical platinum and the alkynyl carbon and between the carbon atoms bonded by the triple bond [Pt(1)–C(1) = 2.013(7) Å, C(1)–C(2) = 1.130(10) Å in **3** and Pt(1)–C(5) = 2.032(9) Å, C(5)–C(6) =1.117(11) Å, Pt(6)–C(18) = 2.073(9) Å, C(18)–C(19) = 1.049(10) Å in **10**] fall in the range commonly found for terminal acetylide ligands bonded to platinum.[27]

This data, with the linear Pt(1)–C(1)–C(2) angle in **3**, and the *ca.* linear Pt(1)–C(5)–C(6) and Pt(6)–C(18)–C(19) angles [175.8(9)° and 176.0(9)°, respectively] in **10**, confirm the σ,η^1 coordination of the alkynyl ligand.[8b-d,13,14,16,17]

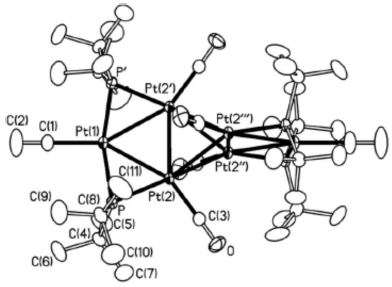


Fig. 5 View of the molecular structure of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 30% probability. ′ = 1 − *x*, 1 − *y*, *z*; ″ = *y*, 1 − *x*, −*z*; ‴ = 1 − *y*, *x*, −*z*.

Table 5 Significant bond lengths (Å) and angles (°) in **3**

Pt(1)–Pt(2)	2.7352(2)	Pt(1)–C(1)	2.013(7)
Pt(2)–Pt(2′)	2.6753(3)	C(1)–C(2)	1.130(10)
Pt(2)–Pt(2″)	2.8563(3)	Pt(2)–C(3)	1.855(5)
Pt(1)–P	2.2698(13)	C(3)–O	1.138(6)
Pt(2)–P	2.2629(11)		
Pt(2)–Pt(1)–Pt(2′)	58.556(8)	Pt(2″)–Pt(2)–Pt(2‴)	55.851(6)
Pt(1)–Pt(2)–Pt(2′)	60.723(4)	P–Pt(1)–Pt(2)	52.77(3)
Pt(2′)–Pt(2)–Pt(2″)	62.075(3)	P–Pt(2)–Pt(1)	53.00(3)
Pt(1)–P–Pt(2)	74.23(4)	O–C(3)–Pt(2)	179.0(5)
P–Pt(2)–C(3)	102.09(16)	Pt(1)–C(1)–C(2)	180.0
Pt(2)–Pt(1)–C(1)	150.722(4)		

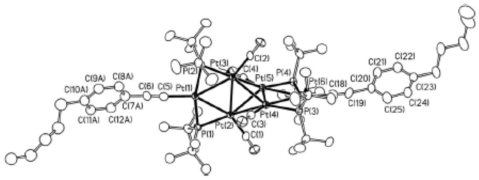


Fig. 6 View of the molecular structure of **10**. Thermal ellipsoids are set at 30% probability. Only the most populated positions of disordered groups are reported, hydrogen atoms are omitted for clarity.

Table 6 Significant bond lengths (Å) and angles (°) in **10**

Pt(1)–Pt(2)	2.7298(4)	Pt(1)–Pt(3)	2.7216(4)
Pt(4)–Pt(6)	2.7259(4)	Pt(5)–Pt(6)	2.7303(4)
Pt(2)–Pt(3)	2.6862(4)	Pt(4)–Pt(5)	2.6756(4)
Pt(2)–Pt(4)	2.8571(4)	Pt(3)–Pt(4)	2.8443(4)
Pt(2)–Pt(5)	2.8483(4)	Pt(3)–Pt(5)	2.8478(4)
Pt(1)–C(5)	2.032(9)	Pt(6)–C(18)	2.073(9)
C(5)–C(6)	1.117(11)	C(18)–C(19)	1.049(10)
Pt(1)–C(5)–C(6)	175.8(9)	Pt(6)–C(18)–C(19)	176.0(9)
C(5)–C(6)–C(7A)	170.3(11)	C(18)–C(19)–C(20)	173.3(11)
C(6)–C(7A)–C(8A)	124.1(9)	C(19)–C(20)–C(21)	120.3(8)

Conclusions

In this work we have described synthetic protocols for the synthesis, in very good yield, of mono- and bis-alkynyl derivatives of general formula $[Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4X(C{\equiv}C\,{-}R)]^{n+}$ (n = 0, X = I, Cl; n = 1, X = CO), $Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4(C{\equiv}C\,{-}R)_2$, $Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4(C{\equiv}C{-}R)(C{\equiv}C{-}R')$, confirming the remarkable robustness of the internal $\{Pt_6\}$ *core* of this class of clusters and their possible employment as synthons for organometallic and macromolecular synthesis, an issue up to now poorly developed but with considerable potential in the chemistry of new cluster-containing materials. In effect, the new ligands are already, or may be easily transformed into bifunctional, and generally conjugated, spacers able to connect cluster units. The electrochemical studies carried out on the derivative $Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4(C{\equiv}C{-}C_6H_5)_2$ (**5**), $Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4(C{\equiv}C{-}C_6H_4\text{-}4\text{-}NO_2)_2$ (**7**), $Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4$ $(C{\equiv}C{-}C_6H_4\text{-}4\text{-}OCH_3)_2$ (**8**), $Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4(C{\equiv}C{-}C_6H_4\text{-}4\text{-}CHO)_2$ (**9**), $Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4(C{\equiv}C{-}C_6H_4\text{-}4\text{-}n\text{-}C_5H_{11})_2$ (**10**) and $Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4(C{\equiv}C{-}C_6H_4\text{-}4\text{-}NO_2)(C{\equiv}C{-}C_6H_4\text{-}4\text{-}OCH_3)$ (**22**) show a dependency of the redox behavior from the para substituent on the ethynylphenyl ligands. In fact, a cathodic shift of the oxidation process centered on the cluster was found with the increasing of the electron donor capability of the apical ligands. An increase of the electron withdrawal ability of the ligands causes the expected anodic shift of the cluster-centered reduction processes, with the exceptions of clusters **7** and **22**, whose reductions are complicated by the nitro groups, which are reduced before the cluster units. Finally, in the time scale of the IR spectroelectrochemical analysis, only the reduced products of complex **9** and **10** show appreciable stability. In conclusion, the chemical and redox features above described make this class of derivatives promising as building blocks for the synthesis of oligomers or molecular wires.

Experimental

General Data. All operations were carried out using standard Schlenk-tube techniques, under an atmosphere of prepurified nitrogen. The reaction vessels were oven dried at *ca*. 150°C prior to use. Commercial grade solvents were purified by employing conventional procedures, distilled and stored over activated molecular sieves under nitrogen atmosphere. Some reagents (NH_4Cl, phenylacetylene, acetylene, ethynyltrimethylsilane, 1-bromo-4-ethynylben-zene, 1-ethynyl-4-nitrobenzene, 1-ethynyl-4-methoxyben-zene, 4-ethynylbenzaldehyde, 1-ethynyl-4-pentylbenzene: Aldrich; CuI: Alfa Aesar, $TlPF_6$: Apollo Scientific) were commercially available and were used without further purification; $Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4ClI$, (**1**),[8d,14b] $Pt_6(\mu\text{-}PBu^t_2)_4$ $(CO)_4Cl_2$, (**2**),[8b,c] 1,4-diethynylbenzene,[28] 1,4-diethynyl-2,5-di-*n*-butylbenzene,[29] were prepared as previously descri-bed. Elemental analyses were performed with a Carlo Erba elemental analyser Mod. 1106. IR spectra (nujol mulls, KBr) were recorded on a Perkin-Elmer Mod. FT-IR 1725X spectrophotometer or with a Perkin-Elmer FT-IR spectrometer equipped with a UATR sampling accessory. NMR spectra were recorded on a Varian Gemini 200 BB instrument (^1H, 200 MHz; ^{13}C, 50.3 MHz; ^{31}P, 81.0 MHz; ^{195}Pt, 42.8 MHz) at room temperature; frequencies are

referenced to the residual resonances of the deuterated solvent (^{1}H, ^{13}C), to 85% H_3PO_4 (^{31}P) and to H_2PtCl_6 (^{195}Pt). The symbol '#' is used to label ^{1}H, ^{13}C and ^{31}P peaks with ^{195}Pt satellites, s = singlet, d = doublet, ddd = double doublet of doublet, t = triplet, dt = double triplet, sept. = septet, vt = virtual triplet and m = multiplet. *J* values are given in Hz. Single crystal X-ray diffraction experiments were performed with a Bruker P4 diffractometer and a Bruker Apex II diffractometer by operating with a graphite-monochromated Mo-K_α radiation.

Electrochemistry and spectroelectrochemistry. Electroche-mical measurements were recorded on a Princeton Applied Research (PAR) 273A Potentiostat/Galvanostat, interfaced to a computer employing PAR M270 electrochemical software, and were performed in dichloromethane solutions containing [nBu4N]PF6 (0.2 mol dm^{-3}) as the supporting electrolyte. HPLC grade dichloromethane (Sigma-Aldrich) was stored under argon over 3-Å molecular sieves. Electrochemical grade [$^{n}Bu_4N$]PF_6 was purchased from Fluka and was used without further purification. Cyclic voltammetries were performed in a three-electrode cell, having a platinum reference electrode, a platinum-spiral counter electrode and a platinum-disc working electrode, and containing 5.10^{-4} M analyte solutions. After recording a sufficient number of voltammograms, a small amount of ferrocene was added to the solution and a further voltammogram was recorded. Potential values were determined by placing the redox couple ferrocenium /ferrocene [E_{redox} calculated as $(E_{pc} + E_{pa})/2$] at +0.39 V *vs* SCE.

Infrared (IR) spectroelectrochemical measurements were carried out using an optically transparent thin-layer electrochemical (OTTLE) cell equipped with CaF_2 windows, platinum minigrid working and auxiliary electrodes and silver wire pseudoreference electrode.[23] During the micro-electrolysis procedures, the electrode potential was controlled by the PAR 273A Potentiostat/Galvanostat. Argon-saturated CH_2Cl_2 solutions (10^{-2} M) of the compound under study, containing [$^{n}Bu_4N$]PF_6 0.2 M as the supporting electrolyte, were used. The *in situ* spectroelectrochemistry has been performed by collecting spectra of the solution at constant time intervals during the reduction process obtained by continuously lowering the initial working potential at a scan rate of 0.5 mV s^{-1}.

General procedure for the synthesis of 3-12. A catalytic amount of CuI (1% in moles per terminal alkyne) was added to a diethylamine solution of $Pt_6(\mu\text{-}PBu^{t}_2)_4(CO)_4Cl_2$, (**2**), and the proper terminal alkyne ligand (molar ratio 1:2). The solution was stirred for 24 h at room temperature and, after this period, the solvent was evaporated under vacuum. The crude product was washed with H_2O and acetone and was dried under vacuum to give the desired product.

Preparation of $\{Pt_6\}(C{\equiv}C\text{-}H)_2$ 3. Reagents: cluster **2** (100 mg, 0.052 mmol), HCCH (1atm) and CuI (0.20 mg, $1.03.10^{-3}$ mmol) in NEt_2H (30 mL); **3** was obtained as a red microcrystalline solid (82 mg, 83%).

Anal. Calcd for $C_{40}H_{74}O_4P_4Pt_6$: C, 25.1; H, 3.90. Found: C, 25.5; H, 3.95. $^{31}P\{^{1}H\}$ NMR (80.9 MHz, CD_2Cl_2, 25°C): δ = 334.7$^{\#}$ (s, 4 P); ^{1}H NMR (200 MHz, CD_2Cl_2, 25°C): δ = 2.91 (s, 2 H, CC*H*), 1.46 (vt, ^{3}J(H,P) + ^{5}J(H,P) = 7.7 Hz, 72 H, CC*H*$_3$); $^{13}C\{^{1}H\}$ NMR (50.3 MHz, CD_2Cl_2, 25°C): δ = 216.4 (s, *C*O), 80.7 (s, PtC≡*C*H), 44.2 (m, P*C*CH$_3$), 31.6 (s, PC*C*H$_3$); $^{195}Pt\{^{1}H\}$ NMR (42.8 MHz, CD_2Cl_2, 25°C): δ = −4685 (m, 2 Pt), −2291 (m, 4 Pt). IR (CH_2Cl_2): 3285 ($\nu_{\equiv C-H}$), 2014 (ν_{CO}), 1969 (ν_{CC}) cm^{-1}.

Preparation of $\{Pt_6\}(C{\equiv}C{-}SiMe_3)_2$ 4. Reagents: cluster **2** (75 mg, 0.039 mmol), $HCCSiMe_3$ (11 μL, d = 0.69 g/mL, 0.078 mmol) and CuI (0.15 mg, $0.79.10^{-3}$ mmol) in NEt_2H (25 mL); **4** was obtained as a red microcrystalline solid (70 mg, 89%).

Anal. Calcd for $C_{46}H_{90}O_4P_4Pt_6Si$: C, 27.2; H, 4.47. Found: C, 27.0; H, 4.46. $^{31}P\{^{1}H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): δ = 333.5$^{\#}$ (s, 4 P); ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ = 1.46 (vt, ^{3}J(H,P) + ^{5}J(H,P) = 6.9 Hz, 72 H, CC*H*$_3$), 0.99 (s, 9 H, SiC*H*$_3$); $^{195}Pt\{^{1}H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): δ = −4672 (m, 2 Pt), −2975 (m, 4 Pt). IR (solid state): 2016 (ν_{CO}) 1977 (ν_{CC}) cm^{-1}.

Preparation of $\{Pt_6\}(C{\equiv}C{-}C_6H_5)_2$ 5. Reagents: cluster **2** (30 mg, 0.015 mmol), phenylacetylene (4 μL, d = 0.93 g/mL, 0.036 mmol) and CuI (0.06 mg, $0.31.10^{-3}$ mmol) in NEt_2H (10 mL); **5** was obtained as a red microcrystalline solid (29 mg, 90%).

Anal. Calcd for $C_{52}H_{82}O_4P_4Pt_6$: C, 30.2; H, 4.00. Found: C, 30.4; H, 4.02. $^{31}P\{^{1}H\}$ NMR (80.9 MHz, CD_2Cl_2, 25°C): δ = 334.9$^{\#}$ (s, 4 P); ^{1}H NMR (200 MHz, CD_2Cl_2, 25°C): δ = 7.23 (m, 10 H, C_6H_5), 1.48 (vt, ^{3}J(H,P) + ^{5}J(H,P) = 7.3 Hz, 72 H, CC*H*$_3$); $^{13}C\{^{1}H\}$ NMR (50.3 MHz, CD_2Cl_2, 25°C): δ = 130.8, 128.3 125.3 (s, C_6H_5), 44.2 (m, P*C*CH$_3$), 31.6 (s, PC*C*H$_3$); $^{195}Pt\{^{1}H\}$ NMR (42.8 MHz, CD_2Cl_2, 25°C): δ = −4678 (m, 2 Pt), −2993 (m, 4 Pt). IR (KBr, Nujol): 2108 (ν_{CC}), 2012 (ν_{CO}) cm^{-1}.

Preparation of $\{Pt_6\}(C{\equiv}C{-}C_6H_4\text{-}4\text{-}Br)_2$ 6. Reagents: cluster **2** (50 mg, 0.026 mmol), 4-bromophenylacetylene (9.4 mg, 0.052 mmol) and CuI (0.10 mg, $0.52.10^{-3}$ mmol) in NEt_2H (20 mL); **6** was obtained as a red microcrystalline solid (49 mg, 88%).

Anal. Calcd for $C_{52}H_{80}BrO_4P_4Pt_6$: C, 29.1; H, 3.76. Found: C, 29.3; H, 3.80. $^{31}P\{^{1}H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): δ = 337.1$^{\#}$ (s, 4 P); ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ = 7.36 (d, ^{3}J(H,H) = 8.6 Hz, 4 H, C_6H_4), 7.17 (d, ^{3}J(H,H) = 8.6 Hz, 4 H, C_6H_4), 1.49 (vt, ^{3}J(H,P) + ^{5}J(H,P) = 7.6 Hz, 72 H, CC*H*$_3$); $^{13}C\{^{1}H\}$ NMR (50.3 MHz, $CDCl_3$, 25°C): δ = 132.1, 130.9, 128.3, 119.7 (s, C_6H_4), 107.6 (s, PtC≡*C*), 90.8 (s, Pt*C*≡C), 44.1 (m, P*C*CH$_3$), 31.3 (s, PC*C*H$_3$); $^{195}Pt\{^{1}H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): δ = −4691 (m, 2 Pt), −3000 (m, 4 Pt). IR (CH_2Cl_2): 2107 (ν_{CC}), 2012 (ν_{CO}) cm^{-1}.

Preparation of $\{Pt_6\}(C{\equiv}C{-}C_6H_4\text{-}4\text{-}NO_2)_2$ 7. Reagents: cluster **2** (50 mg, 0.026 mmol), HC≡C–C_6H_4-4-NO_2 (7.6 mg, 0.052 mmol) and CuI (0.098 mg, $0.517{\cdot}10^{-3}$ mmol) in NEt_2H (15 mL); **7** was obtained as a red microcrystalline solid (45 mg, 82%).

Anal. Calcd for $C_{52}H_{80}N_2O_8P_4Pt_6$: C, 29.0; H, 3.74. Found: C, 28.8; H, 3.78. $^{31}P\{^{1}H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): δ = 337.2$^{\#}$ (s, 4 P); ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ = 8.13 (d, ^{3}J(H,H) = 8.8 Hz, 4 H, C_6H_4), 7.38 (d, ^{3}J(H,H) = 8.8 Hz, 4 H, C_6H_4), 1.51 (vt, ^{3}J(H,P) + ^{5}J(H,P) = 7.5 Hz, 72 H, CC*H*$_3$); $^{13}C\{^{1}H\}$ NMR (50.3 MHz, $CDCl_3$, 25°C): δ = 216.1 (s, *C*O), 144.5 (s, *C*NO_2), 130.7, 123.7, 123.4 (s, C_6H_4), 106.3 (s, PtC≡*C*), 96.7 (s, Pt*C*≡C), 44.1 (m, P*C*CH$_3$), 31.5 (s, PC*C*H$_3$); $^{195}Pt\{^{1}H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): δ = −4678 (m, 2 Pt), −3006 (m, 4 Pt). IR (solid state): 2099 (ν_{CC}), 2014 (ν_{CO}) cm^{-1}.

Preparation of {Pt_6}(C≡C–C_6H_4-4-OCH_3)$_2$ 8. Reagents: cluster **2** (50 mg, 0.026 mmol), 4-ethynylanisole (6.9 mg, 0.052 mmol) and CuI (0.098 mg, $0.517\cdot10^{-3}$ mmol) in NEt_2H (15 mL); **8** was obtained as a red-brownish microcrystalline solid (49 mg, 89%).

Anal. Calcd for $C_{54}H_{86}O_6P_4Pt_6$: C, 30.5; H, 4.08. Found: C, 30.8; H, 3.99. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): δ = 335.4[#] (s, 4 P); ^1H NMR (200 MHz, $CDCl_3$, 25°C): δ = 7.31 (d, ^3J(H,H) = 8.7 Hz, 4 H, C_6H_4), 6.82 (d, ^3J(H,H) = 8.7 Hz, 4 H, C_6H_4), 3.83 (s, 6H, OCH_3), 1.52 (vt, ^3J(H,P) + ^5J(H,P) = 7.2 Hz, 72 H, CCH_3); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25°C): δ = 216.6 (s, *C*O), 157.3 (s, *C*OCH$_3$), 131.9, 122.2, 113.7 (s, C_6H_4), 98.4 (s, PtC≡*C*), 90.4 (s, Pt*C*≡C), 55.3 (s, O*C*H$_3$) 43.9 (m, P*C*CH$_3$), 31.5 (s, PC*C*H$_3$); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): δ = −4671 (m, 2 Pt), −3004 (m, 4 Pt). IR (solid state): 2107 (ν_{CC}), 2010 (ν_{CO}) cm^{-1}.

Preparation of {Pt_6}(C≡C–C_6H_4-4-CHO)$_2$ 9. Reagents: cluster **2** (85 mg, 0.044 mmol), 4-ethynylbenzaldehyde (11.4 mg, 0.088 mmol) and CuI (0.167 mg, $0.88\cdot10^{-3}$ mmol) in NEt_2H (20 mL); **9** was obtained as a dark orange microcrystalline solid (78 mg, 86%).

Anal. Calcd for $C_{54}H_{82}O_6P_4Pt_6$: C, 30.6; H, 3.89. Found: C, 30.3; H, 3.85. $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6, 25°C): δ = 336.2[#] (s, 4 P); ^1H NMR (200 MHz, C_6D_6, 25°C): δ = 9.66 (s, 1 H, C*H*O), 7.59 (d, ^3J(H,H) = 7.5 Hz, 4 H, C_6H_4), 7.53 (d, ^3J(H,H) = 7.5 Hz, 4 H, C_6H_4), 1.48 (vt, ^3J(H,P) + ^5J(H,P) = 7.1 Hz, 72 H, CCH_3); $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 25°C): δ = 217.2 (s, *C*O), 190.3 (s, C*C*HO), 133.7, 130.9, 129.7, 129.1 (s, C_6H_4), 124.1 (s, PtC≡*C*), 94.8 (s, Pt*C*≡C), 44.0, 39.2 (m, P*C*CH$_3$), 31.3 (s, PC*C*H$_3$); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, C_6D_6, 25°C): δ = −4664 (m, 2 Pt), −2998 (m, 4 Pt). IR (solid state): 2101 ($\nu_{C\equiv C}$), 2010 ($\nu_{C\equiv O}$), 1693 ($\nu_{C=O}$) cm^{-1}.

Preparation of {Pt_6}(C≡C–C_6H_4-4-C_5H_{11})$_2$ 10. Reagents: cluster **2** (60 mg, 0.031 mmol), 1-ethynyl-4-pentylbenzene (11 mg, 0.063 mmol) and CuI (0.12 mg, $0.63\cdot10^{-3}$ mmol) in NEt_2H (20 mL); **10** was obtained as a red microcrystalline solid (59 mg, 86%).

Anal. Calcd for $C_{62}H_{102}O_4P_4Pt_6$: C, 33.8; H, 4.66. Found: C, 33.5; H, 4.69. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): δ = 334.9[#] (s, 4 P); ^1H NMR (200 MHz, $CDCl_3$, 25°C): δ = 7.27 (d, ^3J(H,H) = 7.9 Hz, 4 H, C_6H_4), 7.04 (d, ^3J(H,H) = 7.9 Hz, 4 H, C_6H_4), 2.56 (t, ^3J(H,H) = 8.0 Hz, 4 H, C_5H_{11}), 1.48 (vt, ^3J(H,P) + ^5J(H,P) = 7.3 Hz, 72 H, CCH_3), 1.32 (m, 12 H, C_5H_{11}), 0.89 (t, ^3J(H,H) = 6.6 Hz, 6 H, C_5H_{11}); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25°C): δ = 216.9 (s, *C*O), 140.0, 130.8, 128.3, 127.0 (s, C_6H_4), 122.8 (s, PtC≡*C*), 100.1 (s, Pt*C*≡C), 44.2 (m, P*C*CH$_3$), 36.1 (s, C_5H_{11}), 31.8 (s, PC*C*H$_3$), 31.5, 22.9, 14.4 (s, C_5H_{11}); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): δ = −4688 (m, 2 Pt), −2293 (m, 4 Pt); IR (CH_2Cl_2): 2106 (ν_{CC}), 2006 (ν_{CO}) cm^{-1}.

Preparation of {Pt_6}(C≡C–C_6H_4-4-CCH)$_2$ 11. Reagents: cluster **2** (200 mg, 0.10 mmol), 1,4-diethynylbenzene (31.5 mg, 0.25 mmol) and CuI (0.4 mg, $2.1\cdot10^{-3}$ mmol) in NEt_2H (50 mL); **11** was obtained as an orange microcrystalline solid (180 mg, 85%).

Anal. Calcd for $C_{56}H_{82}O_4P_4Pt_6$: C, 31.8; H, 3.91. Found: C, 31.5; H, 3.96. $^{31}P\{^1H\}$ NMR (80.9 MHz, CD_2Cl_2, 25°C): δ = 337.2[#] (s, 4 P); ^1H NMR (200 MHz, CD_2Cl_2, 25°C): δ = 7.2-7.4 (m, 8H, C_6H_4), 3.17 (s, 2 H, CC*H*), 1.49 (vt, ^3J(H,P) + ^5J(H,P) = 7.3 Hz, 72 H, CCH_3); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 25°C): δ = 216.4 (s, *C*O), 132.1, 130.7 (s, C_6H_4), 84.7 (s, C≡*C*H), 44.3 (m, P*C*CH$_3$), 31.8 (s, PC*C*H$_3$); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): δ = −4677 (m, 2 Pt), −3001 (m, 4 Pt). IR (CH_2Cl_2): 3296 ($\nu_{\equiv CH}$), 2100 (ν_{CC}), 2011 (ν_{CO}) cm^{-1}.

Preparation of {Pt_6}(C≡C–C_6H_2-2,5-di-*n*-butyl-4-C≡CH)$_2$ 12. Reagents: cluster **2** (80 mg, 0.041 mmol), 1,4-dietynyl-2,5-di-*n*-butylbenzene (20 mg, 0.084 mmol) and CuI (0.15 mg $0.79\cdot10^{-3}$ mmol) in NEt_2H (25 mL); **12** was obtained as an orange microcrystalline solid (81 mg, 85%).

Anal. Calcd for $C_{72}H_{114}O_4P_4Pt_6$: C, 37.0; H, 4.91. Found: C, 36.8; H, 4.95. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): δ = 334.5[#] (s, 4 P); ^1H NMR (200 MHz, $CDCl_3$, 25°C): δ = 7.22 (s, 2 H, C_6H_2), 7.16 (s, 2 H, C_6H_2), 3.44 (s, 2 H, CC*H*), 2.82 (t, ^3J(H,H) = 7.5 Hz, 8 H, C_4H_9), 1.51 (vt, ^3J(H,P) + ^5J(H,P) = 6.9 Hz, 72 H, CCH_3), 1.32 (m, 16 H, C_4H_9), 0.95 (t, ^3J(H,H) = 7.1 Hz, 12 H, C_4H_9); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25°C): δ = 216.4 (s, *C*O), 141.8, 140.0, 138.5, 132.4, 131.5 (s, C_6H_2), 121.9 (s, PtC≡*C*), 117.3 (s, C_6H_2), 107.7 (s, Pt*C*≡C), 83.4 (s, *C*≡CH), 79.8 (s, C≡*C*H), 44.0, 43.7 (m, P*C*CH$_3$), 33.7, 32.6 (s, C_4H_9), 31.5 (s, PC*C*H$_3$), 26.5, 14.2 (s, C_4H_9); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): δ = −4691 (m, 2 Pt), −2987 (m, 4 Pt); IR (CH_2Cl_2): 3330 ($\nu_{\equiv CH}$), 2090 (ν_{CC}), 2010 (ν_{CO}) cm^{-1}.

General procedure for the synthesis of 13-17. $Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4ClI$, **1**, the proper terminal alkyne (molar ratio 1:1) and a catalytic amount of CuI (1% in moles *per* terminal alkyne) were added to diethylamine under a nitrogen atmosphere. The reaction mixture was stirred overnight at room temperature. The solvent was evaporated under reduced pressure and the crude product was washed several times with H_2O and acetone and then dried under vacuum. The desired product was obtained as a microcrystalline solid.

Preparation of {Pt_6}(C≡C–C_6H_4-4-Br)I, 13. Reagents: cluster **1** (200 mg, 0.099 mmol), 4-bromophenylacetylene (18 mg, 0.099 mmol) and CuI (0.19 mg, $0.99\cdot10^{-3}$ mmol) in NEt_2H (50 mL); **13** was obtained as a red microcrystalline solid (178 mg, 83%).

Anal. Calcd for $C_{44}H_{76}BrIO_4P_4Pt_6$: C, 24.4; H, 3.53. Found: C, 24.2; H, 3.52. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): δ = 336.8[#] (s, 2 P), 331.3[#] (s, 2 P); ^1H NMR (200 MHz, $CDCl_3$, 25°C): δ = 7.36 (d, ^3J(H,H) = 8.3 Hz, 2 H, C_6H_4), 7.19 (d, ^3J(H,H) = 8.3 Hz, 2 H, C_6H_4), 1.55 (vt, ^3J(H,P) + ^5J(H,P) = 7.6 Hz, 36 H, CCH_3), 1.49 (vt, ^3J(H,P) + ^5J(H,P) = 7.6 Hz, 36 H, CCH_3); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25°C): δ = 215.1 (s, *C*O), 132.4, 131.3, 128.4, 121.7 (s, C_6H_4), 118.8 (s, PtC≡*C*), 87.9 (s, Pt*C*≡C), 45.4, 44.3 (m, P*C*CH$_3$), 32.6, 31.8 (s, PC*C*H$_3$); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): δ = −4891 (m, 1 Pt), −4697 (m, 1 Pt), −3302 (m, 2 Pt), −3046 (m, 2 Pt); IR (CH_2Cl_2): 2108 (ν_{CC}), 2014 (ν_{CO}) cm^{-1}.

Preparation of {Pt_6}(C≡C–C_6H_4-4-NO_2)I, 14. Reagents: cluster **1** (300 mg, 0.148 mmol), 4-nitrophenylacetylene (22 mg, 0.15 mmol) and CuI (0.28 mg, $1.50 \cdot 10^{-3}$ mmol) in NEt_2H (60 mL); **14** was obtained as a reddish microcrystalline solid (269 mg, 85%).

Anal. Calcd for $C_{44}H_{76}INO_6P_4Pt_6$: C, 24.7; H, 3.59. Found: C, 24.9; H, 3.63. $^{31}P\{^1H\}$ NMR (80.9 MHz, CD_2Cl_2, 25°C): δ = 337.4[#] (s, 2 P), 332.5[#] (s, 2 P); ^1H NMR (200 MHz, CD_2Cl_2, 25°C): δ = 8.09 (d, ^3J(H,H) = 8.9 Hz, 2 H, C_6H_4), 7.40 (d, ^3J(H,H) = 8.9 Hz, 2 H, C_6H_4), 1.50 (vt, ^3J(H,P) + ^5J(H,P) = 7.1 Hz, 72 H, CCH_3); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 25°C): δ = 216.5, 209.5 (s, *C*O), 146.6 (s, *C*NO_2), 134.8, 132.9, 124.5 (s, C_6H_4), 102.6 (s, PtC≡*C*), 47.3, 46.3 (m, P*C*CH_3), 33.5, 34.4 (s, PC*C*H_3); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, CD_2Cl_2, 25°C): δ = −4885 (m, 1 Pt), −4709 (m, 1 Pt), −3353 (m, 2 Pt), −3015 (m, 2 Pt); IR (solid state): 2102 (ν_{CC}), 2011 (ν_{CO}) cm^{-1}.

Preparation of {Pt_6}(C≡C–C_6H_4-4-C_5H_{11})I, 15. Reagents: cluster **1** (295 mg, 0.146 mmol), 1-ethynyl-4-pentylbenzene (26 mg, 0.151 mmol) and CuI (0.28 mg, $1.50 \cdot 10^{-3}$ mmol) in NEt_2H (60 mL); **15** was obtained as a red microcrystalline solid (262 mg, 83%).

Anal. Calcd for $C_{49}H_{87}IO_4P_4Pt_6$: C, 27.2; H, 4.06. Found: C, 27.0; H, 4.01. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): δ = 336.7[#] (s, 2 P), 330.5[#] (s, 2 P); ^1H NMR (200 MHz, $CDCl_3$, 25°C): δ = 7.25 (d, ^3J(H,H) = 7.8 Hz, 2 H, C_6H_4), 7.05 (d, ^3J(H,H) = 7.8 Hz, 2 H, C_6H_4), 2.56 (t, ^3J(H,H) = 7.4 Hz, 2 H, C_5H_{11}), 1.52 (vt, ^3J(H,P) + ^5J(H,P) = 7.4 Hz, 72 H, CCH_3), 1.33 (m, 6H, C_5H_{11}), 0.89 (t, ^3J(H,H) = 6.4 Hz, 3 H, C_5H_{11}); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25°C): δ = 215.0, 207.1 (s, *C*O), 140.1, 132.2, 130.8, 126.8 (s, C_6H_4), 122.7 (s, PtC≡*C*), 88.6 (s, Pt*C*≡C), 44.4 (m, P*C*CH_3), 36.1 (s, C_5H_{11}), 31.8 (s, PCCH_3), 31.5, 22.9, 14.4 (s, C_5H_{11}); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): δ = −4899 (m, 1 Pt),−4683 (m, 1 Pt), −3323 (m, 2 Pt), −3040 (m, 2 Pt). IR (solid state): 2107 (ν_{CC}), 2009 (ν_{CO}) cm^{-1}.

Preparation of {Pt_6}(C≡C–C_6H_4-4-CCH)I, 16. Reagents: cluster **1** (150 mg, 0.074 mmol), 1,4-diethynylbenzene (9.3 mg, 0.074 mmol) and CuI (0.14 mg, $0.74 \cdot 10^{-3}$ mmol) in NEt_2H (40 mL); **16** was obtained as a red microcrystalline solid (138 mg, 88%).

Anal. Calcd for $C_{46}H_{77}IO_4P_4Pt_6$: C, 26.1; H, 3.67. Found: C, 26.3; H, 3.69. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): δ = 338.9[#] (s, 2 P), 333.3[#] (s, 2 P); ^1H NMR (200 MHz, $CDCl_3$, 25°C): δ = 7.35 (d, ^3J(H,H) = 8.1 Hz, 2 H, C_6H_4), 7.25 (d, ^3J(H,H) = 8.1 Hz, 2 H, C_6H_4), 3.18 (s, 1 H, CC*H*), 1.50 (vt, ^3J(H,P) + ^5J(H,P) = 7.6 Hz, 72 H, CCH_3); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25°C): δ = 215.4 (s, *C*O), 131.9, 130.5, (s, C_6H_4), 118.3 (s, PtC≡*C*), 84.2 (s, *C*≡CH), 77.6 (s, C≡*C*H), 45.4, 44.4 (m, P*C*CH_3), 32.5, 31.7 (s, PC*C*H_3); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): δ = −4891 (m, 1 Pt), −4697 (m, 1 Pt), −3325 (m, 2 Pt), −3052 (m, 2 Pt); IR (solid state): 3266 ($\nu_{≡CH}$), 2099 (ν_{CC}), 2010 (ν_{CO}) cm^{-1}.

Preparation of {Pt_6}(C≡C–C_6H_2-2,5-di-*n*-butyl-4-C≡CH)I, 17. Reagents: cluster **1** (200 mg, 0.099 mmol), 1,4-dietynyl-2,5-di-*n*-butylbenzene (23.6 mg, 0.099 mmol) and CuI (0.19 mg, $0.99 \cdot 10^{-3}$ mmol) in NEt_2H (50 mL); **17** was obtained as a dark orange microcrystalline solid (185 mg, 84%).

Anal. Calcd for $C_{54}H_{93}IO_4P_4Pt_6$: C, 29.1; H, 4.21. Found: C, 29.2; H, 4.23. $^{31}P\{^1H\}$ NMR (80.9 MHz, CD_2Cl_2, 25°C): δ = 336.3[#] (s. 2 P), 331.0[#] (s, 2 P); ^1H NMR (200 MHz, CD_2Cl_2, 25°C): δ = 7.22 (s, 1 H, C_6H_2), 7.16 (s, 1 H, C_6H_2), 3.26 (s, 1 H, CC*H*), 2.73 (m, 2 H, C_4H_9), 1.50-1.54 (m, 8 H, C_4H_9), 1.49 (vt, ^3J(H,P) + ^5J(H,P) = 7.3 Hz, 72 H, CCH_3), 0.94 (t, ^3J(H,H) = 7.3 Hz, 6 H, C_4H_9); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 25°C): δ = 217.4, 209.5 (s, *C*O), 144.1, 142.3, 134.5, 133.6, 131.4 (s, C_6H_2), 123.9 (s, PtC≡*C*), 119.6 (s, C_6H_2), 105.6 (s, PtC≡C), 85.3 (s, *C*≡CH), 82.1 (s, C≡*C*H), 47.2, 46.0 (m, P*C*CH_3), 35.7, 35.6, 34.8, 34.2 (s, C_4H_9), 33.5 (s, PC*C*H_3), 24.9, 24.6, 16.1, 15.9 (s, C_4H_9); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, CD_2Cl_2, 25°C): δ = −4895 (m, 1 Pt), −4761 (m, 1 Pt), −3321 (m, 2 Pt), −3028 (m, 2 Pt); IR (CH_2Cl_2): 3302 ($\nu_{≡CH}$), 2093 (ν_{CC}), 2014 (ν_{CO}) cm^{-1}.

General procedure for the synthesis of 18-19. A mixture of the proper iodo-alkynyl derivative and an excess of $TlPF_6$ was added to dry THF. The reaction mixture was filled with CO and stirred for ca. 24 h. The solution was concentrated and filtered to remove TlI and excess of $TlPF_6$. After adding hexane, a red solid was precipitated out and it was filtered and dried *in vacuo*, affording the desired product as a microcrystalline solid.

Preparation of [{Pt_6}(C≡C–C_6H_4-4-NO_2)(CO)](PF_6), 18. Reagents: cluster **14** (269 mg, 0.126 mmol) and $TlPF_6$ (734 mg, 2 mmol) in THF (15 mL); **18** was obtained as a red microcrystalline solid (210 mg, 77%).

Anal. Calcd for $C_{45}H_{76}F_6O_7P_5Pt_6$: C, 24.9; H, 3.53. Found: C, 25.1; H, 3.51. $^{31}P\{^1H\}$ NMR (80.9 MHz, acetone-d_6, 25°C): δ = 364.7[#] (s, 2 P), 357.0[#] (s, 2 P), −139.1 (sept, ^1J(P,F) = 708 Hz, 1 P); ^1H NMR (200 MHz, acetone-d_6, 25°C): δ = 8.16 (d, ^3J(H,H) = 9.9 Hz, 2 H, C_6H_4), 7.50 (d, ^3J(H,H) = 8.9 Hz, 2 H, C_6H_4), 1.56 (vt, ^3J(H,P) + ^5J(H,P) = 8.0 Hz, 72 H, CCH_3); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2 , 25°C): δ = 217.5, 203.7, 183.4 (s, *C*O), 145.2, 131.2, 125.0, 123.9 (s, C_6H_4), 110.2 (s, PtC≡*C*), 84.3 (s, Pt*C*≡C), 46.2, 45.9 (s, P*C*CH_3), 32.0, 31.6 (s, PCCH_3); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, acetone-d_6, 25°C): δ = −4996 (m, 1 Pt),−4543 (m, 1 Pt), −3092 (m, 4 Pt). IR (solid state): 2105 (ν_{CC}), 2076, 2064, 2044, 2033, 2016 (ν_{CO}) cm^{-1}.

Preparation of [{Pt_6}(C≡C–C_6H_4-4-C_5H_{11})(CO)](PF_6), 19. Reagents: cluster **15** (262 mg, 0.121 mmol) and $TlPF_6$ (734 mg, 2 mmol) in THF (15 mL); **19** was obtained as a red microcrystalline solid (214 mg, 80%).

Anal. Calcd for $C_{50}H_{87}F_6O_5P_5Pt_6$: C, 27.2; H, 3.97. Found: C, 27.4; H, 4.01. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): δ = 357.7[#] (s, 2 P), 354.8[#] (s, 2 P), −142.5 (sept, ^1J(P,F) = 706 Hz, 1 P); ^1H NMR (200 MHz, $CDCl_3$, 25°C): δ = 7.20 (d, ^3J(H,H) = 8.2 Hz, 2 H, C_6H_4), 7.06 (d, ^3J(H,H) = 8.2 Hz, 2 H, C_6H_4), 2.54 (t, ^3J(H,H) = 7.4 Hz, 2 H, C_5H_{11}), 1.51 (vt, ^3J(H,P) + ^5J(H,P) = 7.3 Hz, 72 H, CCH_3), 1.28 (m, 6H, C_5H_{11}), 0.86 (t, ^3J(H,H) = 6.2 Hz, 3 H, C_5H_{11}); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25°C): δ = 207.1, 203.5, 176.0 (s, *C*O), 139.3, 132.2, 131.8, 128.8 (s, C_6H_4), 122.7 (s, PtC≡*C*), 86.1 (s, Pt*C*≡C), 46.3 (m, P*C*CH_3), 36.1 (s, C_5H_{11}), 32.0 (s, PC*C*H_3), 31.1, 22.8, 14.4 (s, C_5H_{11}); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): δ = −4794 (m, 1 Pt),−4065 (m, 1 Pt), −3495 (m, 2 Pt), −3088 (m, 2 Pt). IR (solid state): 2086 (ν_{CC}), 2074, 2052, 2037, 2018 2010 (ν_{CO}) cm^{-1}.

General procedure for the synthesis of 20-21. A solution of NH_4Cl in deionized H_2O was added to a solution of the proper carbonyl-alkynyl derivative in acetone. The reaction mixture was stirred for *ca* 30 min at room temperature, and the solid which precipitated out was filtered off and thoroughly washed with water and acetone. It was finally dried *in vacuo*, affording the desired product as a microcrystalline solid.

Preparation of {Pt_6}(C≡C–C_6H_4-4-NO_2)Cl, 20. Reagents: cluster **18** (210 mg, 0.097 mmol) in acetone (20 mL) and NH_4Cl (53 mg, 1 mmol) in deionized water (3 mL); **20** was obtained as a red microcrystalline solid (188 mg, 95%).

Anal. Calcd for $C_{44}H_{76}ClNO_6P_4Pt_6$: C, 25.8; H, 3.75. Found: C, 25.9; H, 3.77. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): δ = 339.5[#] (s, 2 P), 330.2[#] (s, 2 P); ^1H NMR (200 MHz, $CDCl_3$, 25°C): δ = 8.13 (d, ^3J(H,H) = 8.1 Hz, 2 H, C_6H_4), 7.40 (d, ^3J(H,H) = 8.1 Hz, 2 H, C_6H_4), 1.52 (vt, ^3J(H,P) + ^5J(H,P) = 7.5 Hz, 72 H, CCH_3); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25°C): δ = 144.3, 136.3, 130.7, 123.6 (s, C_6H_4), 44.7, 44.1 (s, PCCH$_3$), 31.6 (s, PCCH$_3$); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): δ = −4712 (m, 1 Pt),−4100 (m, 1 Pt), −3430 (m, 2 Pt), −3044 (m, 2 Pt). IR (solid state) 2103 (ν_{CC}), 2013 (ν_{CO}) cm^{-1}.

Preparation of {Pt_6}(C≡C–C_6H_4-4-C_5H_{11})Cl, 21. Reagents: cluster **19** (214 mg, 0.097 mmol) in acetone (20 mL) and NH_4Cl (53 mg, 1 mmol) in deionized water (3 mL); **21** was obtained as a reddish-orange microcrystalline solid (187 mg, 93%).

Anal. Calcd for $C_{49}H_{87}ClO_4P_4Pt_6$: C, 28.4; H, 4.23. Found: C, 28.2; H, 4.26. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): δ = 336.7[#] (s, 2 P), 326.1[#] (s, 2 P); ^1H NMR (200 MHz, $CDCl_3$, 25°C): δ = 7.26 (d, ^3J(H,H) = 7.7 Hz, 2 H, C_6H_4), 7.06 (d, ^3J(H,H) = 7.7 Hz, 2 H, C_6H_4), 2.56 (t, ^3J(H,H) = 7.4 Hz, 2 H, C_5H_{11}), 1.53 (vt, ^3J(H,P) + ^5J(H,P) = 7.4 Hz, 72 H, CCH_3), 1.33 (m, 6H, C_5H_{11}), 0.90 (t, ^3J(H,H) = 6.4 Hz, 3 H, C_5H_{11}); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25°C): δ = 215.6, 207.1 (s, *C*O), 140.1, 130.8, 128.3, 126.8 (s, C_6H_4), 122.6 (s, PtC≡*C*), 86.1 (s, Pt*C*≡C), 44.8 (m, P*C*CH$_3$), 36.1 (s, C_5H_{11}), 31.8 (s, PC*C*H$_3$), 31.4, 22.9, 14.4 (s, C_5H_{11}); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): δ = −4688 (m, 1 Pt),−4116 (m, 1 Pt), −3426 (m, 2 Pt), −3048 (m, 2 Pt). IR (solid state): 2108 (ν_{CC}), 2006 (ν_{CO}) cm^{-1}.

Preparation of {Pt_6}(C≡C–C_6H_4-4-NO_2)(C≡C–C_6H_4-4-OCH_3), 22. 4-ethynylanisole (12 mg, 0.092 mmol) and CuI (0.17 mg, $0.90\cdot10^{-3}$ mmol) were added to a solution of cluster 20 (188 mg, 0.092 mmol) in NEt_2H (25 mL). The solution was stirred at room temperature for 24 hours, then the solvent was evaporated under vacuum. The crude product was washed with water and the obtained red solid was finally dried *in vacuo* (167 mg, yield 85%).

Anal. Calcd for $C_{53}H_{83}NO_7P_4Pt_6$: C, 29.7; H, 3.91. Found: C, 29.2; H, 3.87. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): δ = 335.9[#] (s, 2 P), 335.0[#] (s, 2 P); ^1H NMR (200 MHz, $CDCl_3$, 25°C): δ = 8.12 (d, ^3J(H,H) = 8.8 Hz, 2 H, C_6H_4-4-NO_2), 7.39 (d, ^3J(H,H) = 8.8 Hz, 2 H, C_6H_4-4-NO_2), 7.22 (d, ^3J(H,H) = 8.8 Hz, 2 H, C_6H_4-4-OCH_3), 6.81 (d, ^3J(H,H) = 8.8 Hz, 2 H, C_6H_4-4-OCH_3), 3.81 (s, 3 H, OCH_3), 1.53 (vt, ^3J(H,P) + ^5J(H,P) = 7.2 Hz, 36 H, CCH_3), 1.51 (vt, ^3J(H,P) + ^5J(H,P) = 7.3 Hz, 36 H, CCH_3); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25°C): δ = 216.8, 215.9 (s, *C*O), 157.5 (s, *C*OCH$_3$), 144.4 (s, *C*NO$_2$), 131.7, 130.7, 123.5 (s, C_6H_4), 122.4, 122.0 (s, PtC≡*C*), 113.6 (s, C_6H_4), 98.5, 97.3 (s, PtC≡C), 55.2 (s, OCH$_3$), 43.9 (m, P*C*CH$_3$), 31.3 (s, PC*C*H$_3$); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): δ = −4691 (m, 1 Pt), −4655 (m, 1 Pt), −3003 (m, 4 Pt). IR (solid state): 2101 (ν_{CC}), 2013 (ν_{CO}) cm^{-1}.

Preparation of {Pt_6}(C≡C–C_6H_4-4-C_5H_{11})(C≡C–C_6H_4-4-CHO), 23. To a stirred solution of **21** (187 mg, 0.090 mmol) in NEt_2H (20 mL), 4-ethynylbenzaldehyde (11.7 mg, 0.090 mmol) and CuI (0.17 mg, $0.90\cdot10^{-3}$ mmol) were added. The solution was stirred at room temperature for 24 hours. Then, the solvent was evaporated under vacuum and the crude product was washed with water. The desired product **23** was obtained as a red microcrystalline solid (171 mg, yield 88%).

Anal. Calcd for $C_{58}H_{92}O_5P_4Pt_6$: C, 32.2; H, 4.29. Found: C, 32.0; H, 4.27. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): δ = 335.3[#] (s, 2 P), 334.2[#] (s, 2 P); ^1H NMR (200 MHz, $CDCl_3$, 25°C): δ = 9.93 (s, 1 H, C*H*O), 7.74 (d, ^3J(H,H) = 8.2 Hz, 2 H, C_6H_4-4-CHO), 7.42 (d, ^3J(H,H) = 8.2 Hz, 2 H, C_6H_4-4-CHO), 7.24 (d, ^3J(H,H) = 7.3 Hz, 2 H, C_6H_4-4-C_5H_{11}), 7.03 (d, ^3J(H,H) = 7.3 Hz, 2 H, C_6H_4-4-C_5H_{11}), 2.55 (t, ^3J(H,H) = 7.1 Hz, 2 H, C_5H_{11}), 1.50 (vt, ^3J(H,P) + ^5J(H,P) = 7.2 Hz, 72 H, CCH_3), 1.34 (m, 6H, C_5H_{11}), 0.89 (t, ^3J(H,H) = 6.3 Hz, 3 H, C_5H_{11}); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): δ = −4672 (m, 2 Pt), −2998 (m, 4 Pt). IR (solid state): 2101 (ν_{CC}), 2010 (ν_{CO}), 1693 ($\nu_{C=O}$) cm^{-1}.

X-ray diffraction studies. The X-ray diffraction experiments were carried out at room temperature by means of a Bruker Smart Breeze CCD diffractometer operating with graphite-monochromated Mo-K_α radiation. The samples were glued on the tip of glass fibres and their lattice parameters were evaluated as a preliminary step to the crystallographic study. The values obtained are reported in table 6. On the basis of those results the intensity data collections were done up to the limits mentioned in the table. The intensities were corrected for Lorentz and polarisation effects and for absorption by means of a multi-scan method.[30] The structure solutions were obtained by the automatic direct methods contained in SHELX97 programme.[31] After the introduction of the hydrogen atoms in calculated positions, the crystal structure of **3** could be refined with anisotropic thermal parameters for heavy atoms till the reliabilty factors listed in table 7. Concerning the refinement of the structure of **10**, the introduction of anisotropic thermal parameters led to thermal ellipsoids abnormally elongated for carbon atoms of four isopropyl groups and of one alkylphenylethinyl group.

The elongation was interpreted as a symptom of a statistical disorder of those groups. These were introduced into the model as each arranged on two different conformations and imposing some restraints on their geometry. After the introduction of hydrogen atoms in calculated positions, the final refinement cycles were done with isotropic thermal parameters for the carbon atoms of disordered groups and anisotropic for the other heavy atoms. The final reliability factors are listed in Table 7.

In addition to the aforementioned software, other control calculations and preparation of publication material were performed with the programs contained in the suite WINGX.[32]

CCDC nnnnnnn contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table 7 Crystal data and structure refinements

	3	10
Empirical formula	$C_{40}H_{74}O_4P_4Pt_6$	$C_{62}H_{102}O_4P_4Pt_6$
Formula weight	1913.41	2205.85
T/K	296	293
λ/Å	0.71073	0.71073
Crystal system	Tetragonal	Monoclinic
Space group	$I\bar{4}2d$	$C2/c$
a/Å	17.3664(2)	24.8698(19)
b/Å	—	17.4794(13)
c/Å	17.6625(2)	33.430(3)
β/°	—	100.5070(10)
U/Å^3	5326.87(14)	14 288.6(19)
Z	4	8
D_{calc}/Mg m^{-3}	2.386	2.051
μ/mm^{-1}	15.850	11.833
No. measured	28 749	82 340
(max	29.623	28.784
No. unique [Rint]	3705 [0.0310]	17 443 [0.0720]
No. parameters	126	572
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0173, 0.0310	0.0378, 0.0771
R_1, wR_2 [all data][a]	0.0241, 0.0323	0.0737, 0.0897
Goodness of fit[a] on F^2	0.986	1.014

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$ where $Q = [MAX(F_o^2, 0) + 2F_c^2]/3$; GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(N - P)]^{1/2}$, where N, P are the numbers of observations and parameters, respectively.

Acknowledgements

This work was supported by the Ministero dell'Istruzione, Università e Ricerca (MIUR), Project PRIN2008 No. 2008RFEB3X and by the Fondazione Cassa di Risparmio di Pisa under the "POLOPTEL" project n. 167/09.

Notes and references

1 (a) N. J. Long and C. K. Williams, *Angew. Chem., Int. Ed. Engl.,* 2003, **42**, 2586; (b) J. R. Berenguer, E. Lalinde and M. T. Moreno, *Coord. Chem. Rev.,* 2010, **254**, 832; (c) R. Buschbeck, P. J. Low and H. Lang, *Coord. Chem. Rev.,* 2011, **255**, 241. (d) T. Ren, *Organometallics,* 2005, **24**, 4854.

2 (a) G. Grelaud, M. P. Cifuentes, F. Paul and M. G. Humphrey, *J. Organomet. Chem.,* 2014, **751**, 181; (b) K. A. Green, M. P. Cifuentes, M. Samoc and M. G. Humphrey, *Coord. Chem. Rev.,* 2011, **255**, 2530.

3 (a) K. M.-C. Wong and V. W.-W. Yam, *Acc. Chem. Res.,* 2011, **44**, 424; (b) J. R. Berenguer, J. Fernandez, B. Gil, E. Lalinde and S. Sanchez, *Inorg. Chem.,* 2010, **49**, 4232; (c) G. S. M. Tong, Y.-C. Law, S. C. F. Kui, N. Zhu, K. H. Leung, D. L. Phillips and C.-M. Che, *Chem. Eur. J.,* 2010, 16, 6540; (d) J. Ni, X. Zhang, Y.-H. Wu, L.-Y. Zhang and Z.-N. Chen, *Chem. Eur. J.,* 2011, 17, 1171; (e) I. O. Koshevoy, A. J. Karttunen, I. S. Kritchenkou, D. V. Krupenya, S. I. Selivanov, A. S. Melnikov, S. P. Tunik, M. Haukka and T. A. Pakkanen, *Inorg. Chem.,* 2013, **52**, 3663.

4 (a) A. Meyer, C. P. Bagowski, M. Kokoschka, M. Stefanopoulou, H. Alborzinia, S. Can, D. H. Vlecken, W. S. Sheldrick, S. Wçlfl and I. Ott, *Angew. Chem. Int. Ed.,* 2012, **51**, 8895; (b) A. Luening, J. Schur, L. Hamel, I. Ott and A. Klein, *Organometallics,* 2013, **32**, 3662.

5 (a) T. Kenny, S. Lamare, S. M. Aly, D. Fortin, G. Brisard and P. D. Harvey, *Inorg. Chem.,* 2012, **51**, 13081; (b) M. S. Khan, M. R. A. Al-Mandhary, M. K. Al-Suti, F. R. Al-Battashi, S. Al-Saadi, B. Ahrens, J. K. Bjernemose, M. F. Mahon, P. R. Raithby, M. Younus, N. Chawdhury, A. Köhler, E. A. Marseglia, E. Tedesco, N. Feeder and S. J. Teat, *Dalton Trans.,* 2004, 2377. (c) W.-Y. Wong and C.-L. Ho, *Acc. Chem. Res.,* 2010, **43**, 1246; (d) J. Mei, K. Ogawa, Y.-G. Kim, N. C. Heston, D. J. Arenas, Z. Nasrollahi, T. D. McCarley, D. B. Tanner, J. R. Reynolds and K. S. Schanze, *ACS Appl. Mater. Interfaces*, 2009, **1**, 150; (d) C. Olivier, B. S. Kim, D. Touchard and S. Rigaut, *Organometallics,* 2008, **27**, 509.

6 (a) I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr.,* 2002, **B58**, 389; (b) F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smith and D. G. Watson, *J. Chem. Inf. Comput. Sci.*, 1991, **31**, 187.

7 (a) *DOFCIM* (Au_8) *and ZABYEG* (Au_3): C.-M. Che, H.-K. Yip, W.-C. Lo and S.-M. Peng, *Polyhedron,* 1994, **13**, 887; (b) *FASSAT* (Au_6Pt): D. E. Smith, A. J. Welch, I. Treumicht and R. J. Puddephatt, *Inorg. Chem.,* 1986, **25**, 4616; (c) *FECGOJ10* (Pt_2Au): L. Manojlovic-Muir, K. W. Muir, I. Treurnicht and R. J. Puddephatt, *Inorg. Chem.,* 1987, **26**, 2418; (d) *IDUBAM and IDUBEQ* (Au_4): T. M. Dau, J. R. Shakirova, A. Domenech, J. Janis, M. Haukka, E. V. Grachova, T. A. Pakkanen, S. P. Tunik and I. O. Koshevoy, *Eur. J. Inorg. Chem.,* 2013, 4976; (e) *MOKJUR* (Os_3): O. A. Kizas, V. V. Krivykh, E. V. Vorontsov, O. L. Tok, F. M. Dolgushin and A. A. Koridze, *Organometallics,* 2001, **20**, 4170; (f) *PINDOH* (Mo_6): M. N. Sokolov, M. A. Mikhailov, K. A. Brylev, A. V. Virovets, C. Vicent, N. B. Kompankov, N. Kitamura and V. P. Fedin, *Inorg. Chem.,* 2013, **52**, 12477; (g) *REFWAB* (Ru_5): J. A. Cabeza, I. del Rio, L. Martinez-Mendez and D. Miguel, *Chem. Eur. J.,* 2006, **12**, 1529; (h) *REMPII* (Mo_6): T. Yamagata, H. Okiyama, H. Imoto and T. Saito, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.,* 1997, **53**, 859; (i) *SELBUG* (Os_3): A. A. Cherkas, N. J. Taylor and A. J. Carty, *J. Chem. Soc., Chem. Commun.,* 1990, 385; (j) *TAQZUH* (Au_5Ag_8): Q.-H. Wei, L.-Y. Zhang, G.-Q. Yin, L.-X. Shi and Z.-N. Chen, *Organometallics,* 2005, **24**, 3818; (k) *VACDOT and VACDUZ* (Pt_2Au): J. H. K.

Yip, J. Wu, K.-Y. Wong, K. P. Ho, C. S.-N. Pun and J. J. Vittal, *Organometallics,* 2002, **21**, 5292; (l) *WIWSIF* (Au_3): J. Vicente, J. Gil-Rubio, N. Barquero, P. G. Jones and D. Bautista, *Organometallics,* 2008, **27**, 646.

8 (a) *VINLUB* (Pt_3): V. Bonuccelli, T. Funaioli, P. Leoni, L. Marchetti and S. Zacchini, *Dalton Trans.,* 2013, **42**, 16898; (b) *BEMFIJ* (Pt_{18}): A. Albinati, P. Leoni, L. Marchetti and S. Rizzato, *Angew. Chem., Int. Ed.,* 2003, **42**, 5990; (c) *ILAJIO* (Pt_6): P. Leoni, F. Marchetti, L. Marchetti and M. Pasquali, *Chem. Commun.,* 2003, 2372; (d) *PAWHOL* (Pt_6): A. Albinati, F. Fabrizi de Biani, P. Leoni, L. Marchetti, M. Pasquali, S. Rizzato and P. Zanello, *Angew. Chem., Int. Ed.,* 2005, **44**, 5701; (e) *YOVWAI* and *YOVWEM* (Pt_3): C. Cavazza, F. Fabrizi de Biani, T. Funaioli, P. Leoni, F. Marchetti, L. Marchetti and P. Zanello, *Inorg. Chem.,* 2009, **48**, 1385.

9 Mainly Group 11 derivatives; selected recent examples: (a) T. U. Connell, S. Sandanayake, G. N. Khairallah, J. M. White, R. A. J. O'Hair, P. S. Donnelly and S. J. Williams, *Dalton Trans.,* 2013, **42**, 4903; (b) F. Gruber, M. Schulz-Dobrick and M. Jansen, *Chem. Eur. J.,* 2010, **16**, 1464; (c) S. C. K. Hau, P.-S. Cheng and T. C. W. Mak, *J. Am. Chem. Soc.,* 2012, **134**, 2922; (d) J. R. Berenguer, J. Fernandez, B. Gil, E. Lalinde and S. Sanchez, *Inorg. Chem.,* 2010, **49**, 4232; (e) T. Yamaguchi, T. Koike and M. Akita, *Organometallics,* 2010, **29**, 6493; (f) X. He, N. Zhu and V. W.-W. Yam, *Dalton Trans.,* 2011, **40**, 9703; (g) I. O. Koshevoy, A. J. Karttunen, S. P. Tunik, M. Haukka, S. I. Selivanov, A. S. Melnikov, P. Y. Serdobintsev and T. A. Pakkanen, *Organometallics,* 2009, **28**, 1369.

10 Selected recent examples: (a) I. S. Krytchankou, D. V. Krupenya, A. J. Karttunen, S. P. Tunik, T. A. Pakkanen, P.-T. Chou and I. O. Koshevoy, *Dalton Trans.,* 2014, **43**, 3383; (b) L.-J. Xu, J.-Y. Wang, L.-Y. Zhang, L.-X. Shi and Z.-N. Chen, *Organometallics,* 2013, **32**, 5402; (c) A. Himmelspach, M. Finze and S. Raub, *Angew. Chem. Int. Ed.,* 2011, **50**, 2628; (d) M. I. Bruce, M. Jevric, B. W. Skelton, A. H. White and N. N. Zaitseva, *J. Organomet. Chem.,* 2010, **695**, 1906; (e) V. Gonzalez-Lopez, M. A. Leyva and M. J. Rosales-Hoz, *Dalton Trans.,* 2013, **42**, 5401; (f) A. S. Estrada-Montano, M. A. Leyva, R. Grande-Aztatzi, A. Vela and M. J. Rosales-Hoz, *J. Organomet. Chem.,* 2014, **751**, 420; (g) M. Hernandez-Sandoval, F. J. Zuno-Cruz, M. J. Rosales-Hoz, M. A. Leyva, N. Andrade, V. Salazar and G. Sanchez-Cabrera, *J. Organomet. Chem.,* 2011, **696**, 4070; (h) T. Hu and T. C. W. Mak, *Eur. J. Inorg. Chem.,* 2013, 5476; (i) G. F. Manbeck, W. W. Brennessel, R. A. Stockland Jr and R. Eisenberg, *J. Am. Chem. Soc.,* 2010, **132**, 12307.

11 (a) H. Lang, D. S. A. George and G. Rheinwald, *Coord. Chem. Rev.,* 2000, **206–207**, 101; (b) W. H. Lam and V. W.-W. Yam, *Inorg. Chem.,* 2010, **49**, 10930; (c) G. Aullon and S. Alvarez, *Organometallics,* 2002, **21**, 2627; (d) U. Rosenthal, *Angew. Chem. Int. Ed.,* 2003, **42**, 1794; (e) G. Erker, W. Frömberg, R. Benn, R. Mynott, K. Angermund and C. Krüger, *Organometallics,* 1989, **8**, 911; (f) P. N. V. Pavan Kumar and E. D. Jemmis, *J. Am. Chem. Soc.,* 1988, **110**, 125; (g) I. Ara, J: R. Berenguer, E. Eguizabal, J. Fornies, E. Lalinde and A. Martin *Eur. J. Inorg. Chem*, 2001, 1631.

12 (a) L.-L. Wen, H. Wang, C.-Q. Wan and T. C. W. Mak, *Organometallics,* 2013, **32**, 5144; (b) Y. Zhao, P. Zhang, B. Li, X. Meng and T. Zhang, *Inorg. Chem.,* 2011, **50**, 9097; (c) F. Gruber, M. Schulz-Dobrick and M. Jansen, *Chem. Eur. J.,* 2010, **16**, 1464; (d) S. C. K. Hau and T. C. W. Mak, *J. Chin. Chem. Soc. (Taipei),* 2013, **60**, 877; (e) L. Zhao, C.-Q. Wan, J. Han, X.-D. Chen and T. C. W. Mak, *Chem. Eur. J.,* 2008, **14**, 10437; (f) L. Zhao and T. C. W. Mak, *J. Am. Chem. Soc.,* 2005, **127**, 14966; (g) T. C. W. Mak and L. Zhao, *Chem. Asian J.,* 2007, **2**, 456.

13 C. Bonaccorsi, F. Fabrizi De Biani, P. Leoni, F. Marchetti, L. Marchetti and P. Zanello, *Chem. Eur. J.,* 2008, **14**, 847.

14 a) P. Leoni, L. Marchetti, V. Bonuccelli, S. K. Mohapatra, A. Albinati and S. Rizzato, *Chem.-Eur. J.,* 2010, **16**, 9468; b) P. Leoni, L. Marchetti, S. K. Mohapatra, G. Ruggeri and L. Ricci, *Organometallics,* 2006, **25**, 4226.

15 a) F. Pevny, E. D. Piazza, L. Norel, M. Drescher, R. F. Winter and S. Rigaut, *Organometallics*, 2010, **29**, 5912; b) C. E. Powell, M. P. Cifuentes, J. P. Morrall, R. Stranger, M. G. Humphrey, M. Samoc, B. Luther-Davies and G. A. Heath, *J. Am. Chem. Soc.*, 2003, **125**, 602; c) M. P. Cifuentes, C. E. Powell, J. P. Morrall, A. M. McDonagh, N. T. Lucas, M. G. Humphrey, M. Samoc, S. Houbrechts, I. Asselberghs, K. Clays, A. Persoons and T. Isoshima, *J. Am. Chem. Soc.*, 2006, **128**, 10819.

16 a) M. Anselmi, V. Bonuccelli, T. Funaioli, P. Leoni, F. Marchetti, L. Marchetti, S. K. Mohapatra and M. Pasquali, Dalton Trans., 2013, 42, 10855; b) P. Leoni, F. Marchetti, L. Marchetti, M. Pasquali and S. Quaglierini, *Angew. Chem., Int. Ed.*, 2001, **40**, 3617.

17 F. Fabrizi de Biani, A. Ienco, F. Laschi, P. Leoni, F. Marchetti, L. Marchetti, C. Mealli and P. Zanello, *J. Am. Chem. Soc.,* 2005, **127**, 3076.

18 a) K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi and N. Nagihara, *J. Organomet. Chem.*, 1978, **145**, 101; b) J. Stahl, J. C. Bohling, T. B. Peters, L. de Quadras and J. A. Gladysz, *Pure Appl. Chem.*, 2008, **80**, 459; c) E. Baralt, E. A. Boudreaux, J. N. Demas, P. G. Lenhert, C. M. Lukehart, A. T. McPhail, D. R. McPhail, J. B. Jr. Myers, L. Sacksteder and W. R. True, *Organometallics*, 1989, **8**, 2417; d) M. Ciriano, J. A. K. Howard, J. L. Spencer, F. G. A. Stone and H. Wadepohl, *J. Chem. Soc., Dalton Trans.*, 1979, 1749; e) S. Crementieri, P. Leoni, F. Marchetti, L. Marchetti and M. Pasquali, *Organometallics*, 2002, **21**, 2575.

19 M. Ravera, R. D'Amato and A. Guerri, *J. Organomet. Chem.*, 2005, **690**, 2376.

20 a) S. K. Hurst, M. P. Cifuentes, A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, I. Asselberghs and A. Persoons, *J. Organomet. Chem.,* 2002, **642**, 259; b) S. Marqués-González, M. Parthey, D. S. Yufit, J. A. K. Howard, M. Kaupp and P. J. Low, *Organometallics*, 2014, **33**, 4947; c) V. W.-W. Yam, R. P.-L. Tang, K. M.-C. Wong, and K.-K. Cheung, *Organometallics*, 2001, **20**, 4476.

21 a) C.-K. Kuo, J.-C. Chang, C.-Y. Yeh, G.-H. Lee, C.-C. Wang and S.-M. Peng, *Dalton Trans.*, 2005, 3696; b) F. Paul, B. G. Ellis, M. I. Bruce, L Toupet, T. Roisnel, K. Costuas, J.-F. Halet, and C. Lapinte, *Organometallics*, 2006, **25**, 649; c) N. Gauthier, N. Tchouar, F. Justaud, G. Argouarch, M. P. Cifuentes, L. Toupet, D. Touchard, J.-F. Halet, S. Rigaut, M. G. Humphrey, K. Costuas and F. Paul, *Organometallics*, 2009, **28**, 2253; d) W. Lu, B.-X. Mi, M. C. W. Chan, Z. Hui, C.-M. Che, N. Zhu and S.-T. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 4958.

22 a) H. M. Wen, Y. H. Wu, Y. Fan, L. Y. Zhang, C. N. Chen and Z. N. Chen, Inorg. Chem., 2010, 49, 2210; b) R. Denis, L. Toupet, F. Paul and C. Lapinte, Organometallics, 2000, 19, 4240; c) V. W.-W. Yam, W. K.-M. Fung and K.-K. Cheung, *J. Cluster Sci.*, 1999, **10**, 37; d) V. W.-W. Yam, W. K.-M. Fung and M.-T. Wong *Organometallics*, 1997, **16**, 1772; e) C. Baik, W.-S. Han, Y. Kang, S. O. Kang and J. Ko, *J. Organomet. Chem.*, 2006, **691**, 5900.

23 M. Krejčik, M. Daněk and F. Hartl, *J. Electroanal. Chem*., 1991, **317**, 179.

24 H. L. M. van Gaal, M.W. M. Graef and A. Van der Ent, *J. Organomet Chem*., 1977, 131,453.

25 a) P. A. Brooksby and A. J. MacQuillan, *J. Phys. Chem. C*, 2010, **114**, 17604; b) A. Gabrielsson, P. Matousek, M. Towrie, F. Hartl, S. Záliš and A. Vlček, Jr., *J. Phys. Chem. A*, 2005, **109**, 6147; c) A. O. Baronetskii and G. M. Kuz'yants, *Russ. Chem. Bullet.*, 1980, **29**, 1267; d) J. Laane and J. R. Ohlsen, *Progr. Inorg. Chem.*, Vol. 27, 465.

26 a) J. H. Wagenknecht, *J. Org. Chem.*, 1977, *11*, 1836. b) J. H. Wagenknecht, G. V. Johnson *J. Electrochem. Soc.*, 1987, **134**, 2754.
27 a) R. Bender, P. Braunstein, A. Dedieu, P. D. Ellis, B. Huggins, P. D. Harvey, E. Sappa and A. Tiripicchio, *Inorg. Chem.*, 1996, **35**, 1223; b) R. Bender, P. Braustein, A. Tiripicchio and M. Tiripicchio Capellini, *Angew. Chem., Int. Ed.*, 1985, **24**, 861; c) J. R. Phillips, G. A. Miller and W. C. Trogler, *Acta Crystallogr., Sect. C (Cr. Str. Comm)*, 1990, **46**, 1648.
28 O. Lavastre, L. Ollivier, P. H. Dixneuf and S. Sibandhit, *Tetrahedron,* 1996, **52**, 5495.
29 A. Pelter and D. E. Jones, *J. Chem. Soc., Perkin Trans.,* **1**, 2000, 2289.
30 Sheldrick, G. M. *SADABS*, Program for empirical absorption correction, University of Göttingen, Germany, **1996**.
31 SHELX97 - Programs for Crystal Structure Analysis (Release 97-2). Sheldrick, G.M., Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
32 Farrugia, L. J. *J. Appl. Crystallogr*., **1999**, *32*, 837-838.