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Synthesis of Co_2Pt, Co_2Pd and $MoPd_2$ mixed-metal clusters with the P–N–P assembling ligands $(Ph_2P)_2NH$ (dppa) and $(Ph_2P)_2NMe$ (dppaMe). Crystal structure of $[Co_2Pt(\mu_3\text{-}CO)(CO)_6(\mu\text{-dppa})]$ ☆

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Abstract

Heterometallic triangular platinum–cobalt, palladium–cobalt and palladium–molybdenum clusters stabilized by one or two bridging diphosphine ligands such as $Ph_2PNHPPh_2$ (dppa) or $(Ph_2P)_2NMe$ (dppaMe) or by mixed ligand sets $Ph_2PCH_2PPh_2$ (dppm)/dppa have been prepared with the objectives of comparing the stability and properties of the clusters as a function of the short-bite diphosphine ligand used and of the metal carbonyl fragment they contain. Ligand redistribution reactions were observed during the purification of $[Co_2Pd(\mu_3\text{-}CO)(CO)_4(\mu\text{-dppa})(\mu\text{-dppm})]$ (**4**) by column chromatography with the formation of $[Co_2Pd(\mu_3\text{-}CO)(CO)_4(\mu\text{-dppm})_2]$ and the dinuclear complex $[(OC)_2\overline{Co(\mu\text{-dppa})_2Pd}Cl]$ (**5**). The latter was independently prepared by reaction of $[Pd(\text{dppa-}P,P')_2](BF_4)_2$ with $Na[Co(CO)_4]$. Attempts to directly incorporate the ligand $(Ph_2P)_2N(CH_2)_3Si(OMe)_3$ (dppaSi) into a cluster or to generate it by *N*-functionalization of coordinated dppa were unsuccessful, in contrast to results obtained recently with related clusters. The crystal structure of $[Co_2Pt(\mu_3\text{-}CO)(CO)_6(\mu\text{-dppa})]$ (**1**) has been determined by X-ray diffraction. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Bimetallic; Clusters; Assembling ligands; Diphosphines

1. Introduction

The short-bite ligand bis(diphenylphosphinoamine) ($Ph_2PNHPPh_2$, dppa) is receiving increasing attention for assembling metal centres in bi- or polynuclear metal complexes owing to both its isoelectronic relationship with the more popular bis(diphenylphosphinomethane) ligand ($Ph_2PCH_2PPh_2$, dppm) and the increased reactivity of its N–H group compared with that of the CH_2 unit in dppm [1]. Thus, the greater acidity of the NH proton versus the CH_2 protons may facilitate subsequent functionalization reactions that would require too drastic conditions in the case of dppm. We have recently exploited this feature to prepare *N*-alkyl derivatives of dppa clusters, including substituents with a trialkoxysilyl group that could subsequently be used for condensation reactions in a sol-gel process with the aim of incorporating metal clusters into a silica matrix in a covalent manner [1g, 2]. Here we report on the synthesis of Co_2Pt, Co_2Pd and $MoPd_2$ mixed-metal clusters containing the dppa ligand and our attempts towards *N*-derivatization. Heterometallic triangular clusters containing two dppa ligands or dppa and dppm (mixed ligand sets) have been prepared by direct incorporation of the second diphosphine ligand.

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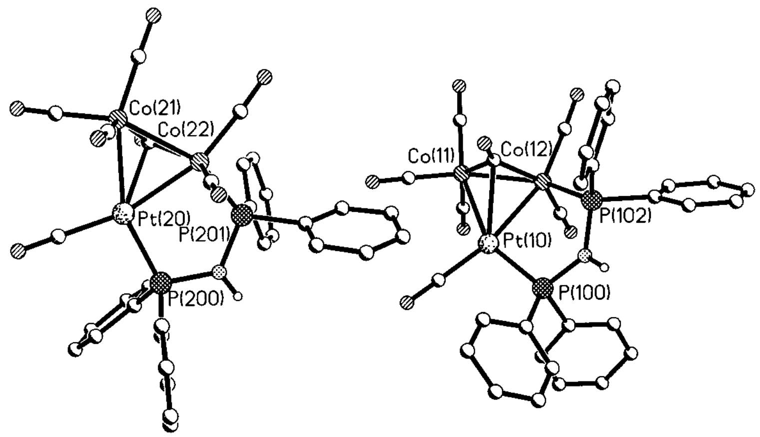
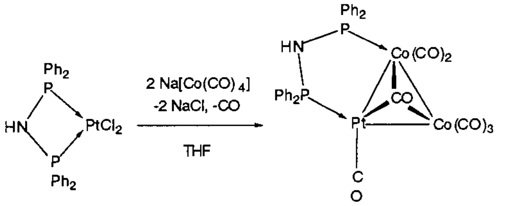


Fig. 1. View of the structure of the two independent molecules of [$Co_2Pt(\mu_3\text{-}CO)(CO)_6(\mu\text{-}dppa)$] (**1**).

2. Results and discussion

2.1. Platinum–cobalt clusters

By analogy with the carbonylmetalate-induced ring-opening reactions observed with [$PtCl_2$(dppm-*P*,*P′*)], which led to a range of mixed-metal clusters [3], we have reacted [$PtCl_2$(dppa-*P*,*P′*)] with two equivalents of Na[$Co(CO)_4$] in THF and isolated in a 93% yield the new cluster [$Co_2Pt(\mu_3\text{-}CO)(CO)_6(\mu\text{-}dppa)$] (**1**) (Eq. (1)):



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(1)

Analytical and spectroscopic data are fully consistent with the structure shown in Eq. (1), which was also confirmed by an X-ray diffraction study (see below). The IR spectrum in the ν(CO) region contains absorptions typical of terminal CO ligands as well as a band at 1772 cm^{-1}, which corresponds to the bridging CO ligand. The proton of the amino group of the coordinated dppa ligand gives rise to a broad multiplet at δ 6.31 in acetone-d_6 because of coupling to the adjacent phosphorus atoms. The $^{31}P\{^1H\}$-NMR resonance for the Pt-bound P atom appears at δ 46.1, with typical values of $^1J(PPt) = 3596$ Hz and $^{2+3}J(PP) = 20$ Hz. The Co-bound P nucleus gives rise to a broad resonance at δ 73.1 owing to the quadrupolar effect of cobalt. These values are consistent with those observed in related clusters [2].

2.1.1. X-ray diffraction study of [$Co_2Pt(\mu_3\text{-}CO)(CO)_6(\mu\text{-}dppa)$] (1)

There are two independent molecules in the unit cell and their molecular structures is shown in Fig. 1. A detailed view of one molecule with the atom numbering scheme is given in Fig. 2. Selected bond distances and angles for one molecule are given in Table 1. The bonding parameters of the second independent molecule are in most cases within the range of the standard deviations of the first molecule and therefore not listed.

The three metal atoms of one molecule form a triangle and the Pt(10)–Co(12) bond is bridged by the dppa ligand. The face of this triangle is capped by an unsymmetrically bonded carbonyl group which has relatively short distances to the two Co atoms [Co(11)–C(122) = 1.98(1), Co(12)–C(122) = 1.89(1) Å] and a rather long distance to the Pt(10) atom (2.55(1) Å). This situation is similar to that of the related triangular cluster compound [$Co_2Pt(\mu_3\text{-}CO)(CO)_7(PPh_3)$] which also shows short Co–C bond distances to the μ_3-bridging carbonyl group (1.88(1), 1.93(1) Å) and a rather long Pt–C distance (2.57(1) Å) [4a]. The coordination sphere around the Pt(10) atom is ideal planar with a sum of

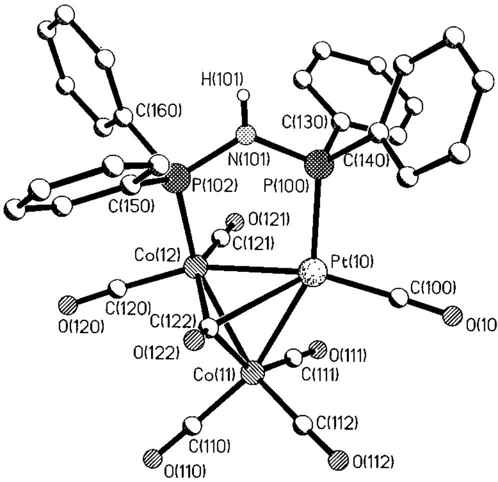


Fig. 2. View of the structure of one molecule of [$Co_2Pt(\mu_3\text{-}CO)(CO)_6(\mu\text{-}dppa)$] (**1**).

the angles of the ligands of 360°. The Co(12) atom has a distorted trigonal bipyramidal coordination sphere where the two terminal and the μ_3-bridging carbonyl groups are in the equatorial plane and the P(102) atom of the dppa ligand and the Co(11) atom are in the axial positions.

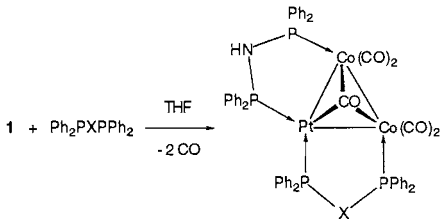
Table 1
Selected bond lengths (Å) and angles (°) for $[Co_2Pt(\mu_3\text{-}CO)(CO)_6(\mu\text{-}dppa)]$ (**1**), molecule A

Bond lengths (Å)			
Pt(10)–C(100)	1.85(2)	Co(11)–C(111)	1.81(2)
Pt(10)–P(100)	2.259(3)	Co(11)–C(122)	1.98(1)
Pt(10)–Co(11)	2.531(2)	Co(12)–C(120)	1.77(2)
Pt(10)–Co(12)	2.508(2)	Co(12)–C(121)	1.80(2)
Co(11)–Co(12)	2.531(2)	Co(12)–C(122)	1.89(1)
Pt(10)–C(122)	2.54(2)	Co(12)–P(102)	2.175(3)
Co(11)–C(112)	1.75(2)	P(100)–N(101)	1.67(1)
Co(11)–C(110)	1.77(2)	N(101)–P(102)	1.699(9)
Bond angles (°)			
Pt(10)–Co(11)–Co(12)	59.40(5)	C(122)–Co(12)–P(102)	100.4(4)
Co(11)–Pt(10)–Co(12)	60.30(5)	C(120)–Co(12)–Pt(10)	161.7(5)
Pt(10)–Co(12)–Co(11)	60.30(6)	C(121)–Co(12)–Pt(10)	87.3(5)
C(100)–Pt(10)–P(100)	101.6(4)	C(122)–Co(12)–Pt(10)	69.0(4)
Co(12)–Pt(10)–C(100)	165.7(4)	P(102)–Co(12)–Pt(10)	94.8(1)
P(100)–Pt(10)–Co(12)	92.68(9)	N(101)–P(100)–Pt(10)	110.1(3)
C(100)–Pt(10)–Co(11)	105.5(4)	P(100)–N(101)–P(102)	121.3(5)
Co(12)–Pt(10)–C(122)	44.0(3)	N(101)–P(102)–Co(12)	112.6(4)
Co(11)–Pt(10)–C(122)	45.9(3)	O(122)–C(122)–Co(12)	142(1)
C(112)–Co(11)–Co(12)	139.6(4)	O(122)–C(122)–Co(11)	137(1)
C(110)–Co(11)–Co(12)	103.5(5)	Co(12)–C(122)–Co(11)	81.6(5)
C(111)–Co(11)–Co(12)	98.6(4)	O(122)–C(122)–Pt(10)	124(1)
C(122)–Co(11)–Co(12)	47.7(4)	Co(12)–C(122)–Pt(10)	67.0(4)
C(120)–Co(12)–P(102)	99.3(5)	Co(11)–C(122)–Pt(10)	66.7(4)
C(121)–Co(12)–P(102)	103.4(5)		

The Co–Pt bond lengths of 2.508(2) and 2.531(2) Å are in the range observed for clusters with Co–Pt cores [4]. The shorter bond is the one that is bridged by the dppa ligand. The P–N–P angle is 121.3(5)°, similar to that of the dppaMe ligands in the triangular cluster $[Pd_2Co(CO)_7(\mu\text{-}dppaMe)_3](PF_6)$ (121.0(4)°) [2]. The Pt–P distance of 2.259(3) Å is in the range found in other chelated Pt(dppa) complexes [1b]. The Co–P bond length (2.175(3) Å) is also comparable with other triangular cluster compounds with bridging dppa ligand [4c].

2.1.2. *Reactions of* $[Co_2Pt(\mu_3\text{-}CO)(CO)_6(\mu\text{-}dppa)]$ *(1)*

In order to evaluate the reactivity of this cluster toward diphosphines that may further enhance the stability of the cluster, an equivalent of dppa was added to a solution of **1** in THF (Eq. (2)). The expected product $[Co_2Pt(\mu_3\text{-}CO)(CO)_4(\mu\text{-}dppa)_2]$ (**2**) was obtained as a red–brown powder. Its IR spectrum shows the disappearance of the band at 2052 cm^{-1} in the precursor, indicating that the Pt-bound CO ligand has been displaced by dppa. The two protons of the amino groups of the coordinated dppa ligands of **2** are equivalent and give rise to a broad multiplet at δ 6.34 ppm in acetone-d_6 because of coupling to the adjacent phosphorus atoms. The $^{31}P\{^1H\}$-NMR resonances for the Pt-bound P atoms appear at δ 56.6, whereas the Co-bound P nuclei give rise to a broad resonance at δ 77.6 owing to the quadrupolar effect of cobalt. A detailed analysis of this AA′BB′ spin system (A = B = P) was not possible owing to insufficient resolution. The ^1J(PPt) value of 3917 Hz is larger than in **1**, which may reflect an increased electron density in **2**. In a similar manner, the dppa/dppm cluster $[Co_2Pt(\mu_3\text{-}CO)(CO)_4(\mu\text{-}dppa)(\mu\text{-}dppm)]$ (**3**) was prepared by reaction of **1** with dppm. This complex could not be isolated pure in the solid-state, it was however fully characterized in solution (see Section 3). Attempts to coordinate the diphosphine ligands $(Ph_2P)_2NMe$ (dppaMe) or $(Ph_2P)_2N(CH_2)_3Si(OEt)_3$ (dppaSi) in a similar manner were unsuccessful. With these two ligands, we have previously observed that their incorporation into a cluster is very sensitive to the nature of the latter [2]. The alternative approach of reacting $[PtCl_2(dppaSi\text{-}P,P')]$ with two equivalents of $Na[Co(CO)_4]$ was unsuccessful.



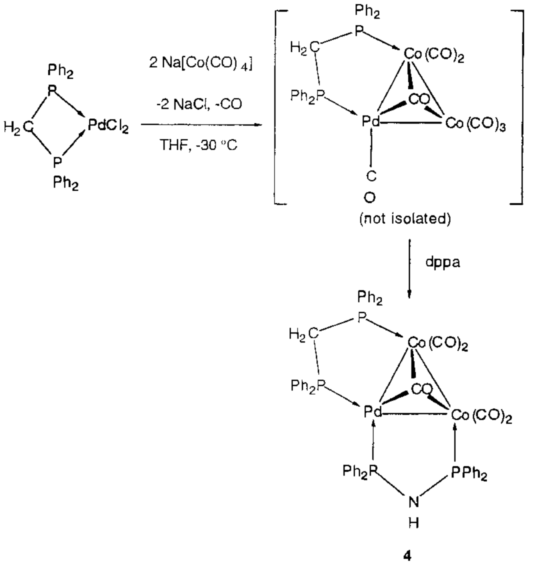
(2)

2 X = NH
3 X = CH_2

We therefore tried to functionalize cluster **1** by reacting a THF solution with excess DBU or KH and then with MeI. The $^{31}P\{^1H\}$-NMR resonances of the functionalized complex show a downfield shift compared with that of **1** (ca. + 20 ppm): the resonance for the Co-bound P atom appears at δ 97.7 and for the Pt-bound P atom at δ 68.1 (^1J(PPt) = 3619 Hz). However, we encountered difficulties in reproducing this alkylation reaction, although this method was recently used to prepare the cluster $[Co_2Pd(\mu_3\text{-}CO)_2(\mu\text{-}dppaMe)_3](PF_6)$ in a 71% yield from $[Co_2Pd(\mu_3\text{-}CO)_2(\mu\text{-}dppa)_3](PF_6)$ [2]. Preliminary experiments were also conducted to functionalize **1** by treating it in THF with an excess of KH, followed by addition of $I(CH_2)_3Si(OMe)_3$. This did not lead to the expected cluster and the brown powder obtained showed no ^{31}P-NMR signal.

2.2. Synthesis of palladium–cobalt and palladium–molybdenum clusters

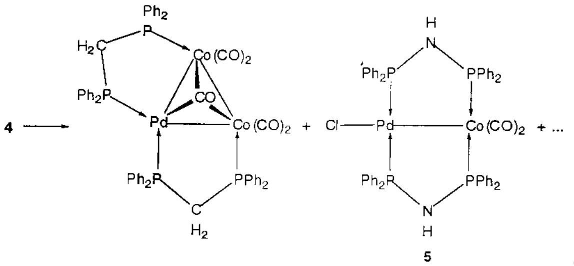
By analogy with procedures originally developed in the dppm chemistry [5], we obtained the mixed-ligand set cluster $[Co_2Pd(\mu_3\text{-}CO)(CO)_4(\mu\text{-}dppa)(\mu\text{-}dppm)]$ (**4**) by reacting $[PdCl_2(dppm\text{-}P,P')]$ with two equivalents of $Na[Co(CO)_4]$ in THF at −30°C, followed by addition of one equivalent of dppa (Eq. (3)). The likely intermediate $[Co_2Pd(\mu_3\text{-}CO)(CO)_6(\mu\text{-}dppm)]$ could not be isolated [4].



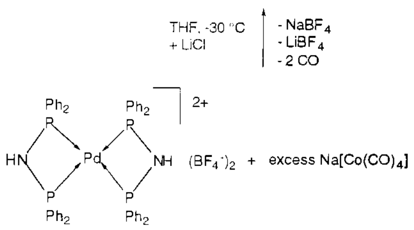
(3)

4

Complex **4** was characterized in solution by $^{31}P\{^1H\}$-NMR spectroscopy but could not be isolated pure in the solid-state (see Section 3). During attempts of purification by column chromatography, formation of $[Co_2Pd(\mu_3\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$ and $[(OC)_2Co(\mu\text{-}dppa)_2PdCl]$ (**5**) was observed (Eq. (4)). The former results from ligand redistribution reactions and was identified by comparison of its spectroscopic data with the literature [5]. By analogy with its dppm analogue [3c], complex **5** was independently prepared by reaction of $[Pd(dppa\text{-}P,P')_2](BF_4)_2$ with a small excess of $Na[Co(CO)_4]$ in THF (Eq. (5)). This new purple dinuclear complex was characterized by $^{31}P\{^1H\}$-NMR spectroscopy (AA′XX′ spin system) where the resonances for the Pd-bound P atoms appear at δ 63.5 and for the Co-bound P atoms at δ 82.0, respectively. The former value is downfield shifted when compared with that of δ 58.3 found for the homodinuclear complex $[Pd_2Cl_2(\mu\text{-}dppa)_2]$ [6]. We have previously isolated the analogous dppm complex $[(OC)_2Co(\mu\text{-}dppm)_2PdCl]$ [3c] as well as the related 32-electron Pd–Mn complex $[(OC)_3Mn(\mu\text{-}dppm)_2PdCl]$ from the reaction of $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ with $Na[Mn(CO)_5]$ [7].

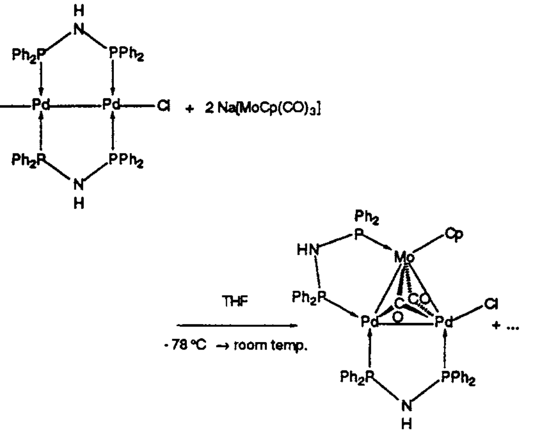


(4)



(5)

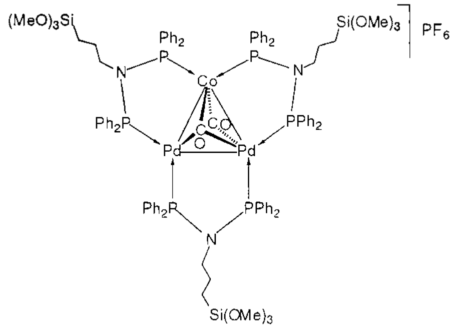
In order to evaluate the influence of the metal carbonyl fragment in this chemistry, we reacted $[Pd_2Cl_2(\mu\text{-}dppa)_2]$ with $Na[MoCp(CO)_3]$ and obtained the cluster $[MoPd_2ClCp(\mu_3\text{-}CO)_2(\mu\text{-}dppa)_2]$ (**6**), as anticipated on the basis of our previous results with dppm as an assembling ligand [8]. Although it could not be isolated pure in the solid-state, its spectroscopic data in solution are fully consistent with the structure shown in Eq. (6).



(6)

6

Functionalization of this cluster by reaction with KH followed by the addition of MeI or EtI afforded $[MoPd_2ClCp(\mu_3\text{-}CO)_2(\mu\text{-}dppaMe)_2]$ (**7**) or $[MoPd_2Cl\text{-}Cp(\mu_3\text{-}CO)_2(\mu\text{-}dppaEt)_2]$ (**8**), respectively. However, reaction with KH and $I(CH_2)_3Si(OMe)_3$ did not lead to the desired *N,N*-derivatized cluster. This is somewhat surprising since $[CoPd_2(\mu_3\text{-}CO)_2\{\mu\text{-}(Ph_2P)_2(CH_2)_3Si\text{-}(OMe)_3\}_3](PF_6)$ (**9**) has been obtained by this method from $[CoPd_2(\mu_3\text{-}CO)_2(\mu\text{-}dppa)_3](PF_6)$ [2]. We have however noted that the outcome of such alkylation reactions very much depends upon the nature of the precursor cluster and direct incorporation of the ligand $(Ph_2P)_2N(CH_2)_3Si(OEt)_3$ (dppaSi) represents an interesting alternative [2].



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Another possible access to $[MoPd_2ClCp(\mu_3\text{-}CO)_2(\mu\text{-}dppaSi)_2]$ could have been the reaction between $[Pd_2Cl_2(\mu\text{-}dppaSi)_2]$ and $Na[MoCp(CO)_3]$. However, this approach was not successful.

Our results provide an easy entry into mixed-metal clusters containing one or two dppa ligands. Systems with different bridging ligands (dppa and dppm) in well-defined positions have also been prepared. The synthetic methods employed explain the regioselectivity with which incorporation of the diphosphine ligands occurs.

3. Experimental

3.1. Reagents and physical measurements

All reactions were performed in Schlenk-type flasks under purified nitrogen. Solvents were dried and distilled under nitrogen by conventional methods. Nitrogen was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water. IR spectra were recorded on a Bruker IFS66 (4000–400 cm^{-1}) spectrometer; samples were prepared as KBr pellets or solutions using CaF_2 cells. The ^1H- and $^{31}P\{^1H\}$-NMR spectra were recorded at 300.13 and 121.5 MHz, respectively, on an FT Bruker AC 300 instrument. The ^1H- and ^{31}P- shifts are given relative to external $SiMe_4$ and H_3PO_4, respectively. The $^{31}P\{^1H\}$-NMR resonances for the Co-bound P nuclei generally give rise to a broad resonance owing to the quadrupolar effect of cobalt. Elemental C, H and N analyses were performed by the Service de microanalyses (Université Louis Pasteur, Strasbourg).

3.2. Synthesis

The ligands $Ph_2PCH_2PPh_2$ (dppm) [9], $Ph_2PNHPPh_2$ (dppa) [6] and $(Ph_2P)_2NCH_2CH_2CH_2Si(OEt)_3$ (dppaSi) [1g] were prepared according to the literature. The complexes $[PtCl_2(dppm\text{-}P,P')]\cdot C_6H_6$ [10], $[PdCl_2(dppm\text{-}P,P')]$ [11], $[PtCl_2(dppa\text{-}P,P')]$ [12], $[Pd_2Cl_2(\mu\text{-}dppa)_2]$ [6], $[Pd_2Cl_2(\mu\text{-}dppaSi)_2]$ [1g], $[PdCl_2(cod)]$ [13], $[PtCl_2(cod)]$ [14] and $[Pd(dppa\text{-}P,P')_2](BF_4)_2$ [15] were prepared according to literature methods. Solutions of $Na[Co(CO)_4]$ and $Na[MoCp(CO)_3]\cdot 2DME$ were prepared according to the literature [16].

3.2.1. $[PdCl_2(dppa\text{-}P,P')]$

A sample of dppa (0.770 g, 2.000 mmol) was dissolved in CH_2Cl_2 (30 cm^3) and added to a CH_2Cl_2 (30 cm^3) solution of $[PdCl_2(cod)]$ (0.571 g, 2.000 mmol). The product immediately precipitated as a colourless solid and stirring was maintained for 30 min. After filtration the solid was washed with Et_2O and *n*-hexane. Yield: 1.029 g (91%). The isolated complex was insoluble in organic solvents and was characterized only by elemental analysis. (Found: C, 51.77; H, 3.41; N, 2.45. $C_{24}H_{21}NP_2Cl_2Pd$ requires C, 51.23; H, 3.76; N, 2.49%).

3.2.2. $[PdCl_2(dppaSi\text{-}P,P')]$

The procedure used was similar to that described for $[PdCl_2(dppa\text{-}P,P')]$, using $[PdCl_2(cod)]$ (0.571 g, 2.000 mmol) and dppaSi (1.178 g, 2.000 mmol). Yield: 1.169 g (76%). (Found: C, 51.81; H, 5.34; N, 2.02. $C_{33}H_{44}NO_3P_2SiCl_2Pd$ requires C, 51.50; H, 5.72; N, 1.82%). NMR ($CDCl_3$): ^1H, δ 7.91–7.51 (m, 20H, aromatic), 3.57 (q, 6H, $^3J = 3$ Hz, OCH_2), 3.02 (m, 2H, NCH_2), 1.25 (m, 2H, NCH_2CH_2), 1.02 (t, 9H, $^3J = 3$ Hz, OCH_2CH_3), 0.19 (t, 2H, $^3J = 3$ Hz, $NCH_2CH_2CH_2Si$); $^{31}P\text{-}\{^1H\}$, δ 30.77 (s, 2P → Pd).

3.2.3. $[PtCl_2(dppaSi\text{-}P,P')]$

The procedure used was similar to that described for $[PdCl_2(dppa\text{-}P,P')]$, using $[PtCl_2(cod)]$ (0.740 g, 2.000 mmol) and dppaSi (1.178 g, 2.000 mmol). Yield: 1.374 g (80%). (Found: C, 46.04; H, 5.06; N, 1.65. $C_{33}H_{44}NO_3P_2SiCl_2Pt$ requires C, 46.15; H, 5.13; N, 1.63%). NMR ($CDCl_3$): ^1H, δ 7.91–7.51 (m, 20H, aromatic), 3.59 (q, 6H, $^3J = 3$ Hz, OCH_2), 2.91 (m, 2H, NCH_2), 1.22 (m, 2H, NCH_2CH_2), 1.04 (t, 9H, $^3J = 3$ Hz, OCH_2CH_3), 0.19 (t, 2H, $^3J = 3$ Hz, $NCH_2CH_2CH_2Si$); $^{31}P\text{-}\{^1H\}$, δ 16.28 (s, 2P → Pt, $^1J(PPt) = 3293$ Hz).

*3.2.4. $[Co_2Pt(\mu_3\text{-}CO)(CO)_6(\mu\text{-}dppa)]$ (**1**)*

A filtered solution of $Na[Co(CO)_4]$ (0.1 M in THF, 6.6 cm^3) was added to a suspension of $[PtCl_2(dppa\text{-}P,P')]$ (0.216 g, 0.332 mmol) in THF (50 cm^3). The mixture was heated (40°C) for 3 h after which time its color had changed from yellow–brown to red–brown and a white precipitate had formed. After filtration the solvent was removed in vacuo and the residue was then extracted with CH_2Cl_2 and filtered on a Celite-padded filter funnel. The filtered solution was concentrated to ca. 30 cm^3 and the addition of *n*-hexane afforded a red–brown microcrystalline powder of **1**. Red single crystals suitable for X-ray diffraction were obtained by layering a THF solution with *n*-hexane. Yield: 0.352 g

(93%). (Found: C, 41.34; H, 2.30; N, 1.45. $C_{31}H_{21}Co_2NO_7P_2Pt$ requires C, 41.63; H, 2.37; N, 1.57%). IR (THF): ν(CO) 2052s, 2033s, 2016s; 1995sh, 1985sh, 1967vs–br; 1887vs–br and 1772m cm^{-1}. IR (KBr): ν(CO) 2057s, 2017s, 1993s, 1980s–sh and 1772w cm^{-1}. NMR (acetone-d_6): ^{1}H, δ 7.37–7.19 (m, 20H, aromatic), 6.31 (m, 1H, NH); ^{31}P-{^{1}H}, δ 73.1 (br, P → Co), 46.1 (d, P → Pt, ^1J(PPt) = 3596 Hz, ^{2+3}J(PP) = 20 Hz).

3.2.5. *$[Co_2Pt(\mu_3\text{-}CO)(CO)_4(\mu\text{-}dppa)_2]$* (**2**)

Upon addition of dppa (0.070 g, 0.182 mmol) to a solution of $[Co_2Pt(CO)_7(\mu\text{-dppa})]$ (**1**) (0.163 g, 0.182 mmol) in THF (20 cm^3) at room temperature (r.t.), gas evolution was observed, indicating that a reaction was occuring. The solvent was removed in vacuo and the solid was washed with toluene (10 cm^3) and *n*-hexane (10 cm^3), affording a red–brown powder (0.085 g, 38%). (Found: C, 51.83; H, 3.31; N, 2.43. $C_{53}H_{42}Co_2N_2O_5P_4Pt$ requires C, 52.00; H, 3.43; N, 2.29%). IR (THF): ν(CO) 1998s, 1967ms, 1950s and 1886s cm^{-1}. NMR (acetone-d_6): ^{1}H, δ 7.60–6.90 (m, 40 H, aromatic), 6.34 (br–m, 2 H, NH); ^{31}P-{^{1}H}, δ 77.6 (br, 2 P → Co), 56.6 (br, 2 P → Pt, ^1J(PPt) = 3917 Hz).

3.2.6. *$[Co_2Pt(\mu_3\text{-}CO)(CO)_4(\mu\text{-}dppa)(\mu\text{-}dppm)]$* (**3**)

This complex was prepared following a similar procedure to that for complex **2**, but starting from $[Co_2Pt(CO)_7(\mu\text{-dppa})]$ (**1**) (0.500 g, 0.560 mmol) and dppm (0.216 g, 0.560 mmol). However, it could not be isolated in pure form and was characterized in solution by its IR (THF): ν(CO) 1997s, 1967s–br, 1950vs and 1885s cm^{-1}, and its ^{31}P{^{1}H}-NMR (acetone-d_6): δ 76.7 (br, P → Co_{dppa}), 54.7 (m, br, P → Pt_{dppa}, ^1J(PPt) = 3973 Hz), 26.5 (m, br, P → Co_{dppm}), 4.0 (m, br, P → Pt_{dppm}, ^1J(PPt) = 3584 Hz). Alternatively, complex (**3**) may be obtained by reaction of $[Co_2Pt(\mu_3\text{-CO})(CO)_6(\mu\text{-dppm})]$ (0.500 g, 0.560 mmol) with dppa (0.216 g, 0.560 mmol) under similar conditions.

3.2.7. *$[Co_2Pd(\mu_3\text{-}CO)(CO)_4(\mu\text{-}dppa)(\mu\text{-}dppm)]$* (**4**)

A solution of $Na[Co(CO)_4]$ (0.1 M in THF, 5 cm^3) was added dropwise to a suspension of $[PdCl_2(\text{dppm-}P,P')]$ (0.140 g, 0.249 mmol) in THF (20 cm^3) at − 30°C. The color of the suspension slowly turned from light yellow to red. After this, solid dppa (0.096 g, 0.25 mmol) was added and the solution was further stirred for 3 h. The reaction mixture was filtered on a Celite-padded filter funnel to remove insoluble material, containing NaCl. The ^{31}P{^{1}H}-NMR spectrum (THF/acetone-d_6) of the reaction mixture revealed the presence of **4**, $[Co_2Pd(\mu_3\text{-CO})(CO)_4(\mu\text{-dppm})_2]$ and $[(OC)_2\overline{Co(\mu\text{-dppa})_2Pd}\,Cl]$ (**5**). The solution was impregnated on silica gel, evaporated to dryness and the residue was chromatographed on a silica gel column. Elution with a mixture of hexane (75%) and toluene (25%) gave first a pale yellow solution of unreacted compounds. Elution with a mixture of hexane (25%) and toluene (75%) afforded a light purple solution of $[Co_2Pd(\mu_3\text{-CO})(CO)_4(\mu\text{-dppm})_2]$ [5a] characterized by IR and ^{31}P{^{1}H}-NMR spectroscopics methods. Elution with pure toluene afforded a dark purple solution of **5** characterized by IR and ^{31}P{^{1}H}-NMR spectroscopic methods. Further elution with THF afforded a small amount of a mixture of **4** and **5**. Some dark purple material remained on top of the column that could not be eluted with THF or CH_2Cl_2.

Complex **4** could not be isolated in pure form and was characterized in solution by its ^{31}P{^{1}H}-NMR spectrum (acetone-d_6): δ 78.7 (br, m, P → Co_{dppa}), 48.9 (m, P → Pd_{dppa}), 27.55 (br, m, P → Co_{dppm}), − 13.7 (d, P → Pd_{dppm}, ^2J(PP) = 34 Hz).

3.2.8. *$[(OC)_2\overline{Co(\mu\text{-}dppa)_2Pd}\,Cl]$* (**5**)

A filtered solution of $Na[Co(CO)_4]$ (0.1 M in THF, 2.8 cm^3) and $[Pd(\text{dppa-}P,P')_2](BF_4)_2$ (0.279 g, 0.266 mmol) in THF (20 cm^3) was stirred for 2 h at − 30°C. The color of the mixture rapidly turned from light yellow to brown. After this time LiCl (0.011 g, 0.266 mmol) was added. The solvent was evaporated to dryness under reduced pressure, the residue was extracted with dichloromethane (20 cm^3) and the solution was filtered through a Celite-padded filter funnel. The solvent was removed in vacuo and the residue was recrystallized from a mixture of THF (15 cm^3) and pentane (60 cm^3) at − 20°C to afford green–brown microcrystalline powder of (**5** · THF) (0.155 g, 53% based on Pd). (Found: C, 58.37; H, 4.33; N, 2.58. $C_{50}H_{42}PdN_2O_2P_4ClCo \cdot THF$ requires C, 58.98; H, 4.58; N, 2.55%). IR (THF): ν(CO) 1959vs and 1895s–br cm^{-1}. NMR (acetone-d_6): ^{1}H, δ 7.78–7.24 (m, 40H, aromatic), 6.29 (br, 2H, NH), 3.63 and 1.80 (THF signals); ^{31}P-{^{1}H}, δ 82.0 (br, P → Co), 63.5 (t, P → Pd, $N = |J(P_AP_X) + J(P_AP_{X'})| = 116$ Hz).

3.2.9. *$[MoPd_2ClCp(\mu_3\text{-}CO)_2(\mu\text{-}dppa)_2]$* (**6**)

A filtered solution of $Na[MoCp(CO)_3] \cdot 2DME$ (0.1 M in THF, 6.8 cm^3) was added to a cooled (− 78°C) and stirred suspension of $[Pd_2Cl_2(\mu\text{-dppa})_2]$ (0.360 g, 0.342 mmol) in 20 cm^3 THF. The reaction was progressively raised to ambient temperature while stirring was maintained for 2 h. The yellow–brown mixture was filtered to remove insoluble NaCl. The filtrate was evaporated to dryness and the residue extracted with CH_2Cl_2. Precipitation with *n*-hexane yielded **6** (0.152 g, 62%) contaminated with $[Pd_2Cl_2(\mu\text{-dppa})_2]$ (25% by NMR). Attemps to isolate pure **6** were unsuccessful. Data for **6**: IR (THF): ν(CO) 1795mw and 1745s cm^{-1}. NMR (acetone-d_6): ^{1}H, δ 7.48–7.19 (m, 40H, aromatic), 6.39 (m, 1H, NH), 6.18 (m, 1H, NH); ^{31}P-{^{1}H}, δ 100.2 (m, P → Mo), 45.1 (m, 2P → Pd), 42.5 (m, P → Pd).

3.2.10. *[MoPd$_2$ClCp(μ_3-CO)$_2${μ-(Ph$_2$P)$_2$NMe}$_2$]* (**7**)

To a solution of [MoPd$_2$ClCp(μ_3-CO)$_2$(μ-dppa)$_2$] (**6**) (0.249 g, 0.201 mmol) in 20 cm^3 THF was added an excess of KH (2 mmol), gas evolution was observed, indicating that a reaction was occuring. When gas evolution stopped an excess of MeI (2 mmol) was added and stirring was maintained for 3 h. After filtration the solvent was removed in vacuo and the residue was then recrystallized from CH$_2$Cl$_2$–*n*-pentane, affording a green–brown microcrystalline powder of **7** (0.094 g, 37%). (Found: C, 54.36; H, 4.29; N, 1.96. C$_{57}$H$_{50}$Pd$_2$N$_2$O$_2$P$_4$-ClMo requires C, 54.18; H, 3.96; N, 2.22%). IR (KBr): ν(CO) 1797m and 1747s cm^{-1}. NMR (acetone-d_6): ^{1}H, δ 7.56–7.14 (m, 40H, aromatic), 1.99 (br, 6H, CH$_3$); ^{31}P-{^{1}H}, δ 118.3 (m, P → Mo, $|^{2+3}J(\mathrm{PP})| = 27$ Hz), 70.0 (m, P → Pd), 67.2 (m, P → Pd), 64.9 (m, P → Pd). The other coupling constants were not determined.

3.2.11. *[MoPd$_2$ClCp(μ_3-CO)$_2${μ-(Ph$_2$P)$_2$NEt}$_2$]* (**8**)

This complex was obtained following a procedure similar to that detailed for **7**, using [Pd$_2$MoClCp(μ_3-CO)$_2$(μ-dppa)$_2$] (**6**) (0.249 g, 0.201 mmol) and EtI (2 mmol). Recrystallization of the product from CH$_2$Cl$_2$–*n*-hexane led to the formation of a green–brown microcrystalline powder containing **8** and [Pd$_2$MoClCp(μ_3-CO)$_2$(μ-dppa)$_2$] (**6**). The two products could not be separated or purified. Complex **8** was characterized by its ^{31}P{^{1}H}-NMR spectrum (acetone-d_6): δ 119.6 (m, P → Mo, $|^{2+}3J(\mathrm{PP})| = 28$ Hz), 71.8 (m, P → Pd), 65.9 (m, P → Pd), 63.7 (m, P → Pd). The other coupling constants were not determined.

3.3. *X-ray structure determination for [Co$_2$Pt(μ_3-CO)(CO)$_6$(μ-dppa)]* (**1**)

Crystal data and experimental details are given in Table 2. The X-ray data of the compound were collected on a Siemens SMART CCD area detector diffractometer using graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å), a nominal crystal-to-detector distance of 3.85 cm and 0.3° ω-scan frames. Corrections for Lorentz polarization effects as well as an empirical adsorption correction with the program SADABS were applied [17]. The structures were solved by direct methods (SHELXS86). Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL93) with anisotropic thermal parameters for all non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in idealized positions.

4. Supplementary material

All the crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 103340. 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.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 2
Crystal data and structure refinement for [Co$_2$Pt(μ_3-CO)(CO)$_6$(μ-dppa)] (**1**)

Empirical formula	C$_{31}$H$_{21}$Co$_2$NO$_2$P$_2$Pt
Formula weight (g mol^{-1})	894.38
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.9719(2)
b (Å)	13.9234(2)
c (Å)	21.8041(2)
α (°)	87.249(1)
β (°)	83.265(1)
γ (°)	74.873(1)
V (Å^3)	3192.80(8)
Z	4
$D_{\mathrm{calc.}}$ (g cm^{-3})	1.861
T (K)	293(2)
μ (mm^{-1}) (Mo–K$_\alpha$)	5.545
Absorption correction	Empirical
F(000)	1728
Crystal size (mm)	0.22 × 0.18 × 0.04
θ range (°)	0.94–25.00
Indices ranges	$-11 \le h \le 15$, $-19 \le k \le 19$, $-22 \le l \le 31$
Reflections collected	18181
Independent reflections	11067 [$R_{\mathrm{int}} = 0.0572$]
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.982
Final R indices [$I = 2\sigma(I)$]	$R = 0.0593$, $R_w = 0.1130$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0492{*}P)^2]$ with $P = (\max(F_o^2, 0) + 2{*}F_o^2)/3$
Diff. Fourier peaks min./max. (e Å^{-3})	$-2.436/2.303$

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