

Some complexes containing Pt-C₅-Co₃ fragments: Molecular structure of *trans*-Pt{C≡CC≡C-μ₃-C[Co₃(μ-dppm)-(CO)₆(PPh₃)]₂(PPh₃)₂ determined using synchrotron radiation

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Abstract

Reactions of platinum(II) chloro-phosphine complexes with Co₃(μ₃-CC≡CC≡CSiMe₃)(μ-dppm)(CO)₇ in the presence of NaOMe have given the compounds Pt{C≡CC≡C-μ₃-C[Co₃(μ-dppm)(CO)₇]}₂(dppe) (**1**), *trans*-Pt{C≡CC≡C-μ₃-C[Co₃(μ-dppm)(CO)₇]}₂(PEt₃)₂ (**2**) and *trans*-Pt{C≡CC≡C-μ₃-C[Co₃(μ-dppm)(CO)₆(PPh₃)]₂(PPh₃)₂ (**3**), each of which contains two Co₃ clusters linked by C₅ chains to the Pt centre. Electrochemical studies (CVs) show the presence of both oxidation and reduction processes, the latter probably occurring on the CCo₃ cores. Ready reductive elimination of {Co₃(μ-dppm)(CO)₇}₂(μ₃:μ₃-C₁₀) occurs from **1** upon heating. The X-ray study of **3** was carried out using synchrotron radiation (Advanced Photon Source, Argonne, IL) to confirm its structure. © 2005 Elsevier B.V. All rights reserved.

Keywords: Cobalt cluster; Platinum; Poly-yne; X-ray structure; Synchrotron radiation

1. Introduction

There is continuing interest in the chemistry and properties of metal complexes containing carbon chains linking transition metal centres [1,2]. This arises in part from their potential as materials with potential for opto-electronic applications [3] and as models for molecular scale wires [4], as well as on account of their inherent interest. A considerable amount of work has been reported using platinum(II)-phosphine complexes as end groups, which includes the extensive studies of Gladysz and coworkers [2b] on ever-longer chains and the construction of sequences containing two or more platinum centres. While our own studies of platinum complexes have so far been limited to the construction of neutral molecular squares containing C₄ chains linking the metal centres [5], we have recently become interested in the preparation of heterome-

tallic systems containing odd-numbered carbon chains [6]. Recently, we were able to prepare compounds which contain two C₅ chains linking platinum centres with tricobalt clusters, and to characterise one of these structurally. This chemistry is described below.

2. Results and discussion

The preparation of platinum(II) alkynyl complexes by reaction of appropriate 1-alkynes with complexes of the type PtX₂(P)₂ [X = halide, *cis* or *trans* isomers for monodentate P = PR₃, (P)₂ = bidentate phosphines] in the presence of sodium methoxide was described many years ago [7]. More recently, it has become apparent that similar complexes are directly accessible from the often more stable trimethylsilyl-substituted alkynes, desilylation occurring in situ [8]. Most recently, the in situ desilylation and oxidative coupling of the resulting alkynes has been used to effect the synthesis of several long chain complexes including {*trans*-Pt(tol)[P(tol)₃]₂}₂{μ-(C≡C)₁₄} which

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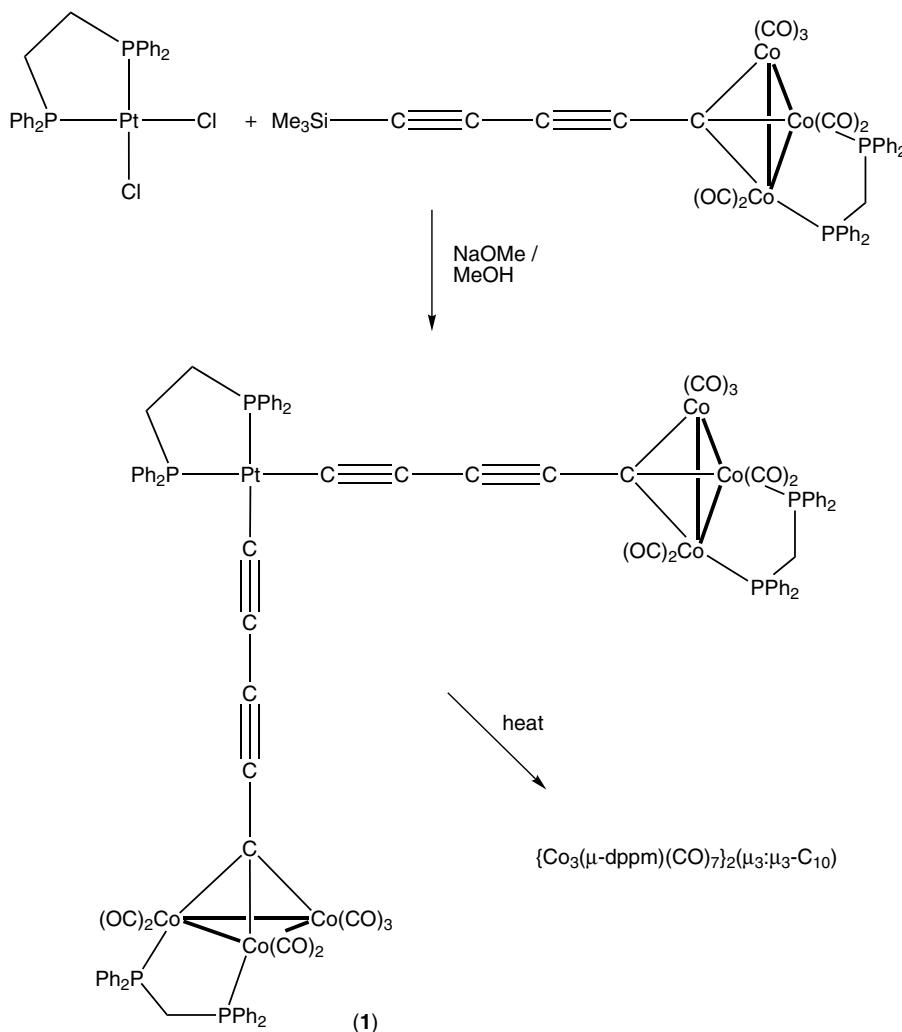
contains the longest chain linking two metal centres that has so far been characterised [9].

Application of the original methodology to reactions between $\text{PtCl}_2(\text{PR}_3)_2$ [$(\text{PR}_3)_2 = \text{dppe}$, $\text{PR}_3 = \text{PEt}_3$, PPh_3] and two equivalents of $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CC}\equiv\text{CSiMe}_3)(\mu\text{-dppm})(\text{CO})_7$ [6b] has resulted in the successful preparation of the compounds $\text{Pt}\{\text{C}\equiv\text{CC}\equiv\text{C}-\mu_3\text{-C}[\text{Co}_3(\mu\text{-dppm})(\text{CO})_7]\}_2(\text{dppe})$ (**1**; Scheme 1), *trans*- $\text{Pt}\{\text{C}\equiv\text{CC}\equiv\text{C}-\mu_3\text{-C}[\text{Co}_3(\mu\text{-dppm})(\text{CO})_7]\}_2(\text{PEt}_3)_2$ (**2**) and *trans*- $\text{Pt}\{\text{C}\equiv\text{CC}\equiv\text{C}-\mu_3\text{-C}[\text{Co}_3(\mu\text{-dppm})(\text{CO})_6(\text{PPh}_3)]\}_2(\text{PPh}_3)_2$ (**3**; Scheme 2), each of which contains two C_5 chains linking the Pt centre with Co_3 clusters. The complexes are obtained in low to moderate yields as red to brown solids which have been characterised through a combination of elemental analyses and spectroscopic methods and, in the case of **3**, by an X-ray structural determination.

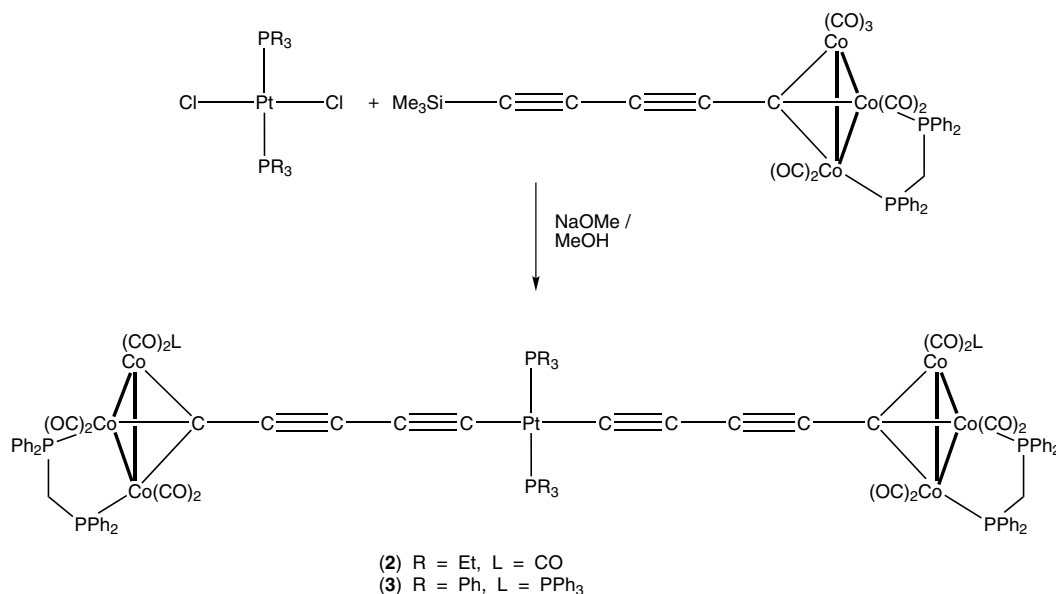
Complex **1** was obtained in the highest yield (52%), but on standing or heating in solution (particularly in chlorinated solvents), some decomposition resulted with formation of the C_{10} derivative $\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}_2(\mu_3\text{:}\mu_3\text{-C}_{10})$, identified by comparison with an authentic sample [11]. The IR spectrum of **1** contains a weak $\nu(\text{CC})$ band at

2152 cm^{-1} and terminal $\nu(\text{CO})$ bands between 2090 and 1962 cm^{-1} with a pattern characteristic of the substituted $\text{Co}_3(\text{CO})_7$ cluster. Resonances characteristic of the dppe and dppe ligands are found in the ^1H and ^{31}P NMR spectra, the latter containing two signals at δ_{P} 34.0 (s, dppe) and 40.86 [triplet with $J(\text{PPt}) = 2269\text{ Hz}$, dppe] in a 2/1 ratio. The magnitude of $J(\text{PPt})$ in the latter confirms the expected *cis* geometry. In the ^{13}C NMR spectrum, resonances at δ 95.30, 97.49 and 103.90 are assigned to atoms in the C_5 chain, the Co_3C nucleus being too broadened by the cobalt quadrupole to be observed, while the PtC resonance is probably not found because of coupling to P and Pt. The Co–CO resonances occur at δ 202.56, 210.41 and 224.31. The overall composition is confirmed by ions in the electrospray mass spectrum (ES MS) at m/z 2251 $[\text{M} + \text{Na}]^+$ and 2336 $[\text{M} + \text{Ag}]^+$, obtained from solutions containing NaOMe or Ag^+ , respectively.

Thin red needles of *trans*- $\text{Pt}\{\text{C}\equiv\text{CC}\equiv\text{C}-\mu_3\text{-C}[\text{Co}_3(\mu\text{-dppm})(\text{CO})_7]\}_2(\text{PEt}_3)_2$ (**2**) were obtained similarly from *trans*- $\text{PtCl}_2(\text{PEt}_3)_2$, but disappointingly were not suitable for an X-ray study. The IR spectrum contained $\nu(\text{CC})$ at 2142 and $\nu(\text{CO})$ between 2079 and 1963 cm^{-1} . The ^1H



Scheme 1.



Scheme 2.

NMR spectrum contained the expected resonances from the PEt_3 and dppm ligands, with the corresponding ^{31}P signals at δ 12.87 [$J(\text{PPt})$ 2232 Hz] and 34.06, respectively, confirming the *trans* geometry about Pt. No ^{13}C NMR spectrum could be obtained on account of the low solubility of **2** in suitable solvents.

A 30% yield of **3** was obtained from *trans*- $\text{PtCl}_2(\text{PPh}_3)_2$ as dark brown micro crystals. The IR spectrum contained, in addition to the $\nu(\text{CC})$ band at 2146 cm^{-1} , $\nu(\text{CO})$ absorptions between 2082 and 1934 cm^{-1} , with a pattern suggesting that the anticipated $\text{Co}_3(\text{CO})_7$ cluster was no longer present. There are three ^{31}P resonances at δ 18.3 [$J(\text{PPt}) = 2203\text{ Hz}$], 33.47 and 48.84 (ratio 1/2/1) which can be assigned to the Pt- PPh_3 , dppm and Co- PPh_3 ligands, respectively, found by the X-ray structure. Evidently during the reaction, transfer of PPh_3 from platinum to the cobalt cluster has occurred.

2.1. Molecular structure of **3**

The small size of crystals of **3** entailed using synchrotron radiation to procure a structure. Fig. 1 shows a plot of a molecule of **3**, selected bond distances and angles being presented in Table 1. The central square-planar Pt atom is attached to two PPh_3 ligands [Pt-P(1,2) 2.290(2), 2.296(2) Å] and two C_5 chains [Pt-C(1,6) 2.007(8), 2.013(8) Å], each pair of ligands being mutually *trans* [P(1)–Pt–P(2) 173.22(8), C(1)–Pt–C(6) 179.1(3)°]. The two C_5 chains are end-capped by $\text{Co}_3(\mu\text{-dppm})(\text{CO})_6(\text{PPh}_3)$ clusters of conventional geometry and dimensions [including Co–P(dppm) 2.188–2.203(2), Co–P(PPh_3) 2.212(2) and 2.208(2) Å] [10]. The Co–Co separations are between 2.449(1) and 2.510(2) Å, but show no dependence on the positions of the tertiary phosphine ligands. Individual distances and angles show no significant departures from

values determined earlier for related compounds and merit no further comment here.

Of most interest in the present context are the carbon chains. Atoms C(5,10) are μ_3 -bonded to the Co_3 cluster [Co–C 1.876(8)–1.943(7) Å] with bond lengths again independent of whether the Co atom is attached to dppm or PPh_3 ligands. Along the chain from the Pt centre, the short–long–short–long bond alternation confirms the presence of a diynyl unit attached to Pt at one end and to the μ_3 -C atom at the other, the latter separations being 1.42(1), 1.38(1) Å. There appears to be little if any electron delocalisation along the chain, perhaps not unexpected given the difficulty of rehybridising the cluster-bonded carbon atoms. Angles at individual carbon atoms are close to linear, ranging between $172.7(8)^\circ$ and $179.5(9)^\circ$.

2.2. Electrochemistry

We have recorded cyclic voltammograms (CVs) for the three complexes described above. For **1**, a reversible reduction wave occurs at -1.17 V and two oxidation waves at $+0.59$ and $+0.83\text{ V}$. For **2** and **3**, the reduction waves are found at -1.17 and -1.395 V , respectively, with poorly resolved irreversible oxidation waves at $+0.82$ and $+0.68\text{ V}$. The reduction processes are two-electron events, while the oxidation events appear to involve 1-e steps. We assign the reduction events to addition of electrons to the two Co_3 cores, these being independent of each other, suggesting that there is no electronic interaction between the two clusters. The oxidation processes probably occur on the carbon chain or at the Pt centres and, in this connection, we recall that the HOMOs of the neutral $\text{Pt}(\mu\text{-C}\equiv\text{C}\equiv\text{CH})_2(\text{dHpe})$ ($\text{dHpe} = \text{PH}_2\text{CH}_2\text{CH}_2\text{PH}_2$) are calculated to be delocalised over the entire $\text{Pt}(\text{C}_4\text{H})_2$ core, so that oxidation processes may affect the entire molecule [5].

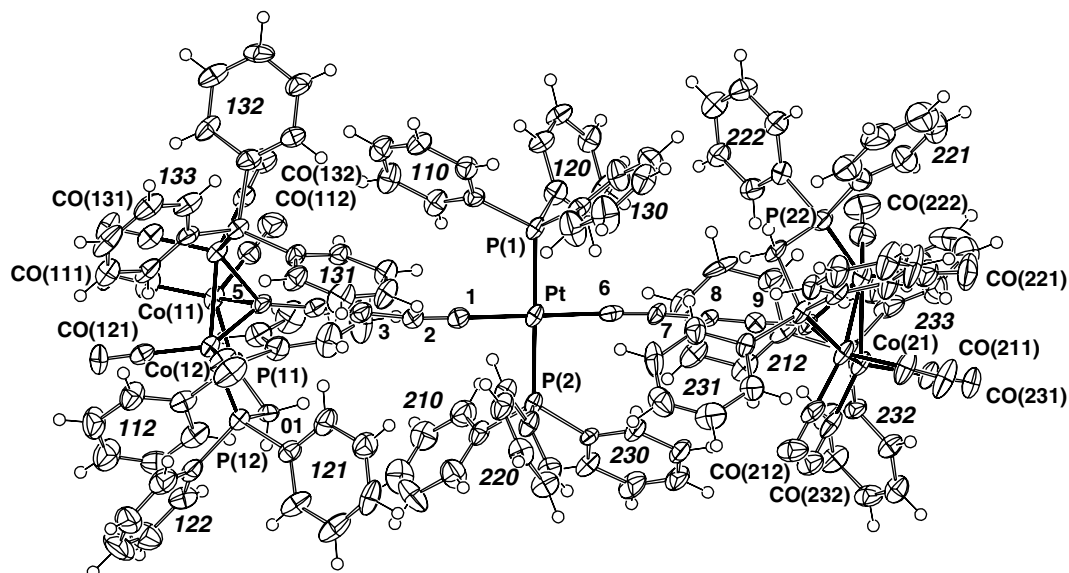


Fig. 1. Plot of a molecule of *trans*-Pt{C≡CC≡C-μ₃-C[Co₃(μ-dppm)(CO)₆(PPh₃)₂]₂(PPh₃)₂ (**3**).

Table 1
Selected bond distances (Å) and angles (°) for complex **3**

Bond distances (Å)			
Co(11)–Co(12)	2.497(2)	Co(21)–Co(22)	2.478(2)
Co(11)–Co(13)	2.449(1)	Co(21)–Co(23)	2.476(2)
Co(12)–Co(13)	2.484(1)	Co(22)–Co(23)	2.510(2)
Co(11)–P(11)	2.188(2)	Co(21)–P(21)	2.203(2)
Co(12)–P(12)	2.191(2)	Co(22)–P(22)	2.202(2)
Co(13)–P(13)	2.212(2)	Co(23)–P(23)	2.208(2)
Pt–P(1)	2.290(2)	Pt–P(2)	2.296(2)
Co(11)–C(5)	1.900(8)	Co(21)–C(10)	1.938(8)
Co(12)–C(5)	1.876(8)	Co(22)–C(10)	1.904(8)
Co(13)–C(5)	1.919(7)	Co(23)–C(10)	1.943(7)
Pt–C(1)	2.007(8)	Pt–C(6)	2.013(8)
C(1)–C(2)	1.19(1)	C(6)–C(7)	1.20(1)
C(2)–C(3)	1.37(1)	C(7)–C(8)	1.37(1)
C(3)–C(4)	1.21(1)	C(8)–C(9)	1.22(1)
C(4)–C(5)	1.42(1)	C(9)–C(10)	1.38(1)
Bond angles (°)			
P(1)–Pt–P(2)	173.22(8)	C(1)–Pt–C(6)	179.1(3)
P(1)–Pt–C(1)	91.8(2)	P(2)–Pt–C(1)	87.4(2)
P(1)–Pt–C(6)	88.2(2)	P(2)–Pt–C(6)	92.8(2)
Co(11)–C(5)–C(4)	127.5(6)	Co(21)–C(10)–C(9)	126.6(6)
Co(12)–C(5)–C(4)	133.7(6)	Co(22)–C(10)–C(9)	136.3(5)
Co(13)–C(5)–C(4)	131.9(6)	Co(23)–C(10)–C(9)	132.0(6)
Pt–C(1)–C(2)	177.8(8)	Pt–C(6)–C(7)	176.8(7)
C(1)–C(2)–C(3)	173.5(8)	C(6)–C(7)–C(8)	175.6(8)
C(2)–C(3)–C(4)	179.5(9)	C(7)–C(8)–C(9)	177.3(8)
C(3)–C(4)–C(5)	177.8(8)	C(8)–C(9)–C(10)	172.7(8)

3. Conclusions

We have made the first examples of complexes containing odd-numbered carbon chains (C₅) linking two different metal centres. These three complexes contain eleven-atom C₅–Pt–C₅–chains, bent for **1** and approximately linear for **2** and **3**. The geometries about platinum reflect those of the precursor chloro-phosphine-platinum(II) complexes, while in the reaction which leads to the formation of **3**, the cobalt

cluster acts in part as a PPh₃-scavenger, with one CO ligand on a non-dppm-bridged Co(CO)₃ fragment of the cluster being replaced by this ligand, sourced from the platinum(II) precursor. Of some interest is the ready reductive elimination of the C₅CO₃ fragments from the platinum(II) centre in **1**, followed by their coupling to give the known {Co₃(μ-dppm)(CO)₇}₂(μ₃:μ₃-C₁₀) [**6a**], this reaction no doubt being facilitated by the mutually *cis* orientation of these fragments in **1**. Notably, neither **2** nor **3** undergo any similar reaction.

4. Experimental

4.1. General

All reactions were carried out under dry nitrogen, although normally no special precautions to exclude air were taken during subsequent work-up. Common solvents were dried, distilled under argon and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates (20 × 20 cm²) coated with silica gel (Merck, 0.5 mm thick).

4.2. Instruments

IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH₂Cl₂ were obtained using a 0.5 mm path-length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Varian 2000 instrument (¹H at 300.13 MHz, ¹³C at 75.47 MHz, ³¹P at 121.503 MHz) with solutions in CDCl₃ contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ¹H and ¹³C NMR spectra and external H₃PO₄ for ³¹P NMR spectra. Electro-spray mass spectra (ESMS) were obtained from samples dissolved in MeOH unless otherwise indicated. Solutions were injected into a Varian Platform II spectrometer via a 10 ml injection loop. Nitrogen was used as the drying and nebulising gas. Chemical aids to ionisation were used [11]. Electrochemical samples (1 mM) were dissolved in CH₂Cl₂ containing 0.5 M [NBu₄]BF₄ as the supporting electrolyte for the spectro-electrochemical experiments. Cyclic voltammograms were recorded using a PAR model 263 apparatus, with a saturated calomel electrode, with ferrocene as internal calibrant (FeCp₂/[FeCp₂]⁺ = +0.46 V). A 1 mm path-length cell was used with a Pt-mesh working electrode, Pt wire counter and pseudo-reference electrodes. Elemental analyses were by CMAS, Belmont, Vic., Australia.

4.3. Reagents

PtCl₂(dppe) [12], *trans*-PtCl₂(PR₃)₂ (R = Et, Ph) [13] and Co₃(μ₃-CC≡CC≡CSiMe₃)(μ-dppm)(CO)₇ [6b] were obtained by the cited methods.

4.4. Pt{C≡CC≡C-μ₃-C[Co₃(μ-dppm)(CO)₇]₂(dppe) (1)

PtCl₂(dppe) (25 mg, 0.038 mmol) was dissolved in a mixture of thf and MeOH (13 ml, 10/3) by stirring for 30 min at 40 °C. Addition of Co₃(μ₃-CC≡CC≡CSiMe₃)(μ-dppm)(CO)₇ (67 mg, 0.076 mmol) and NaOMe (excess in MeOH, 1 ml) was followed by stirring overnight at r.t. The filtered solution was then evaporated and the residue extracted into CH₂Cl₂ and purified by preparative t.l.c. (acetone/hexane 1/2). The major green-brown band (R_f 0.16) contained Pt{C≡CC≡C-μ₃-C[Co₃(μ-dppm)-

(CO)₇]₂(dppe) (**1**) (43.3 mg, 52%), obtained as a brown solid. Anal. Calc. for C₁₀₀H₆₈Co₆O₁₄P₆Pt: C, 53.91; H, 3.08. Found: C, 54.00; H, 3.03%. *M*, 2228. IR (CH₂Cl₂, cm⁻¹): ν(CC) 2152vw; ν(CO) 2090vw, 2054s, 2006vs, 1982 (sh), 1962 (sh). ¹H NMR: δ 2.62 (m, 4H, CH₂), 3.25, 4.44 (2 × m, 2 × 2H, dppm), 6.99–7.93 (m, 60H, Ph). ¹³C NMR: δ 29.97 (m, dppe), 41.07 [s (br), dppm], 95.30, 97.49, 103.90 (carbon chain), 128.28–136.36 (m, Ph), 202.56, 210.41, 224.31 [3 × s (br), Co–CO]. ³¹P NMR: δ 34.1 [s (br), dppm], 40.86 [t, J(PPt) = 2269 Hz, dppe], ratio 2/1. ES-MS (positive ion, MeOH + NaOMe, *m/z*): 2251, [M + Na]⁺; (CH₂Cl₂/MeOH + Ag⁺, *m/z*): 2336, [M + Ag]⁺.

Slow decomposition occurs in solution (especially in chlorinated solvents) to give as one product {Co₃(μ-dppm)(CO)₇]₂(μ₃:μ₃-C₁₀), identified by comparison (IR, t.l.c.) with an authentic sample [6a].

4.5. *trans*-Pt{C≡CC≡C-μ₃-C[Co₃(μ-dppm)(CO)₇]₂-(PEt₃)₂ (2)

A solution of Co₃(μ₃-CC≡CC≡CSiMe₃)(μ-dppm)(CO)₇ (50 mg, 0.056 mmol) in thf/MeOH (12 ml, 10/2) was treated with an excess of NaOMe in MeOH. After 15 min, *trans*-PtCl₂(PEt₃)₂ (14.6 mg, 0.028 mmol) was added and the mixture was stirred for 5 h. at r.t. Removal of solvent, extraction of the residue with CH₂Cl₂ and separation by preparative t.l.c. (acetone/hexane 3/7) gave one major band (R_f 0.56) which contained *trans*-Pt{C≡CC≡C-μ₃-C[Co₃(μ-dppm)(CO)₇]₂(PEt₃)₂ (**2**) (8.6 mg, 15%), obtained as thin red needles. Anal. Calc. C₈₆H₇₇Co₆O₁₄P₆Pt: C, 50.00; H, 3.61. Found: C, 49.98; H, 3.65%. *M*, 2066. IR (CH₂Cl₂, cm⁻¹): ν(CC) 2152vw; ν(CO) 2090vw, 2054s, 2006vs, 1982 (sh), 1962 (sh). ¹H NMR: δ 1.25 (m, 18H, PCH₂Me), 2.15 (m, 12H, PCH₂Me), 3.35, 4.49 (2 × m, 2 × 2H, dppm), 7.10–7.50 (m, 40H, Ph). ³¹P NMR: δ 12.87 [t, J(PPt) 2232, PEt₃], 34.06 [s (br), dppm], ratio 1/2.

4.6. *trans*-Pt{C≡CC≡C-μ₃-C[Co₃(μ-dppm)(CO)₆-(PPh₃)₂]₂(PPh₃)₂ (3)

A mixture of *trans*-PtCl₂(PPh₃)₂ (22 mg, 0.028 mmol) and Co₃(μ₃-CC≡CC≡CSiMe₃)(μ-dppm)(CO)₇ (50 mg, 0.056 mmol) dissolved in thf/MeOH (22 ml, 10/1) was treated with NaOMe in MeOH (excess, 1 ml) and left to stir overnight. Removal of solvent and extraction of the residue with CH₂Cl₂ was followed by separation by preparative t.l.c. (acetone–hexane 3/7). The major green-brown band (R_f 0.32) afforded dark red microcrystals of *trans*-Pt{C≡CC≡C-μ₃-C[Co₃(μ-dppm)(CO)₆-(PPh₃)₂]₂(PPh₃)₂ (**3**) (22.7 mg, 29%) from C₆H₆/MeOH, initially identified by an X-ray structural determination. An analytical sample was obtained from CH₂Cl₂/MeOH. Anal. Calc. for C₁₄₄H₁₀₄Co₆O₁₂P₈Pt · 2CH₂Cl₂: C, 58.61; H, 3.64. Found: C, 58.14; H, 3.64%. *M* (unsolvated), 2823. IR (CH₂Cl₂, cm⁻¹): ν(CC) 2146w; ν(CO) 2082w,

2056m, 2022s, 1986vs (br), 1968s (br), 1934 (sh). ^1H NMR: δ 2.90, 3.94 ($2 \times \text{m}$, $2 \times 2\text{H}$, dppm), 5.30 [s (br), CH_2Cl_2], 7.05–7.77 (m, 100H, Ph). ^{31}P NMR: δ 18.30 [t, $J(\text{PPt}) = 2203$ Hz, Pt- PPh_3], 33.37 [s (br), dppm], 48.84 [s (br), Co- PPh_3], ratio 1/2/1.

4.7. Structure determination

Full spheres of diffraction data were measured at ca. 103 K using a synchrotron (Sector 15 of the Advanced Photon Source at the Argonne National Laboratory, Argonne, IL, USA). 189 533 reflections were merged to 25 204 unique ($R_{\text{int}} = 0.085$) after “empirical”/multiscan absorption correction (proprietary software) and used in the full-matrix least-squares refinements on F^2 . All data were measured using synchrotron radiation, $\lambda = 0.48595$ Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms. All solvent molecules were resolved and refined, one only being refined as a rigid body and with site occupancy set at 0.5 after initial trial refinement. Conventional residuals are $R [I > 2\sigma(I)] = 0.071$, $R_w(F^2) = 0.137$ [weights: $(\sigma^2(F^2) + 21F^2)^{-1}$]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system [14]. Pertinent results are given in Fig. 1 (which shows non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and in Table 1.

4.8. Crystal and refinement data

trans-Pt{C \equiv CC \equiv C- μ_3 -C[Co $_3$ (μ -dppm)(CO) $_6$ (PPh $_3$)] $_2$ - (PPh $_3$) $_2$ · 3.5C $_6$ H $_6$ ≡C $_{144}$ H $_{104}$ Co $_6$ O $_{12}$ P $_8$ Pt · 3.5C $_6$ H $_6$, $M_w = 3096.27$. Monoclinic, space group $P2_1/c$, $a = 17.332(1)$, $b = 19.426(2)$, $c = 41.744(3)$ Å, $\beta = 97.409(3)$, $V = 13938$ Å 3 , $Z = 4$. $2\theta_{\text{max}} = 34.0^\circ$. $D_c = 1.476$ g cm $^{-3}$, $\mu = 0.64$ mm $^{-1}$, $T_{\text{min/max}} = 0.37$. Crystal $0.11 \times 0.05 \times 0.003$ mm.

5. Supplementary material

Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC 280612. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ,

UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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