Metallochain Cluster Complexes and Metallomacrocyclic Triangles Based on Coordination Bonds between Palladium or Platinum and Diphosphinoacetylene Ligands

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Abstract: To explore the potential of the coordination chemistry of Pd and Pt halides with phosphinoacetylene ligands for the generation of novel, highly metallated organometallic coordination polymers, investigations on model compounds $[MX_2(PPh_2C{\equiv}CPh)_2]$ that exhibit *trans*-configured Pd centers and *cis*-configured Pt centers have been performed. The molecular structure of the *trans*-Pd complexes **2** (M = Pd, X = Br) and **5** (M = Pd, X = I) appeared suitable for the generation of linear materials, whereas the *cis*-Pt complex **6** (M = Pt, X = I) suggested the prospective formation of ring systems. The presence of acetylene moieties allowed for further increase of metal concentration by cluster formation with $[Co_2(CO)_8]$. Two novel bimetal cluster complexes **7** and **8** were obtained from **5** and **6**, respectively, and these exhibit a bridging iodine ligand as an interesting structural motif leading to heterocyclic systems with M-I-Co-C-P skeletons (M = Pd or Pt). A similar approach with $[Fe_2(CO)_9]$ led to the formation of several products, including an unusual Pd–Fe cluster-containing compound **10**. The extension of the coordination strategy to rigid bis(phosphinoacetylene) ligands gave rise to strained ring systems. Surprisingly, for the *cis*-configured $PtCl_2$ center, a rarely observed triangular structure **12** was obtained exclusively. The corresponding PtI_2 analog, **13a** rearranged over time to form a "ring-fused" system **13b** with an extended BINAP-like ligand.

Keywords: cluster compounds · metallocycles · platinum · ring-opening polymerization · self-assembly

Introduction

The incorporation of metal atoms into macromolecular structures and supramolecular assemblies offers considerable promise for the development of new functional materials with novel properties.[1–4] For example, the presence of transition metal centers has been shown to permit redox control of the size and shape of a macroscopic object[5] and the "wiring" of enzymes to electrodes,[6] selective binding and sensing,[7] and the generation of liquid crystallinity[8] and magnetic nanoparticle composites,[9, 10] etch resistance to plasmas,[11, 12] as well as other desirable physical and chemical characteristics.[13] The use of covalent bonds to create main-chain metallopolymers is now relatively well-developed as illustrated by the cases of extensively studied systems such as polyferrocenes and polymetallaynes.[3, 14, 15] Coordinate bonds provide an attractive, alternative approach to the construction of metallopolymers. However, only over the past decade have soluble examples of such materials been convincingly characterized. Most work in this area to date has focused on the use of bidentate, π-conjugated N-donor ligands as spacer units.[2, 16]

Despite the ubiquitous nature of phosphine ligation in transition-metal chemistry, the utility of metal–P-donor interactions for the creation of metallopolymers is relatively unexplored.[17–22] The first examples of polymers based on bisphosphine linkers were reported by Cowie in 1988[21] and Wright in 1992.[22] However, the analysis and structural characterization of the materials were limited owing to their reduced solubility. In 1993 partially soluble Au-containing materials **I** based on rigid bisphosphines were reported by Puddephatt et al.[17] In this case the presence of bulky side groups is necessary for appreciable solubility. The polymers show luminescence in solution and solid state due to conjugation along the backbone indicating interesting electronic properties.[18, 19] More recently, James et al. demonstrated the ring-opening polymerization (ROP) of strained silver bis(diphenylphosphino)acetylene cage molecules **II** (Ag_2L_3) to give the corresponding coordination polymers

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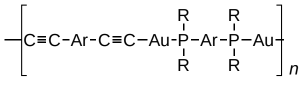
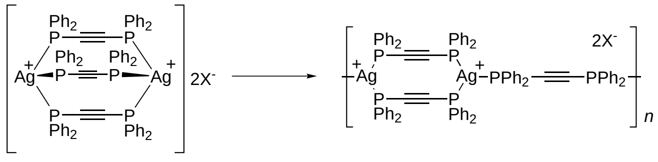


I

R = Ph, *i*Pr; Ar = phenylene, biphenylene



II **III**

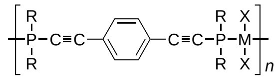
X = OTf, NO_3, BF_4

III.[20] Although the resulting materials were insoluble in common solvents, characterization by single-crystal X-ray diffraction was possible.

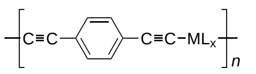
As part of our research on the development of processable, highly metallated macromolecular materials we have targeted novel Pd and Pt bis(phosphinoacetylene) coordination structures. The formation of cluster complexes with the acetylenic units present in such materials would provide an additional possibility for the introduction of metal atoms to high-molecular-weight coordination polymers. With these ultimate aims in mind, in this paper we report our initial studies in this area and describe model compounds for prospective high polymers, including metallochain model compounds, cluster species, and unusual Pt containing metallomacrocycles.

Results and Discussion

We have targeted on the preparation of novel Group 10 coordination structures **IV** that can be considered as "inverse" Hagihara-type polymetallynes, such as **V**, as they possess skeletal M–P and P–C≡C bonds rather than M–C≡C bonds.



IV M = Pd, Pt
X = Cl, Br, I

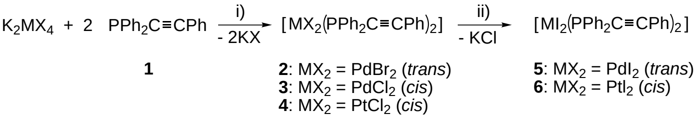


V M = Ni, Pd, Pt, Ru
L = PR_3

We chose Group 10 metal halides for our investigations as they are known to form strong bonds with phosphine ligands and the resulting complexes are stable towards the atmosphere. As a result of their square-planar coordination geometry, only two possible isomers, *cis* and *trans*, exist. Centers with the latter geometry are of particular interest for our purpose as the formation of polymers **IV** rather than rings would be expected to be thermodynamically preferred.

Synthesis and characterization of phosphinoacetylene complexes: The coordination chemistry of monophosphinoacetylene ligands with Group 10 metals has been previously explored by Carty et al.[23–26] These investigations showed that the *cis* or *trans* geometry preference for such complexes is primarily dictated by the nature of the metal or the halide. Thus, the Pt complexes appear to always possess the *cis* configuration, irrespective of the nature of the halide substituents.[23, 24] In the case of Pd complexes, on the other hand, the geometry of the complex is determined by the nature of the halide.[23] Chloro substituents generally afford *cis* complexes, whereas iodo substituents afford *trans* species. However, in the case of $PdBr_2$ the complex geometry is influenced by the nature of the phosphine substituents as well; both complex isomers can be obtained with different ligands.[23]

We prepared the new complex **2** as well as the previously reported species **3** and **4**, according to the known procedure by reaction of the phosphinoacetylene **1** with the corresponding tetrahalo metallate {K_2PdBr_4 or K_2MCl_4 (M = Pd or Pt)} in a mixture of H_2O/EtOH (1:2).[23] Subsequent transhalogenation of the chloro complexes **3** and **4** with KI in acetone[23a] afforded the iodinated complexes **5** and **6** in quantitative yield (Scheme 1). In the ^{31}P NMR spectra of the two new species **2** and **5**, and the previously described **6** single resonances (**2**: $\delta = 6.6$; **5**: $\delta = -14.8$; **6**: $\delta = -11.8$ ppm, $J(Pt,P) = 3475$ Hz) were observed, indicating the formation of one isomer only. It is interesting to note that, although phosphinoacetylene complexes of Group 10 metals have been known for more than 30 years, very few have been structurally characterized by X-ray crystallography. In this context, *trans*-configured complexes are completely unexplored, and very few examples of *cis* isomers are described in the literature.[24, 26] The geometry of complexes **2**, **5**, and **6**[27] was therefore verified by single-crystal X-ray structure analyses. The molecular structures of **5** and **6** are depicted in Figure 1.



$$K_2MX_4 + 2\ PPh_2C{\equiv}CPh \xrightarrow[-2KX]{i)} [MX_2(PPh_2C{\equiv}CPh)_2] \xrightarrow[-KCl]{ii)} [MI_2(PPh_2C{\equiv}CPh)_2]$$

1

2: $MX_2 = PdBr_2$ (*trans*)
3: $MX_2 = PdCl_2$ (*cis*)
4: $MX_2 = PtCl_2$ (*cis*)

5: $MX_2 = PdI_2$ (*trans*)
6: $MX_2 = PtI_2$ (*cis*)

Scheme 1. Synthesis of the model compounds **2**–**6**. Reaction conditions: i) H_2O/EtOH (1:2), RT, 24 h; ii) KI, acetone, RT, 30 min.

The isostructural Pd complexes **2** and **5** were found to possess *trans* geometries, whereas for the Pt complex the configuration was *cis*, as anticipated. The structural parameters of the PtI_2 complex **6**, as presented in Table 1, are unexceptional and are similar to those of **4**.[24] The same

Table 1. Selected bond lengths [Å] and angles [°] for **2**, **5**, and **6**.

	2	**5**	**6**
M–P	2.3201(7)	2.3266(9)	2.2566(15) 2.2661(15)
M–X	2.4341(3)	2.6055(2)	2.6287(6) 2.6483(6)
P–C_α	1.752(3)	1.754(4)	1.759(6) 1.753(6)
C_α–C_β	1.202(4)	1.204(5)	1.202(8) 1.196(6)
P-M-P	180.00(2)	180.00(3)	92.73(6)
X-M-X	180.000(17)	180.000(9)	88.25(3)
M-P-C_α	114.39(10)	115.86(13)	119.08(19) 109.5(2)
P-C_α-C_β	168.1(3)	168.0(3)	165.9(5) 173.2(5)

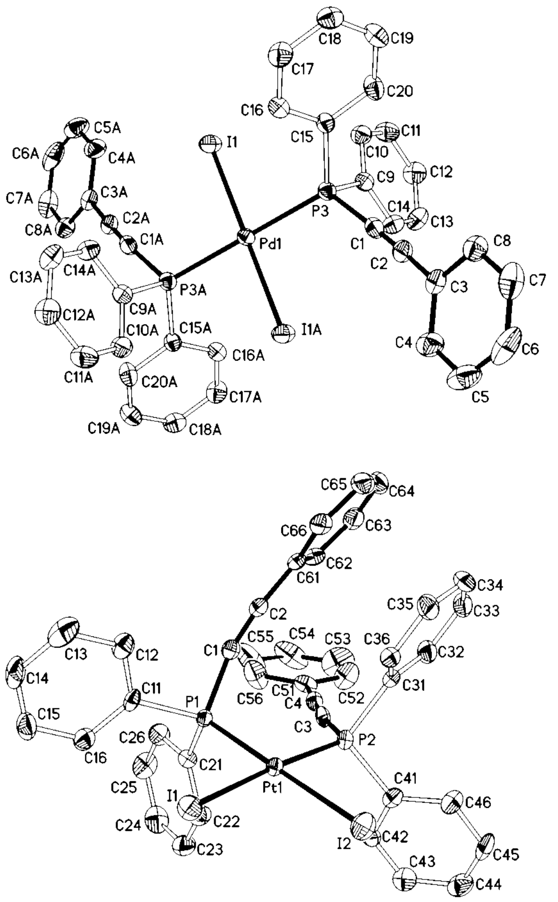
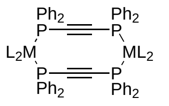


Figure 1. Molecular structure of **5** (top) and **6** (bottom) with thermal ellipsoids at the 50% probability level. H atoms and one $CHCl_3$ solvent molecule (**6**) are omitted for clarity.

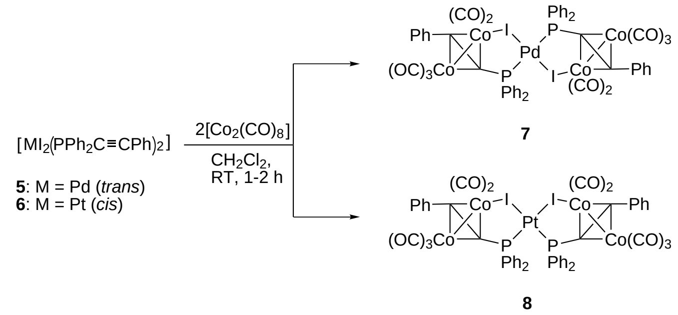
applies for **2** and **5**, whose structural data are comparable to those of the related complexes $[Pd(PPh_3)_2Br_2]$[28a] and $[Pd(PPh_3)_2I_2]$.[28b] It should be mentioned that the two acetylene units in **6** do not have a coplanar arrangement with respect to the central PtI_2P_2 plane. As observed for **4**,[24] the two P–C≡C units exhibit a *cisoid* arrangement with a torsion angle (τ) at Pt of 69.4° between them. However, the X-ray structures, which confirm the *trans* nature of **2** and **5**, reinforce the notion that the formation of coordination polymers should be favored for the Pd systems. The Pt complex **6** on the other hand, indicates that a macrocycle formation may be preferred in this case. Indeed, cyclic dimers based on *cis*-configured Pt or Pd complexes with bis(diphenylphosphino)acetylene ligands are well known.[29]



M = Pd, Pt
L = halogen, PR_3, bipy

Synthesis and characterization of phosphinoacetylene cluster complexes

Reaction with $[Co_2(CO)_8]$: As noted previously, phosphinoacetylene complexes are potentially interesting precursors to highly metallated cluster-containing organometallic materials. As a cluster component, we investigated the tetrahedral, redox-active acetylene-dicobaltcarbonyl unit, accessible by reaction of $[Co_2(CO)_8]$ with alkynes.[30] Reaction of **5** with two equivalents of $[Co_2(CO)_8]$ affords the cluster model compound **7** in good yield (82%; Scheme 2). The reaction was performed in CH_2Cl_2 at room temperature and was easily monitored by the evolution of CO. The black cluster compound **7** gave a single ^{31}P NMR resonance at $\delta = 50.3$ ppm, and the downfield shift of the signal relative to **5** suggested the formation a five-membered ring system.[31] The ^1H and ^{13}C NMR data were unexceptional and in accordance with literature data for comparable tetrahedral Co cluster compounds.[32] We were able to obtain suitable black crystals of **7** for an X-ray diffraction study at room temperature from a concentrated solution of **7** in CH_2Cl_2. The structural data show the former triple bonds capped by a $\{Co_2(CO)_6\}$ unit, as expected (Figure 2). The bond lengths and angles of the cluster unit as presented in Table 2 are similar to those of comparable Co_2C_2 cluster compounds.[32] The complex geometry is not affected by the cluster formation. The phosphine ligands as well as the iodine ligands are *trans* to each other as



Scheme 2. Synthesis of the Co-cluster compounds **7** and **8**.

Table 2. Selected bond lengths [Å] and angles [°] for **7** and **8**.

	7	8
M–I	2.6197(4)	2.6718(6) 2.6566(6)
M–P	2.3459(15) 2.3460(15)	2.2599(19) 2.2723(19)
Co–I	2.5949(9)	2.5979(11) 2.5944(12)
P–C_α	1.770(6)	1.760(8) 1.781(7)
Co1–C1	1.945(6)	1.928(7)
Co3–C8[a]		1.921(7)
C_α–C_β	1.364(8)	1.362(10) 1.361(10)
P-M-P	180.00(7)	96.73(7)
I-M-I	180.00(2)	85.216(18)
M-P1-C1	109.1(2)	107.9(3)
Pt1-P2-C8[a]		110.1(2)
P1-C1-Co1	124.6(3)	128.3(4)
P2-C8-Co3[a]		126.3(4)
C1-Co1-I1	91.22(17)	89.9(2)
C8-Co3-I2[a]		89.7(2)
Co1-I1-M	104.60(2)	103.18(3)
Co3-I2-Pt1[a]		104.16(3)

[a] Only applicable for **8**.

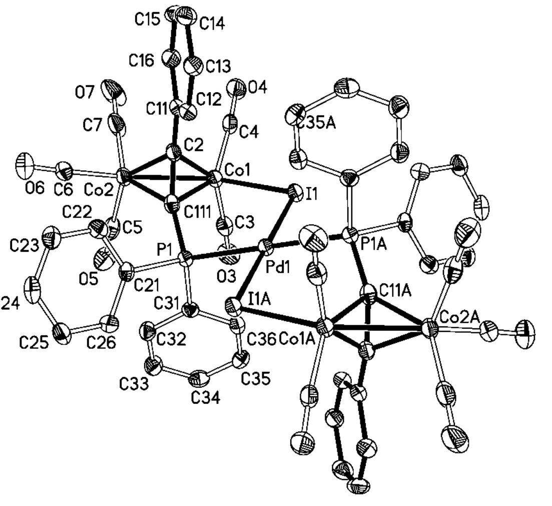


Figure 2. Molecular structure of **7** with thermal ellipsoids at the 50% probability level. H atoms and two CH_2Cl_2 solvent molecules are omitted for clarity.

observed for the starting material. However, a very intriguing feature of the structure of **7** are the iodine atoms bridging the central Pd atom and one of the Co atoms, thereby replacing one of the carbonyl ligands. Owing to the bridging mode the Pd–I bonds are slightly elongated (2.6197(4) Å vs 2.6055(2) Å in **5**). The Co–I bonds amount to 2.5949(9) Å, which is significantly shorter than in the few other structurally characterized iodine-substituted cobalt carbonyl compounds (c.f. 2.642(2);[33] 2.649(1), 2.639(1);[34] 2.630(2)/2.623(3), 2.604(2)/2.610(2) Å[35]). This suggests an electronic interaction between the central Pd atom and the Co atom through the bridging iodine, which is potentially interesting for the electronic properties of the material. To the best of our knowledge a bridging halide has not previously been observed in tetrahedral Co–acetylene clusters.

The only examples for bridging atoms involve S[36] and P[37] atoms utilized in enantioselective Pauson–Khand reactions. It is interesting to note that the bridging iodine atoms in **7** do not distort the environment of the Pd atom. A near perfect square-planar geometry is maintained (angles: P-Pd-P/I-Pd-I = 180.00(2)°). However, the interaction leads to a distortion of the former acetylene units; both terminating phenyl groups are rotated approximately 80° each out of the PdI_2P_2 plane, compared with about 31° in the noncluster compound **5**. However, due to the simultaneous rotation they still exhibit a *trans* arrangement to each other, which is also favorable for a possible polymeric structure.

We also synthesized and characterized the corresponding Pt analogue. Species **8** is accessible in a similar reaction by treatment of **6** with two equivalents of $[Co_2(CO)_8]$. The ^{31}P NMR resonance of $\delta = 37.9$ ppm ($J(Pt,P) = 3695$ Hz) is again shifted downfield from the starting material **6** ($\delta = -11.8$ ppm; $J(Pt,P) = 3475$ Hz), due to the ring-contribution of the five-membered ring system.[31] The single-crystal X-ray structure analysis of **8** shows that the *cis*-configured cluster–Pt model compound also contains iodine bridges (Figure 3). As a consequence, the Pt–I bonds of 2.6566(6) and 2.6718(6) Å are slightly elongated relative to **6** (2.6287(6), 2.6483(6) Å). The Co–I bonds of 2.5979(11) and 2.5944(12) Å are in the same range as those found in **7**. The other structural features are similar to those observed for **7** (Table 2). However, the environment at the central Pt atom in **8** is affected by the binding to the cluster in this case. Thus, the I-Pt-I angle of 85.22(2)° is slightly smaller than that in **6** (88.25(3)°), whereas the P-Pt-P angle is slightly wider (96.73(7) vs 92.73(6)° in **6**). Due to the bridging iodine an intriguing structural motif is formed in **7** and **8**: a bimetallic, spirocyclic system with the Pd or Pt atom as central atoms. The monocyclic subunits consist of five different atoms (Pd-P-C-Co-I or Pt-P-C-Co-I) and exhibit an envelope conformation.

Another striking structural feature in **8** is the *trans* orientation of the terminating phenyl groups (angle ≈155°) as observed for **7** before. The corresponding angle for the starting material **6** amounts to ≈70°, that is, a *cisoid* orientation of the terminating phenyl groups.

To compare the bridging character of different halides, we also attempted to synthesize the corresponding chloro- and bromo-substituted complexes. However, the reaction of **2** or **4** with two equivalents of $[Co_2(CO)_8]$ afforded a variety of products. In the case of the Pt precursor **4**, one minor product appeared to be similar to compounds **7** and **8**, based on the presence of a ^{31}P NMR resonance at $\delta = 31.6$ ppm ($J(Pt,P) = 3255$ Hz). However, the appearance of several other resonances in the ^{31}P NMR spectrum without Pt satellites indicate that decomplexation reactions are likely in the case of the Cl- and Br-substituted complexes. In the case of related Co-cluster-bridged phosphinoacetylenes dimeric decomplexation products were observed that support this assumption.[38]

Reaction with $[Fe_2(CO)_9]$: To investigate a possible extension of our synthetic approach to iron clusters, we attempted to

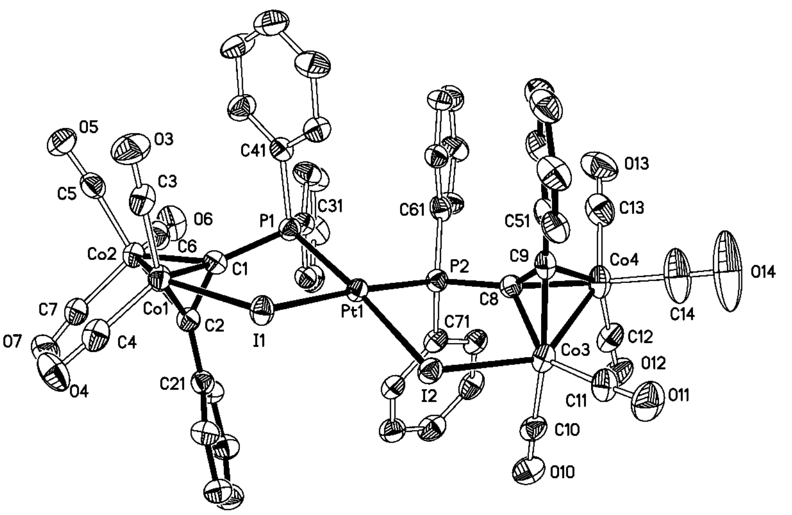
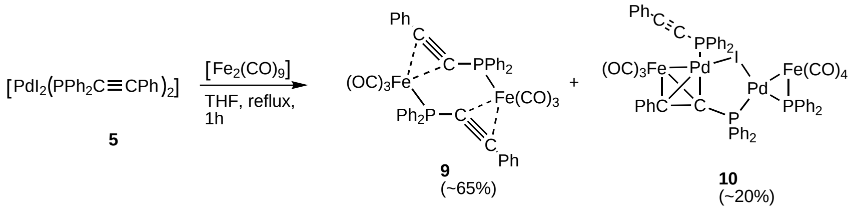


Figure 3. Molecular structure of **8** with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.

react the phosphinoacetylene model complexes with $[Fe_2(CO)_9]$. However, reaction of **2**, **5**, or **6** with varying amounts of $[Fe_2(CO)_9]$ (2, 4, 8, equiv) in refluxing THF resulted in the formation of several products in every case. The major product, the cyclic dimer **9**,[39] is observed in almost all reactions (Scheme 3); this compound apparently arises from decomplexation of the phosphine ligand from the Pd or Pt center and subsequent dimerization. This observation mirrors the increased reactivity of $[Fe_2(CO)_9]$ towards acetylenes.

Table 3. Selected bond lengths [Å] and angles [°] for **10**.

Pd1–I1	2.6884(8)	Pd1–Fe1	2.5165(12)	C8-P2-Pd2	110.8(2)
Pd2–I1	2.6783(7)	Fe1–C8	1.999(8)	P2-Pd2-I1	91.38(5)
Pd2–P2	2.306(2)	Fe1–C9	1.884(7)	Pd2-Fe2-P3	53.09(6)
P2–C8	1.759(8)	C8–C9	1.356(10)	Fe2-Pd2-P3	54.06(6)
C8–Pd1	2.100(6)			Fe2-P3-Pd2	72.85(6)
Pd2–Fe2	2.6425(12)	Pd1-I1-Pd2	98.06(2)	Fe1-Pd1-C9	45.95(18)
Pd2–P3	2.211(2)	I1-Pd1-C8	95.5(2)	Fe1-Pd1-C8	50.3(2)
Fe2–P3	2.239(2)	Pd1-C8-P2	122.9(4)	C8-Fe1-C9	40.7(3)



Scheme 3. Reaction of **5** with $[Fe_2(CO)_9]$.

However, in the reaction of **5** with four equivalents of $[Fe_2(CO)_9]$, we were able to isolate one of the minor products **10** (approx. 20% abundance). The ^{31}P NMR spectrum of **10** has three resonances, one of which is surprisingly shifted to low field ($\delta = 165.2$ ppm), whereas the other two resonances appear at higher field ($\delta = 37.5$ and -0.4 ppm), in the expected range for cluster-bound phosphinoacetylenes. The low-field ^{31}P NMR resonance is consistent with a μ^2-phosphido bridge,[40a,b] presumably generated by transition-metal-promoted cleavage of a P–C≡C bond. We were able to obtain brown single crystals of **10** at -30°C from CH_2Cl_2/MeCN (1:1) that were suitable for an X-ray structure analysis, confirming the formation of a very unusual cluster compound (important structural data are given in Table 3). The molecular structure of **10** is depicted in Figure 4. The surprising structural motifs include a diphenylphosphido unit bridging an Fe and Pd moiety,[40c] as anticipated from the ^{31}P NMR data, as well as the novel tetrahedral $PdFeC_2$ cluster unit. It is interesting to note, that although apparently two molecules of **5** were involved in the generation of **10**, only one iodine substituent and two phosphinoacetylene units, apart from the μ^2-phosphido bridge, are still present. As a result of the bridging mode of the remaining iodine substituent, another interesting structural feature is the five-membered heterocycle consisting of a Pd_2ICP skeleton, which is related to the heterocycles in **7** and **8**. Of further interest is the observation that one of the original phosphinoacetylene ligands still possesses an uncomplexed acetylene unit, although an excess of $[Fe_2(CO)_9]$ was used in the reaction. In conclusion to this section, the X-ray structure of **10** underlines the increased reactivity of $[Fe_2(CO)_9]$ towards acetylenes and suggests that the Fe-cluster chemistry is likely to be less useful than that with Co for our purpose.

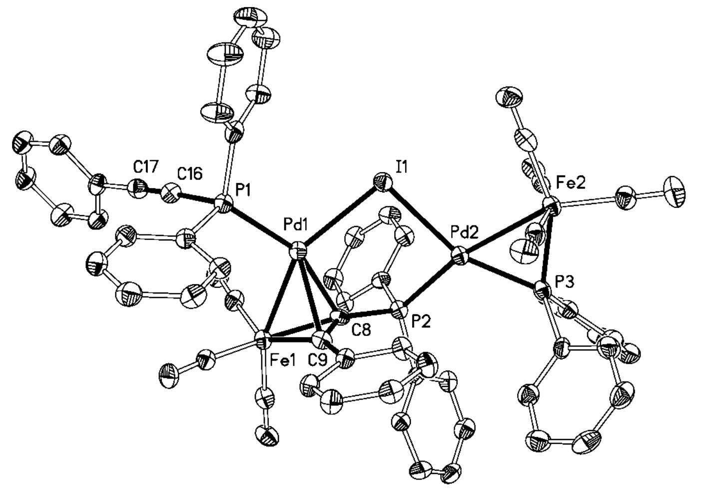


Figure 4. Molecular structure of **10** with thermal ellipsoids at the 30% probability level. H atoms, one CH_3CN, and two H_2O solvent molecules are omitted for clarity.

Synthesis and characterization of Pt-based macrocycles: As macrocyclic systems represent interesting models for the corresponding high-molecular-weight coordination polymers and are of intrinsic interest themselves,[41, 42] we explored the formation of such species in the case of Pt. Our investigations focused on the use of the rigid 1,4-diethynylbenzene-based bisphosphine **11** (Scheme 4), which is significantly longer than the bis(diphenylphosphino)acetylene (dppa) ligand usually used in the literature.[29] The steric effect associated with the presence of a phenylene moiety in **11** was expected to help suppress the formation of cyclic dimers in favor of larger rings. Moreover, phenylene moieties would, if necessary, allow the facile introduction of solubilizing substituents to polymers and a degree of electronic communication between the metal centers might be possible due to the π-conjugated nature of the ligand.

Reaction of K_2PtCl_4 with **11** in $CHCl_3$ for three days at room temperature selectively afforded the product **12** in quantitative yield. A single ^{31}P NMR resonance at $\delta = -8.4$ ppm ($J(Pt,P) = 3745$ Hz) indicated the formation of a product with *cis*-Pt centers and equivalent phosphorus atoms.

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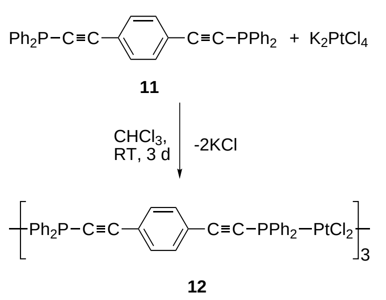


Scheme 4. Synthesis of **12**.

However, the exact structure could not be derived from experimental data in solution. Suitable colorless single crystals for an X-ray structure analysis were obtained at room temperature from a concentrated solution of **12** in $CHCl_3$/CH_2Cl_2/MeCN (1:1:1). The molecular structure of **12** is depicted in Figure 5. The structural data reveal the formation of the first cyclic trimer of a neutral Pt–bis(phosphine) complex and show an interpenetrating arrangement of the three ligands, linked by *cis*-configured square-planar $PtCl_2$ fragments perpendicular to the ring plane.

Surprisingly, the rarely observed exclusive[43] formation of a cyclic trimer seems to be favored here, although the square-planar complex geometry would allow for less strained, supramolecular squares.[44] Usually, triangular structures are only observed in coexistence with corresponding squares.[44] However, the interesting perpendicular arrangement seems to allow the Pt center to maintain its square-planar geometry. The Pt−Cl bond lengths of 2.336(2) or 2.338(2) Å and the Pt−P bond lengths of 2.242(2) or 2.243(2) Å are statistically the same and in agreement with the complex *cis*-$[PtCl_2(PPh_2C{\equiv}CPh)_2]$ (**4**) (2.335(2), 2.350(2), and 2.235(2), 2.237(2) Å, respectively[24]). The same is true for the corresponding angles (average P-Pt-P: ≈95.5(5)°; Cl-Pt-Cl: ≈88.0(8)°; vs 94.16(6)° and 88.64(7)°).

As a result of the unusual triangle motif in **12**, the torsion angles at the Pt centers indicate some strain present within the ring. Thus, the torsion angle τ (see discussion of the structure of **6** above) at Pt2 is significantly smaller ($\tau = 59.0°$) than those at Pt1 ($\tau = 69.0°$) and Pt3 ($\tau = 68.7°$), which are in agreement with those in **4** and **6** ($\tau = 69.4°$).[24] The apparently slightly strained nature of the ring system in **12** is potentially interesting for a ring-opening polymerization process.[44d] However, the reaction of **12** with KI in acetone proceeded through halogen exchange without any discernable ring-opening reactions. Triangle **13a** was found to slowly rearrange at room temperature over time (>weeks) to afford the "ring-fused" cyclic trimer **13b** (Scheme 5). The rearrangement proceeds through a [2+2+2]-cycloaddition with subsequent 1,3-H shift in a manner similar to that observed previously by Carty et al. for thermal reactions involving monophosphinoacetylene systems.[24] It is interesting to note that heating of the sample is not necessary to achieve the coupling chemistry required for the formation of **13b**. This is in contrast to the literature, in which rearrangement was only observed thermally (80 °C, refluxing benzene). The slightly strained nature the cyclic trimer ring may trigger the coupling process at lower temperatures. However, the rearrangement is only observed at two of the Pt centers, whereas the third Pt center remains unaffected. The ^{31}P NMR spectrum of **13b** showed three different resonances at $\delta = 49.7$, 36.2, and −9.3 ppm. The low-field shift of two of the phosphorus centers can be explained by the missing shielding effect of a neighboring acetylene unit, whereas for the third, high-field-shifted phosphorus resonance it is still present. The ^1H NMR spectrum clearly indicated the formation of a naphthalene unit with resonances similar to BINAP ($\delta = 8.13$, 6.76, 6.20, 5.87 ppm).

We were able to obtain single crystals that were suitable for X-ray structure analysis from a concentrated solution of **13b** in $CHCl_3$/CH_2Cl_2/MeCN (1:1:1) at room temperature. The molecular structure of **13b** (Figure 6) reveals that the fusion of the four acetylene units with two of the linking phenylene units generates an extended BINAP-like ligand structure with helical chirality. Differences to BINAP are an additional phenylene spacer, which links the two newly formed naphthalene subunits, and the two acetylene spacers between the naphthalene systems and P2 or P1, respectively. The bond lengths at the Pt centers (Pt2 and Pt3) are unexceptional (see Table 4), and the slight deviation of the bond angles from a perfect square-planar geometry can be explained by steric effects of the chelating bis(phosphino)phenylene ligands. The structural motif at the Pt1 center is comparable to the Pt centers in **13a** with a torsion angle of $\tau = 70.6°$. The Pt−P bond lengths of

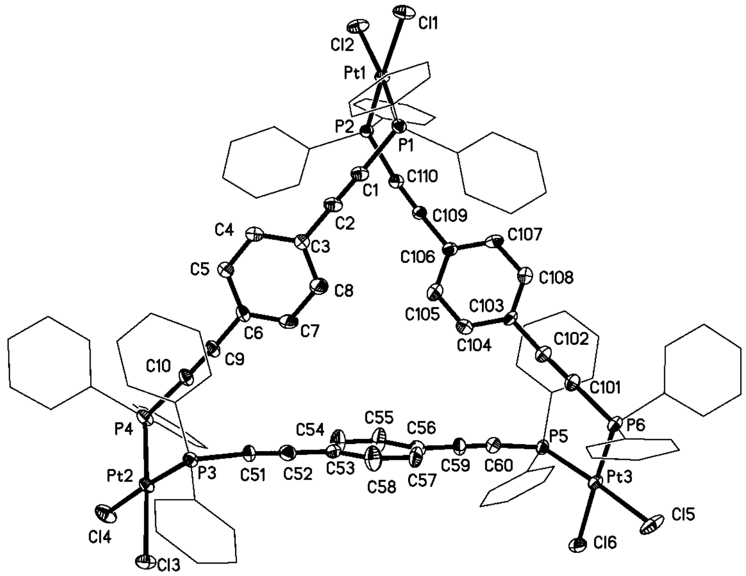
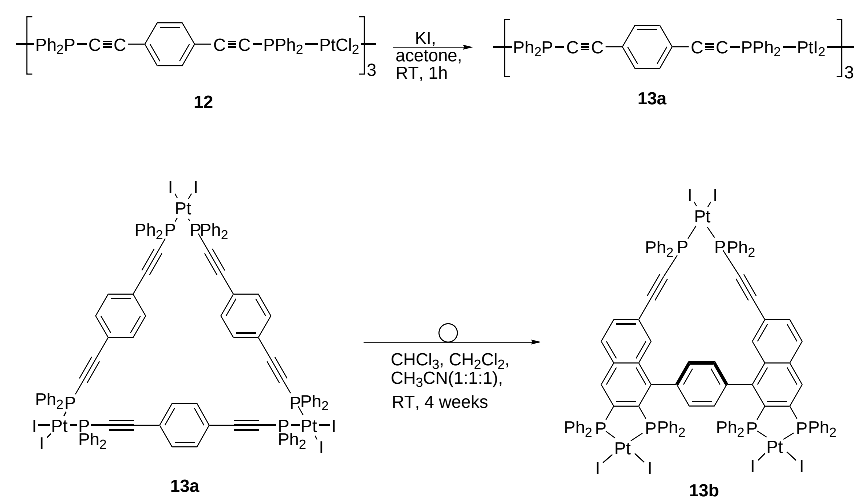


Figure 5. Molecular structure of **12** with thermal ellipsoids at the 30% probability level. H atoms and two $CHCl_3$ solvent molecules are omitted for clarity.



Scheme 5. Synthesis and reactivity of **13a**.

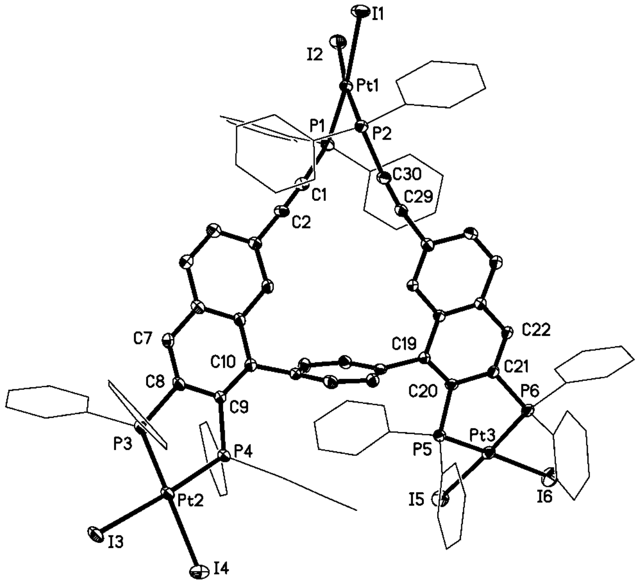


Figure 6. Molecular structure of **13b** with thermal ellipsoids at the 30% probability level. H atoms and two $CHCl_3$ solvent molecules are omitted for clarity.

2.2461(17) and 2.2520(16) Å are elongated compared to **13a** and the corresponding Pt–P distances at Pt2 and Pt3. The P1-Pt1-P2 angle of 91.80(6)° is slightly smaller than in **13a** (c.f. average P-Pt-P: ≈95.5(5)°). The slight differences can be attributed to the strained nature of the ring system caused by the BINAP-like ligand.

However, attempts to ring-open the triangle **13a** in solution were unsuccessful. Refluxing **13a** in toluene for 24 hours resulted in the formation of about 50% of the ring-fused triangle **13b** in addition to unreacted **13a**. This again emphasizes the templating effect of the triangular structure in **13a** to lead to an *intra*molecular rearrangement rather than an *inter*molecular polymerization process caused by the proximity of the acetylene ligands.

Conclusion

Our initial investigations on the potential for the use of Pd and Pt complexes for the generation of novel organometallic coordination polymers led to the synthesis and structure characterization of two new Pd phosphinoacetylene complexes **2** and **5** and the verification of the *cis*-configured structure of the ligands in the Pt complex **6**. Compounds **5** and **6** were transformed into the novel bimetal cluster complexes **7** and **8**, which exhibit interesting structural features such as bridging iodine atoms between Co and Pd leading to heterocycles with M-I-Co-C-P skeletons, and an *anti* conformation of the terminal phenyl groups. A similar reaction with $[Fe_2(CO)_9]$ emphasized the increased reactivity of $[Fe_2(CO)_9]$ towards acetylenes and led to the formation of several products, including the very unusual Pd–Fe-cluster-containing complex **10** with a bridging PPh_2 moiety leading to a cyclic Pd-Fe-P unit. The use of extended, rigid bis(phosphinoacetylene) ligands allowed the synthesis of rarely observed molecular triangles with *cis*-configured Pt centers. The triangular structure in the PtI_2 complex **13a** and the resulting proximity of the acetylene moieties templated a rearrangement reaction; this led to the formation of the "fused-ring" system **13b** with an extended BINAP-like structure at room temperature. However, attempts the ring-open the triangular complex **13a** in solution were unsuccessful. Due to the

Table 4. Selected bond lengths [Å] and angles [°] for **12** and **13b**.

	12	**13b**
Pt1–P	2.242(2)	2.2461(17)
	2.2429(19)	2.2520(16)
Pt2–P	2.231(2)	2.2092(17)
	2.245(2)	2.2425(15)
Pt3–P	2.236(2)	2.2183(17)
	2.240(2)	2.2380(15)
Pt1–X	2.3362(19)	2.6372(5)
	2.338(2)	2.6542(5)
Pt2–X	2.336(2)	2.6557(5)
	2.338(2)	2.6584(6)
Pt3–X	2.337(2)	2.6440(5)
	2.342(2)	2.6542(6)
P-Pt1-P	95.27(7)	91.80(6)
P-Pt2-P	95.27(7)	87.61(6)
P-Pt3-P	96.48(8)	84.13(6)
X-Pt1-X	88.24(8)	88.078(17)
X-Pt2-X	87.29(8)	90.559(17)
X-Pt3-X	88.62(8)	90.823(19)

templating nature of the ring system *intra*molecular formation of **13b** was observed exclusively.

Interestingly, the structures of the cluster model compounds **7** and **8** indicate that ring-opening polymerization of **12** and **13a** might be induced by reaction with $[Co_2(CO)_8]$. Both model compounds clearly indicate this possibility through the *trans* arrangement of the terminating phenyl rings; this would increase the strain in the corresponding ring systems dramatically. Moreover, the coordination chemistry the *trans*-oriented Pd system should favor the formation of macromolecules rather than ring systems and this possibility is also currently under detailed investigation.

Experimental Section

General procedures: Reactions, unless otherwise noted, were carried out in dry glassware and under inert atmosphere of purified nitrogen by using Schlenk techniques. Solvents were dried over appropriate drying agents and then distilled or they were obtained by the Grubbs method.[45] Phenylethynyl(diphenyl)phosphine (**1**),[46] $[MCl_2(PPh_2C{\equiv}CPh)_2]$ (**3**: M = Pd,[23] **4**: M = Pt[24]) and *p*-Bis(diphenylphosphinoethynyl)benzene (**11**)[47] were prepared according to literature procedures. KI and $[Fe_2(CO)_9]$ were purchased from Aldrich and used as received. K_2PtCl_4, K_2PdCl_4, K_2PdBr_4, and $[Co_2(CO)_8]$ were purchased from Strem and used as received. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Varian Gemini 300, Mecury 300 or Unity 400 MHz spectrometers. Chemical shifts were referenced to solvent peaks. Mass spectra were obtained with the use of a VG 70–250S mass spectrometer operating in electron impact (EI) mode. The calculated isotopic distribution for each ion was in agreement with experimental values. Elemental analyses were performed by Quantitative Technologies, Whitehouse, NJ.

X-ray diffraction studies: Crystal data and details of the data collection are provided in Tables 5 and 6. Diffraction data were collected on a Nonius Kappa-CCD using graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). A combination of 1° ϕ and ω (with κ offsets) scans were used collect sufficient data. The data frames were integrated and scaled by using the Denzo-SMN package. The structures were solved and refined with the SHELXTL-PC V5.1 software package. Refinement was by full-matrix least-squares on F^2 using all data (negative intensities included). In all structures hydrogen atoms bonded to carbon atoms were included in calculated positions and treated as riding atoms.

CCDC-180449 (**7**), CCDC-180450 (**8**), CCDC-180451 (**2**), CCDC-180452 (**5**), CCDC-180453 (**10**), CCDC-180454 (**6**), CCDC-180455 (**12**), and CCDC-180456 (**13b**), contain the supplementary, crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Synthesis of complex 2: (Inert conditions were not necessary for this procedure.) Phosphine ligand **1** (1.14 g; 4 mmol), dissolved in ethanol (2 mL), was added to a solution of K_2PdBr_4 (1.0 g, 2 mmol) in water (4 mL). The reaction mixture was stirred for 24 h at room temperature and the solvent then removed under vacuum. The residue was taken up in CH_2Cl_2 (10 mL) and filtered through a frit to remove the KCl/KBr. Slow evaporation of the solvent afforded **2** in a quantitative yield as yellow crystals (1.67 g, 99%). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ = 6.6 ppm; ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): δ = 7.85 (brdd, 8H; Ph), 7.51 to 7.40 (m, 14H; Ph), 7.22 (brt, 4H; Ph), 6.97 ppm (brd, 4H; Ph); $^{13}C\{^1H\}$ NMR: δ = 134.1 (d, *J*(C,P) = 12.9 Hz; Ph), 134.0 (s; Ph), 132.1 (s; Ph), 131.6 (s; Ph), 130.6 (s; Ph), 128.6 (d, *J*(C,P) = 13.0 Hz; Ph), 128.5 (d, *J*(C,P) = 8.3 Hz; Ph), 120.5 (s; Ph), 110.7 (br; C≡C), 95.7 ppm (br; C≡C); MS: *m/z* (%): 837 (3) $[M^+]$, 759 (15) $[M^+ - Br]$, 286 (100) $[Ph_2PCCPh^+]$, 77

Table 5. Crystal data and structure refinement for **2**, **5**, and **6**.

	2	**5**	**6** · $CHCl_3$
formula	$C_{40}H_{30}Br_2P_2Pd$	$C_{40}H_{30}I_2P_2Pd$	$C_{41}H_{31}Cl_3I_2P_2Pt$
M_r	838.80	932.78	1140.84
T [K]	150(1)	150(1)	150(1)
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a [Å]	10.3323(3)	10.3684(3)	11.7902(2)
b [Å]	16.6952(3)	17.0295(4)	14.0487(2)
c [Å]	10.4290(3)	10.4871(3)	24.0427(5)
α [°]	90	90	90
β [°]	109.1280(10)	110.0940(10)	91.770(6)
γ [°]	90	90	90
V [Å^3]	1699.68(8)	1738.98(8)	3980.46(12)
Z	2	2	4
ρ_{calcd} [Mg m^{-3}]	1.639	1.781	1.904
μ [mm^{-1}]	3.019	2.429	5.387
F(000)	832	904	2168
crystal size [mm^3]	0.32 × 0.20 × 0.20	0.18 × 0.16 × 0.16	0.35 × 0.28 × 0.20
θ range [°]	3.20–27.50	3.16–27.51	2.79–25.06
index ranges	$0 \le h \le 13$	$0 \le h \le 13$	$0 \le h \le 14$
	$0 \le k \le 21$	$0 \le k \le 21$	$0 \le k \le 16$
	$-13 \le l \le 12$	$-13 \le l \le 12$	$-28 \le l \le 28$
reflections collected	13720	14243	24150
independent reflections	3897 [*R*(int) = 0.065]	3974 [*R*(int) = 0.055]	6966 [*R*(int) = 0.048]
completeness to θ [°]	27.50, 99.7%	27.51, 99.6%	25.06, 98.7%
absorption correction	multi-scan	multi-scan	semi-empirical
max./min. transmission	0.5835/0.4450	0.6973/0.6690	0.4121/0.2543
data/restraints/parameters	3897/0/206	3974/0/206	6966/0/443
goodness-of-fit on F^2	1.057	1.033	1.013
final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0360$, $wR2 = 0.0878$	$R1 = 0.0337$, $wR2 = 0.0753$	$R1 = 0.0338$, $wR2 = 0.0857$
R indices (all data)	$R1 = 0.0480$, $wR2 = 0.0932$	$R1 = 0.0502$, $wR2 = 0.0827$	$R1 = 0.0445$, $wR2 = 0.0914$
extinction coefficient	0.0018(6)	0.0014(3)	0.00072(9)
largest diff. peak/hole [e Å^{-3}]	0.928/−1.030	1.223/−0.754	1.569/−1.178

Table 6. Crystal data and structure refinement for **7**, **8**, **10**, **12**, and **13b**.

	7 $\cdot 2\,CH_2Cl_2$	**8**	**10** $\cdot 0.5\,MeCN \cdot 2\,H_2O$	**12** $\cdot 2\,CHCl_3$	**13b** $\cdot 2.5\,CHCl_3$
formula	$C_{52}H_{34}Cl_4Co_4I_2O_{10}P_2Pd$	$C_{50}H_{30}Co_4I_2O_{10}P_2Pt$	$C_{60}H_{45.50}Fe_2IN_{0.50}O_9P_3Pd_2$	$C_{104}H_{74}Cl_{12}P_6Pt_3$	$C_{104.50}H_{73.50}Cl_{7.50}I_6P_6Pt_3$
M_r	1618.45	1537.29	1461.78	2520.12	3127.50
T [K]	150(1)	150(1)	150(1)	150(1)	150(1)
crystal system	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [Å]	9.6702(10)	14.7065(10)	9.6077(3)	27.3897(3)	17.9913(2)
b [Å]	11.1270(10)	18.0698(14)	14.4550(5)	19.9725(4)	18.1767(2)
c [Å]	13.4841(14)	20.1236(13)	23.2666(11)	21.6238(6)	1.2848(2)
α [°]	99.413(5)	90	95.8000(10)	90	67.4270(10)
β [°]	90.983(5)	108.446(5)	93.5850(10)	109.228(8)	76.3250(10)
γ [°]	105.873(6)	90	107.4460(10)	90	74.8940(10)
V [Å^3]	1373.8(2)	5073.0(6)	3052.1(2)	11169.2(4)	6132.23(11)
Z	1	4	2	4	2
ρ_{calcd} [Mg m^{-3}]	1.956	2.013	1.591	1.499	1.694
μ [mm^{-1}]	2.936	5.365	1.683	4.163	5.204
$F(000)$	784	2928	1446	4904	2940
crystal size [mm^3]	0.25 × 0.25 × 0.23	0.23 × 0.16 × 0.13	0.30 × 0.10 × 0.06	0.15 × 0.13 × 0.06	0.15 × 0.13 × 0.10
θ range [°]	2.59–27.60	2.69–25.03	2.87–26.06	2.57–25.05	2.84–27.57
index ranges	$0 \leq h \leq 12$ $-14 \leq k \leq 13$ $-17 \leq l \leq 17$	$0 \leq h \leq 17$ $0 \leq k \leq 21$ $-22 \leq l \leq 22$	$0 \leq h \leq 11$ $-17 \leq k \leq 17$ $-28 \leq l \leq 28$	$-32 \leq h \leq 30$ $-23 \leq k \leq 0$ $0 \leq l \leq 25$	$0 \leq h \leq 23$ $-22 \leq k \leq 23$ $-26 \leq l \leq 27$
reflections collected	41665	72051	24379	58481	96470
independent reflections	6195 [$R(int) = 0.058$]	8359 [$R(int) = 0.062$]	11516 [$R(int) = 0.078$]	19405 [$R(int) = 0.051$]	28117 [$R(int) = 0.048$]
completeness to θ [°]	27.60, 96.8 %	25.03, 93.2 %	26.06, 95.5 %	25.05, 98.1 %	27.57, 99.0 %
absorption correction	multi-scan	multi-scan	semi-empirical	semi-empirical	semi-empirical
max/min transmission	0.5516/0.5273	0.5422/0.3717	0.9058/0.6322	0.7883/0.5740	0.6241/0.5090
data/restraints/parameters	6195/12/359	8359/0/622	11516/2/713	19405/15/1102	28117/36/1158
goodness-of-fit on F^2	1.035	1.082	1.014	1.029	1.031
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0537$, $wR2 = 0.1139$	$R1 = 0.0445$, $wR2 = 0.0954$	$R1 = 0.0615$, $wR2 = 0.1495$	$R1 = 0.0503$, $wR2 = 0.1169$	$R1 = 0.0475$, $wR2 = 0.1298$
R indices (all data)	$R1 = 0.0859$, $wR2 = 0.1276$	$R1 = 0.0648$, $wR2 = 0.1049$	$R1 = 0.1015$, $wR2 = 0.1729$	$R1 = 0.0824$, $wR2 = 0.1266$	$R1 = 0.0655$, $wR2 = 0.1399$
extinction coefficient	none	none	0.0019(4)	none	0.00064(6)
largest diff. peak/hole [e Å^{-3}]	1.468/ – 0.986	1.429/ – 1.025	1.245/ – 1.192	2.416/ – 2.120	6.083/ – 2.207

(90) [Ph$^+$]; elemental analysis calcd (%) for $C_{40}H_{30}Br_2P_2Pd$ (837.3): C 57.27, H 3.60; found: C 57.24, H 3.53.

Synthesis of complexes 5 and 6: The chloro-substituted compounds **3** (1.49 g, 2 mmol) and **4** (1.67 g, 2 mmol) were each dissolved in acetone (15 mL). KI (0.67 g, 4 mmol) was added, and the reaction mixture stirred for 30 min at room temperature. The solvent was removed under vacuum, and the residue taken up in CH_2Cl_2 (10 mL) and filtered through a frit subsequently. Slow evaporation of the solvent at room temperature afforded **5** (1.86 g, 99 %) and **6** (2.04 g, 99 %) as red/yellow crystals in quantitative yield.

Complex 5: $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = -14.8$ ppm; ^1H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 7.78$ (m, 8H; Ph), 7.61 (m, 4H; Ph), 7.42–7.29 ppm (m, 18H; Ph); $^{13}C\{^1H\}$ NMR: $\delta = 134.1$ (d, J(C,P) = 13.3 Hz; Ph), 134.0 (s; Ph), 132.8 (s; Ph), 131.4 (s; Ph), 130.8 (s; Ph), 128.9 (d, J(C,P) = 25.8 Hz; Ph), 128.7 (d, J(C,P) = 11.7 Hz; Ph), 125.9 (s; Ph), 101.5 (br; C≡C), 87.1 ppm (br; C≡C); MS: m/z (%): 932 (2) [M^+], 805 (5) [$M^+ - I$], 204 (95) [PhI$^+$], 77 (100) [Ph$^+$]; elemental analysis calcd (%) for $C_{40}H_{30}I_2P_2Pd$ (931.9): C 51.50, H 3.24; found: C 51.15, H 3.21.

Complex 6: $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 20 °C): $\delta = -11.8$ ppm (^1J(P,Pt) = 3475 Hz); ^1H NMR (300 MHz, C_6D_6, 20 °C): $\delta = 7.96$ (m, 8H; Ph), 7.10–6.73 ppm (m, 22H; Ph); $^{13}C\{^1H\}$ NMR: $\delta = 134.2$ (d, J(C,P) = 11.4 Hz; Ph), 134.2 (s; Ph), 132.0 (s; Ph), 131.4 (s; Ph), 130.4 (s; Ph), 128.3 (d, J(C,P) = 2.2 Hz; Ph), 128.3 (d, J(C,P) = 6.1 Hz; Ph), 120.6 (s; Ph), 108.9 (br; C≡C), 95.7 ppm (br; C≡C); MS: m/z (%): 1021 (5) [M^+], 894 (55) [$M^+ - I$], 178 (100) [PhCCPh$^+$], 77 (40) [Ph$^+$]; elemental analysis calcd (%) for $C_{40}H_{30}I_2P_2Pt$ (1021.5): C 47.03, H 2.96; found: C 47.25, H 2.87.

Synthesis of the Co-cluster model compounds: [$Co_2(CO)_8$] (0.75 g, 2.2 mmol) was added at room temperature to a solution of the complex **5** (0.93 g; 1 mmol) or **6** (1.02 g; 1 mmol) in CH_2Cl_2 (30 mL). The reaction mixture was stirred for 1–2 h, until no further CO evolution was observed. The solvent and any unreacted [$Co_2(CO)_8$] were then evaporated under vacuum. The residue was dissolved in CH_2Cl_2 (15 mL) and filtered through neutral alumina. The cluster-bound product was obtained from the concentrated solution at −30 °C as black crystals in good yield (**7**: 1.33 g, 82 %; **8**: 1.20 g, 78 %).

Complex 7: $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 20 °C): $\delta = 50.3$ ppm; ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): $\delta = 8.26$ (br m, 4H; Ph), 8.03 (br m, 4H; Ph), 7.42 (br m, 6H; Ph), 7.42–6.88 ppm (m, 16H; Ph); $^{13}C\{^1H\}$ NMR: $\delta = 198.7$ (br; CO), 196.1 (br; CO), 134.1 (br; Ph), 133.0 (br; Ph), 132.8 (s; Ph), 132.2 (s; Ph), 131.4 (s; Ph), 130.8 (s; Ph), 129.1 (d, J(C,P) = 9.0 Hz; Ph), 128.7 (d, J(C,P) = 6.6 Hz; Ph), 100.5 (br; C≡C), 78.7 ppm (br; C≡C); IR (solid, nujol): $\tilde{\nu} = 2064$, 2016, 2007, 1994, 1963 cm^{-1} (C≡O); MS (FAB positive ionization): m/z (%): 1448 (10) [M^+], 1421 (15) [$M^+ - CO$], 1364 (100) [$M^+ - 3CO$], 1336 (60) [$M^+ - 4CO$]; elemental analysis calcd (%) for $C_{52}H_{34}Cl_4Co_4I_2O_{10}P_2Pd$ (1618.5): C 38.59, H 2.12; found: C 38.31, H 2.27.

Complex 8: $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 20 °C): $\delta = 37.9$ ppm (J(P,Pt) = 3695 Hz); ^1H NMR (300 MHz, C_6D_6, 20 °C): $\delta = 8.13$ (br m, 8H; Ph), 7.17 (br, 10H; Ph), 6.75 (br, 4H; Ph), 6.53 (br, 4H; Ph), 6.32 ppm (br, 4H; Ph); $^{13}C\{^1H\}$ NMR: $\delta = 204.1$ (br; CO), 200.9 (br; CO), 197.8 (br; CO), 141.1 (br; Ph), 136.3 (br; Ph), 132.7 (br; Ph), 131.7 (br; Ph), 130.4 (br; Ph), 130.0 (s; Ph), 128.8 (s; Ph), 127.6 (s; Ph), 106.2 (br; C≡C), 96.4 ppm (br; C≡C); IR (solid, nujol): $\tilde{\nu} = 2068$, 2027, 2020, 1996, 1989 cm^{-1} (C≡O); MS (FAB pos ionization): m/z (%): 1482 (5) [$M^+ - 2CO$], 1453 (35) [$M^+ - 3CO$], 1398 (25) [$M^+ - 5CO$], 1342 (50) [$M^+ - 7CO$], 1314 (50) [$M^+ - 8CO$], 1286 (50) [$M^+ - 9CO$], 1257 (100) [$M^+ - 10CO$]; elemental analysis calcd (%) for $C_{50}H_{30}Co_4I_2O_{10}P_2Pt$ (1538.2): C 39.06, H 1.97; found: C 38.86, H 2.19.

Synthesis of Fe-cluster model compounds: Complex **5** (0.93 g, 1 mmol) was dissolved in THF (25 mL) and [$Fe_2(CO)_9$] (1.45 g, 4 mmol), suspended in THF (25 mL), was added at room temperature. The reaction mixture was then refluxed for 1 h. After cooling to room temperature, the solution was analyzed by ^{31}P NMR spectroscopy. The analysis revealed the generation of about 65 % of **9**, 20 % of **10** and approx. 15 % of unidentified products. The solvent was then evaporated under vacuum, the residue taken up in CH_2Cl_2 (25 mL) and filtered over neutral alumina. The red solution was evaporated to dryness again and toluene (10 mL) and MeCN (5 mL) were added.

Brown crystals of **10** were obtained after 6 days at -30 °C in 15 % yield (0.10 g).

Complex 9: $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 20 °C): $\delta = 50.8$ ppm; ^1H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 7.90$ (br d, J(H,P) = 7.5 Hz, 8 H; Ph), 7.75 (m, 4 H; Ph), 7.42–7.27 ppm (m, 18 H; Ph); $^{13}C\{^1H\}$ NMR: $\delta = 213.0$ (d, J(C,P) = 19.2 Hz; CO), 134.2 (d, J(C,P) = 57.5 Hz; Ph), 132.4 (s; Ph), 132.0 (d, J(C,P) = 12.3 Hz; Ph), 131.2 (d, J(C,P) = 2.6 Hz; Ph), 130.5 (s; Ph), 128.9 (d, J(C,P) = 11.7 Hz; Ph), 128.7 (s; Ph), 121.0 (s; Ph), 111.7 (d, J(C,P) = 15.8 Hz; C≡C), 83.0 ppm (d, J(C,P) = 96.7 Hz; C≡C).

Complex 10: $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 166.4$, 37.1, -0.5 ppm; ^1H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 8.16$ (d, J(H,P) = 6.8 Hz, 4 H; Ph), 8.13 (d, J(H,P) = 7.2 Hz, 2 H; Ph), 8.10 (d, J(H,P) = 6.8 Hz, 2 H; Ph), 7.65–7.06 (m, 24 H; Ph), 6.96–6.84 (m, 8 H; Ph); $^{13}C\{^1H\}$ NMR: $\delta = 215.1$ (br; CO), 207.1 (br; CO), 136.9 (d, J(C,P) = 13.8 Hz; Ph), 134.0–122.3 (m, 40 C; Ph), 113.5 (s; Ph), 95.7 (br; C≡C), 71.9 ppm (br; C≡C); elemental analysis calcd (%) for $C_{59}H_{40}Fe_2IO_7P_3Pd_2$ (1405.3): C 50.43, H 2.87; found: C 48.87, H 2.95.

Synthesis of 12: (Inert conditions were not necessary for this procedure.) Bisphosphine **11** (0.19 g, 0.4 mmol), dissolved in $CHCl_3$ (15 mL) was added to a suspension of K_2PtCl_4 (0.17 g, 0.4 mmol) in $CHCl_3$ (20 mL) at room temperature. The reaction mixture was stirred for 3 d, the solvent removed under vacuum, and the residue taken up in water (10 mL). The product was filtered off and evaporated to dryness again, and the residue taken up in $CHCl_3/CH_2Cl_2$/MeCN (60 mL; 1:1:1 mixture). Slow evaporation of the solvent at room temperature afforded **12** as colorless crystals in 54 % yield (0.49 g). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 20 °C): $\delta = -8.4$ ppm (s, J(P,Pt) = 3745 Hz); ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): $\delta = 7.61$ (dd, J = 12.6, 7.8 Hz, 24 H; Ph), 7.58–7.37 (m, 36 H; Ph), 6.72 ppm (s, 12 H; C_6H_4); $^{13}C\{^1H\}$ NMR: $\delta = 134.0$ (br; Ph), 132.8 (s; Ph), 131.3 (s; ar-CH), 129.0 (s; Ph), 128.8 (s; Ph), 122.1 (s; ar-C), 100.2 (br; C≡C), 89.4 ppm (br; C≡C); MS (FAB positive ionization): m/z (rel. intensity) 2244(5) [M^+-Cl], 1251(100) [M^+-2$PtCl_2$-L]; elemental analysis calcd (%) for $C_{102}H_{72}Cl_6P_6Pt_3$ (2281.5): C 53.70, H 3.18; found: C 53.33, H 3.24.

Synthesis of 13a: (Inert conditions were not necessary for this procedure.) The triangle **12** (0.45 g, 0.2 mmol) was dissolved in acetone (20 mL) and KI (0.20 g, 1.2 mmol) was added at room temperature. The reaction mixture was stirred for 1 h, the solvent removed under vacuum, and the residue taken up in CH_2Cl_2 (15 mL). The product was filtered off and evaporated to dryness to afford **13a** in quantitative yield (0.56 g, 99 %) as orange powder. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 20 °C): $\delta = -11.5$ ppm (s, J(P,Pt) = 3502 Hz); ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): $\delta = 7.79$ (dd, J = 5.2, 2.8 Hz, 24 H; Ph), 7.48–7.31 (m, 36 H; Ph), 6.55 (s, 12 H; C_6H_4); $^{13}C\{^1H\}$ NMR: $\delta = 134.6$ (br; Ph), 132.2 (s; Ph), 131.0 (s; ar-CH), 128.9 (s; Ph), 128.8 (s; Ph), 122.2 (s; ar-C), 106.7 (br; C≡C), 85.3 ppm (br; C≡C); elemental analysis calcd (%) for $C_{102}H_{72}I_6P_6Pt_3$ (2830.2): C 43.29, H 2.56; found: C 42.54, H 2.24.

Synthesis of 13b: (Inert conditions were not necessary for this procedure.) A solution of **13a** (0.40 g; 0.14 mmol) in $CHCl_3/CH_2Cl_2$/MeCN (30 mL, 1:1:1 mixture) was kept for 3 weeks at room temperature. Subsequent slow evaporation of the solvent at room temperature afforded **13b** as yellow crystals in 56 % yield (0.22 g). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 20 °C): $\delta = 49.7$ (s, J(P,Pt) = 3301 Hz), 36.2 (s, J(P,Pt) = 3233 Hz), -9.3 ppm (s, J(P,Pt) = 3500 Hz); ^1H NMR (400 MHz, CD_2Cl_2, 20 °C): $\delta = 8.13$ (d, J = 10.0 Hz, 2 H; ar-H), 8.01 (dd, J = 14.1, 7.2 Hz, 4 H; ar-H), 7.82 (dd, J = 11.7, 6.3 Hz, 4 H; ar-H) 7.87–6.99 (m, 48 H; ar-H), 6.76 (d, J = 8.0 Hz, 2 H ar-H), 6.53 (br, 4 H; ar-H), 6.47 (s, 4 H; ar-H), 6.20 (d, J = 8.0 Hz, 2 H; ar-H), 5.87 ppm (d, J = 8.5 Hz, 2 H; ar-H); $^{13}C\{^1H\}$ NMR: $\delta = 144.6$–128.0 (br; naphthyl-C), 121.3 (s; ar-C), 117.1 (s; ar-C), 105.4 (br; C≡C), 89.3 ppm (br; C≡C). elemental analysis calcd (%) for $C_{102}H_{72}I_6P_6Pt_3 \cdot CHCl_3$ (2949.54): C 41.94, H 2.49; found: C 41.63, H 2.39.

Acknowledgements

T.B. would like to thank the Deutsche Forschungsgemeinschaft (DFG) for a research fellowship. S.S. thanks the Deutscher Akademischer Austauschdienst (DAAD) for a research fellowship. I.M. thanks the NSERC for an E.W.R. Steacie Fellowship (1997–1999), the University of Toronto for a McLean Fellowship (1997–2003), the Ontario Government for a PREA Award (1999–), and the Canadian Government for a Canada Research Chair (2001–) for the duration of the work described.

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Received: March 1, 2002 [F3918]