

REACTIVITY OF ANIONIC METAL CARBONYL HYDRIDES TOWARD BIS(DIPHENYLPHOSPHINO)METHANE COMPLEXES OF PALLADIUM AND PLATINUM *

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Summary

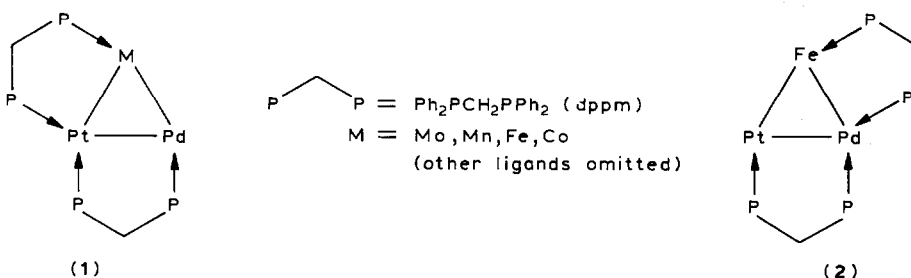
The reactions between $[\text{PPN}][\text{HFe}(\text{CO})_4]$ or $[\text{PPN}][\text{HFeCr}(\text{CO})_9]$ and $[\text{PdPt}(\mu\text{-dppm})_2\text{Cl}_2]$ (**3**) in THF have been shown to give the trimetallic cluster $[\text{FePdPt}(\mu\text{-dppm})_2(\text{CO})_4]$; because of the residual acidity of the H ligand in the starting anions, they behave as precursors of $[\text{Fe}(\text{CO})_4]^{2-}$. Hydride transfer followed by molecular rearrangement takes place in the reactions between $[\text{Et}_4\text{N}][\text{HM}(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{W}$) and $[\text{PtCl}_2(\text{dppm})]$, which give $[\text{Pt}_2(\mu\text{-H})(\mu\text{-dppm})_2\text{H}_2][\text{MCl}(\text{CO})_5]$. Products resulting from redox exchange and intermolecular dppm (and sometimes CO) transfer were isolated from the reactions of $[\text{Pd}_2(\mu\text{-dppm})_2\text{Cl}_2]$ with $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ or $[\text{Et}_4\text{N}][\text{HCr}(\text{CO})_5]$, and of the latter anion with **3**. Whereas reaction of this anion with *trans*- $[\text{PdCl}_2(\text{PEt}_3)_2]$ led to reduction to palladium metal, *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ was converted into $[\text{Pt}_4(\mu\text{-CO})_5(\text{PEt}_3)_4]$ (79% yield).

Introduction

The use of bis(diphenylphosphino)methane ($\text{Ph}_2\text{PCH}_2\text{PPh}_2 = \text{dppm}$) as a stabilising ligand capable of holding two metal centers in close proximity has met with considerable success [1,2]. There is now a large number of homo- and hetero-bi-nuclear complexes and clusters containing one or more dppm ligands whose presence largely determine the structural [3], chemical, or electrochemical [4] molecular properties. We recently reported methods of making mixed-metal cluster compounds containing one or more dppm ligands [5,6]. An easy route to such clusters containing three different metal atoms involves the reaction of the bi-

* Dedicated to Professor Jean Tirouflet, with good wishes for a long and happy retirement.

metallic complex $[\text{PdPt}(\mu\text{-dppm})_2\text{Cl}_2]$ with carbonylmetallate anions [7,8], which affords molecules containing the almost planar core MPdPtP_4 (1).



The regioselective insertion of the metal carbonyl fragment M into the palladium–phosphorus bond of the precursor complex has been observed with the carbonylmetallate anions $[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$, $[\text{Mn}(\text{CO})_5]^-$, $[\text{Fe}(\text{CO})_3\text{NO}]^-$ and $[\text{Co}(\text{CO})_4]^-$ [7]. In the case of $[\text{Fe}(\text{CO})_4]^{2-}$, however, the kinetically favoured isomer of type 1 readily isomerizes to a type 2 structure, which is that of the slightly preferred thermodynamic isomer of $[\text{FePdPt}(\text{CO})_4(\mu\text{-dppm})_2]$ [8].

We have found that reactions of $[\text{Pd}_2(\mu\text{-dppm})_2\text{Cl}_2]$ and $[\text{PdPt}(\mu\text{-dppm})_2\text{Cl}_2]$ with carbonylmetallates generally give clusters which are structurally closely related, although reactions with the former substrate are much faster than those with the latter [7,8].

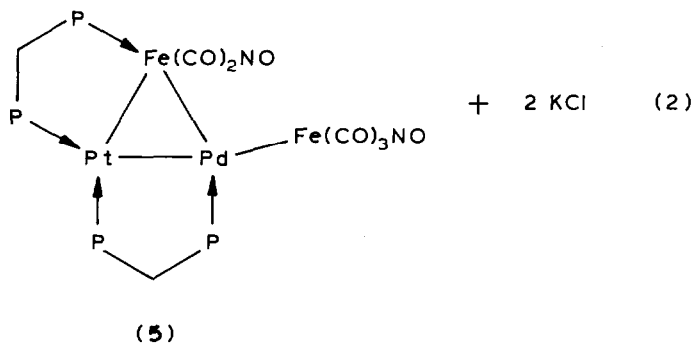
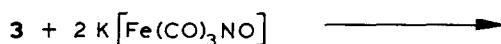
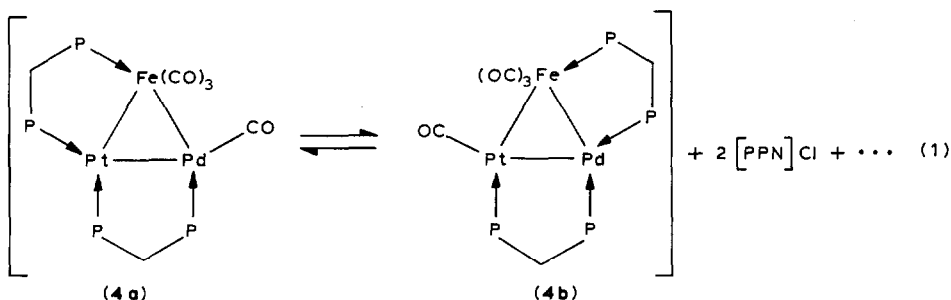
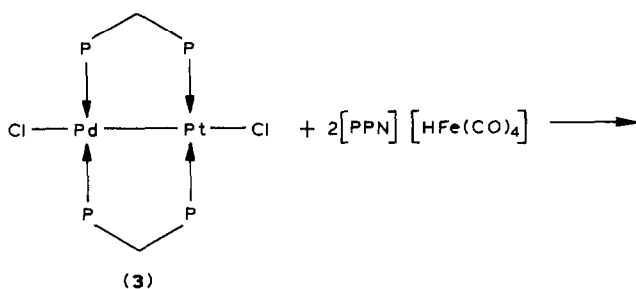
In view of the current interest in (i) selective syntheses of and metal–ligand interactions in mixed-metal cluster compounds [9,10], and (ii) the reactions of metal carbonyl hydrides, which may behave inter alia as acids [11] or as hydride donors [12], we decided to investigate the reactions of anionic iron and group 6 mono- and di-nuclear carbonyl hydrides with mono- and di-nuclear palladium and/or platinum dppm complexes. These reactions are described below along with others with related systems.

Results and discussion

The bimetallic complex $[\text{PdPt}(\mu\text{-dppm})_2\text{Cl}_2]$ (3) reacts with 2 equivalents of $[\text{PPN}][\text{HFe}(\text{CO})_4]$ ($\text{PPN} = \text{Ph}_3\text{PNPPH}_3$) in tetrahydrofuran (THF) at 60°C to give complex 4 as a mixture of two structural isomers (eq. 1).

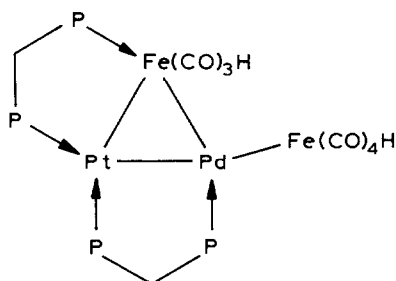
The cluster $[\text{FePdPt}(\mu\text{-dppm})_2(\text{CO})_4]$ (4) has previously been isolated in high yield from the reaction of 3 with $\text{Na}_2[\text{Fe}(\text{CO})_4]$ and the isomerization of the kinetically favoured isomer 4a into 4b has been monitored by IR ($\nu(\text{CO})$) and ^{31}P NMR spectroscopy and shown to reach an equilibrium with isomers in a ca. 1/1 ratio [8]. It is noteworthy that in this reaction $[\text{HFe}(\text{CO})_4]^-$ behaves as a precursor of $[\text{Fe}(\text{CO})_4]^{2-}$, and that the hydride ligand neither remains associated with Fe nor is transferred onto another metal centre. This is consistent with the known acidity of the iron carbonyl hydrides [11] and with the observation that $[\text{HFe}(\text{CO})_4]^-$ does not transfer H^- to $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Cr, W}$) either [13].

It is interesting to compare the reaction of eq. 1 with the related one involving the anion $[\text{Fe}(\text{CO})_3\text{NO}]^-$, which gave the stable and well-characterized cluster $[\text{Fe}_2\text{PdPt}(\mu\text{-dppm})_2(\text{CO})_5(\text{NO})_2]$ (5) [7b] (eq. 2).



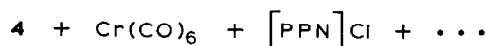
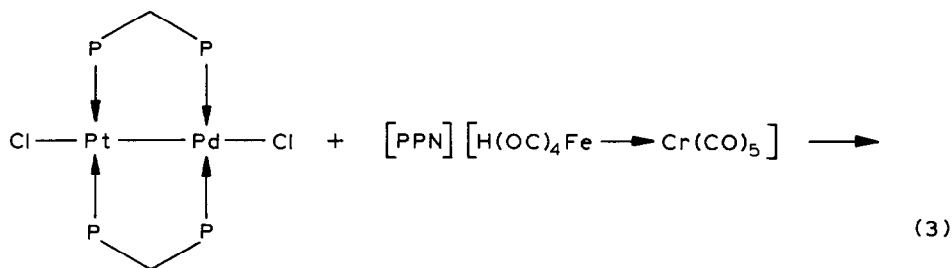
In view of the isolobal analogy between the trigonal pyramidal fragment $[(\text{ON})(\text{OC})_3\text{Fe}]^-$ and the distorted square pyramidal fragment $[\text{H}(\text{OC})_4\text{Fe}]^-$ (viewed as a protonated $[\text{Fe}(\text{CO})_4]^{2-}$, it is possible that a product such as **6**, similar to **5**, was formed by the reaction of eq. 1, but we were unable to identify it. (Formal elimination of $\text{H}_2\text{Fe}(\text{CO})_3$ from **6** would lead to **4**). Thus we cannot unambiguously decide whether loss of H^+ from $[\text{HFe}(\text{CO})_4]^-$ occurs at an early stage in the reaction of eq. 1, or whether **4** is formed via a labile intermediate, such as **6**, in which metal-metal interactions are expected to lower the electron density at the Fe centres and thus enhance the acidity of the H ligand. The latter suggestion would be

consistent with the experimental that in the reaction of eq. 1, 2 equivalents of $[\text{HFe}(\text{CO})_4]^-$ are necessary for complete consumption of **3**.

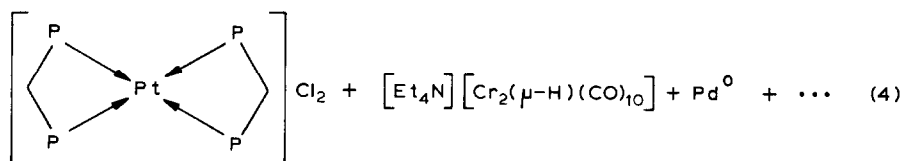


(6)

Reaction of **3** with one equivalent of the bimetallic complex $[\text{PPN}][\text{HFeCr}(\text{CO})_9]$ took place with rupture of the $\text{Fe} \rightarrow \text{Cr}$ bond, and **4** was again isolated (eq. 3). As previously noted [14], the lability of the dative $\text{Fe} \rightarrow \text{Cr}$ bond accounts for the formation of these products and somewhat limits the use of this and related bimetallic anions in the synthesis of mixed-metal clusters. The isolation of some unchanged **3** suggests that two equivalents of the dimetal carbonylate anion are also necessary in this reaction (see above).

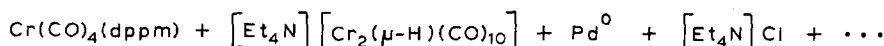
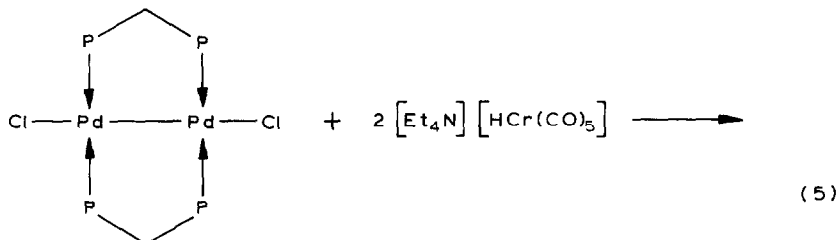


We were unable to isolate any heterometallic complex from the reaction of **3** with 2 equivalents of $[\text{Et}_4\text{N}][\text{HCr}(\text{CO})_5]$. Electron transfer occurred instead, and formal disproportionation of the $\text{Pd}^{\text{I}}-\text{Pt}^{\text{I}}$ dimer **3** gave the bis-dppm- Pt^{II} complex $[\text{Pt}(\text{dppm})_2]^{2+}$ together with Pd metal (eq. 4).



Hydride transfer from $[\text{HCr}(\text{CO})_5]^-$ evidently takes place during the reaction, leaving the unsaturated neutral fragment $[\text{Cr}(\text{CO})_5]$ to combine with unchanged $[\text{HCr}(\text{CO})_5]^-$ and affording the stable hydride-bridged dichromium carbonylate $[\text{Cr}_2(\mu\text{-H})(\text{CO})_{10}]^-$ [15].

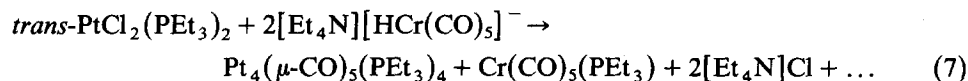
A somewhat related reaction occurred between $[\text{Pd}_2(\mu\text{-dppm})_2\text{Cl}_2]$ and $[\text{HCr}(\text{CO})_5]^-$, but with complete reduction of Pd^{II} to Pd^0 (eq. 5).



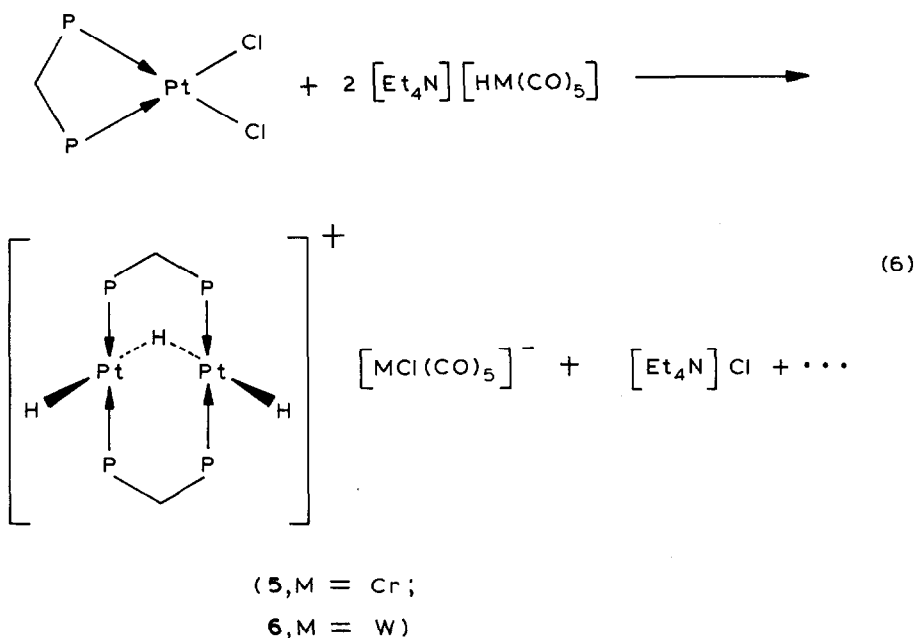
These results are consistent with electrochemical data, which indicate that reduction of $[\text{Pd}_2(\mu\text{-dppm})_2\text{Cl}_2]$ is easier than that of $[\text{PdPt}(\mu\text{-dppm})_2\text{Cl}_2]$ [4a]. On the other hand, the dianion $[\text{Cr}_2(\text{CO})_{10}]^{2-}$ reacts with $[\text{Pd}_2(\mu\text{-dppm})_2\text{Cl}_2]$ to give the A-frame complex $[\text{Pd}_2(\mu\text{-CO})(\mu\text{-dppm})_2\text{Cl}_2]$ [16] (55% yield) and some $[\text{Cr}(\text{CO})_4(\text{dppm})]$ [17]. This indicates that $[\text{Cr}_2(\text{CO})_{10}]^{2-}$ is less reducing than $[\text{HCr}(\text{CO})_5]^-$ towards $[\text{Pd}_2(\mu\text{-dppm})_2\text{Cl}_2]$.

Such redox reactions would be expected to be sensitive to the oxidation state of the palladium or platinum atom(s) in the precursor complex and thus, reaction of $[\text{Pt}(\text{dppm})\text{Cl}_2]$ with 2 equivalents of $[\text{HM}(\text{CO})_5]^-$ ($\text{M} = \text{Cr}, \text{W}$) resulted in hydride transfer and formation of the known trihydridodiplatinum cation $[\text{Pt}_2(\mu\text{-H})(\mu\text{-dppm})_2\text{H}_2]^+$ [18] (eq. 6).

The identities of complexes **5** and **6** were determined by elemental analysis and comparison of the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of their cations with those of the cations of $[\text{Pt}_2(\mu\text{-H})(\mu\text{-dppm})_2\text{H}_2]\text{PF}_6$ [19] and also of the IR($\nu(\text{CO})$ region) spectra of their anions with those of the anions in the corresponding $[\text{Et}_4\text{N}][\text{MCl}(\text{CO})_5]$ complexes [20]. In reactions with other carbonylmetallates, e.g. $[\text{Mn}(\text{CO})_5]^-$, $[\text{Mo}(\text{or W})(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$ or $[\text{Fe}(\text{CO})_4]^{2-}$, we recently found that use of $[\text{PtCl}_2(\text{dppm})]$ leads to heterometallic clusters containing at least one bridging dppm ligand [6]. Such a dppm-assisted process is also involved in the reaction shown in eq. 6, although in this case the ligand holds in proximity two identical metals, and thus stabilizes a Pt dimer. In the absence of ligands, such as dppm, capable of stabilizing a dinuclear complex, $[\text{HCr}(\text{CO})_5]^-$ reduces Pt^{II} phosphine complexes to Pt^0 carbonyl clusters (eq. 7).



This known Pt_4 cluster [21] is likely to have a butterfly structure, as established for the case in which the phosphine is PMe_2Ph [21,22]. A similar reaction has been observed between $\text{trans-}[\text{PtCl}_2(\text{PEt}_3)_2]$ and 2 equivalents of $[\text{Mn}(\text{CO})_5]^-$ or $[\text{Fe}(\text{CO})_3\text{NO}]^-$, which afforded the Pt^0 cluster $[\text{Pt}_5(\mu\text{-CO})_5(\text{CO})(\text{PEt}_3)_4]$ [23]. Reac-



tion of *trans*-[PdCl₂(PEt₃)₂] with 2 equivalents of [HCr(CO)₅][−] led to [Cr(CO)₅(PEt₃)] [24] (52% yield) and reduction to palladium metal. This contrasts with the corresponding reaction involving e.g., [Cr(CO)₃(η-C₅H₅)][−], which yielded the heterometallic cluster [Pd₂Cr₂(η-C₅H₅)₂(CO)₆(PEt₃)₂] [25].

It has been shown that transition metal hydride anions can convert organic halides RX into RH by various pathways, such as electron transfer and nucleophilic displacement [26,27]. The reaction rate is slower for [HFe(CO)₄][−] than for e.g., [HCr(CO)₅][−] [28]. On the other hand, the acidities of the group 8 carbonyl hydrides are known to decrease in the order Fe > Ru > Os [11]. This is consistent with the observation of a direct hydride transfer from [HRu(CO)₄][−], but not from [HFe(CO)₄][−], to a carbonyl ligand on another metal centre, a key step in formyl ligand formation [12]. In the present study the dinuclear complex [Pt₂(μ-H)(μ-dppm)₂H₂]⁺ has been shown to result from hydride transfer from [HM(CO)₅][−] (M = Cr, W) to [Pt(dppm)Cl₂], accompanied by molecular rearrangement. Reactions between [HFe(CO)₄][−] or [HFeCr(CO)₉][−] and [PdPt(μ-dppm)₂Cl₂] (3) have led to the trimetallic cluster [FePdPt(μ-dppm)₂(CO)₄], independently prepared from 3 and [Fe(CO)₄]^{2−}, and confirm the significant residual acidity of the H ligand in these uninegative anions. Other reactions have been investigated, involving other Pd^I, Pd^{II} or Pt^{II} complexes or [Cr₂(CO)₁₀]^{2−}, which proceed by redox exchange. Obviously, platinum tends to form metal–metal bonded complexes more easily than palladium. The oxidation state of the metal centres and the characteristics of the coordinated phosphine ligands (dppm vs. monodentate phosphines) largely determine the nature of the reaction products.

Experimental

All manipulations were carried out in standard Schlenk glassware under purified N₂. All solvents were distilled under N₂ from appropriate drying agents: Na/benzo-

phenone (THF, Et₂O, toluene, hexane), P₄O₁₀ (CH₂Cl₂), or activated 4 Å molecular sieves (acetone). The compounds [Pd₂(μ-dppm)₂Cl₂] [16], [PdPt(μ-dppm)₂Cl₂] [29], *trans*-[PtCl₂(PEt₃)₂] [30], [PPN][HFe(CO)₄] [31], [Et₄N][HCr(CO)₅] [15], Na[Cr₂(CO)₁₀] [32] and [Et₄N][Cr₂(μ-H)(CO)₁₀] [33] were prepared by published procedures. [PtCl₂(dppm)] was prepared by dropwise addition of a stoichiometric amount of a solution of dppm in CH₂Cl₂ to a suspension of [PtCl₂(PhCN)₂] in CH₂Cl₂. After 12 h stirring the precipitate was filtered off and recrystallized from CH₂Cl₂/hexane. The solid was then kept in vacuo at 160 °C for 4 h to remove the solvent of crystallisation [34]. The bimetallic complex [PPN][HFeCr(CO)₉] was prepared by a method analogous to a published procedure [13] but involving reaction of [Cr(CO)₅(NMe₃)] with [PPN][HFe(CO)₄].

The instruments used were described previously [25]. Elemental analyses were performed by the Service Central de Microanalyses du CNRS.

Reaction of [PdPt(μ-dppm)₂Cl₂] (3) with [PPN][HFe(CO)₄]. THF (50 ml) was added at 25 °C to a solid mixture of **3** (0.57 g, 0.50 mmol) and [PPN][HFe(CO)₄] (0.38 g, 0.51 mmol). No reaction occurred at room temperature and the reaction mixture was heated and stirred at 60 °C for 2 h, during which the solution turned red. The solid was filtered off and washed with THF (10 ml) and then with MeOH (30 ml), to remove [PPN]Cl, dried under vacuum, and shown to be unchanged **3** (0.26 g, 0.23 mmol). The red filtrate was evaporated to dryness and the residue extracted with toluene (3 × 10 ml); evaporation of the extract gave **4** which was recrystallized from CH₂Cl₂/hexane (0.51 g, 82% based on reacted **3**), and identified by comparison of its spectroscopic data with those in the literature [8].

When the reaction was carried out with 2 equivalents of [PPN][HFe(CO)₄], complete conversion of **3** was observed, and **4** was isolated in similar yield.

Reaction of [PdPt(μ-dppm)₂Cl₂] with [PPN][HFeCr(CO)₉]. THF (30 ml) was added at 0 °C to a solid mixture of [PdPt(μ-dppm)₂Cl₂] (0.28 g, 0.25 mmol) and [PPN][HFeCr(CO)₉] (0.23 g, 0.26 mmol). No reaction occurred at 0 °C and the mixture was stirred for 12 h at room temperature. Removal of some unchanged **3** and [PPN]Cl by filtration left a red solution, which was evaporated to dryness under reduced pressure. Extraction with toluene (2 × 10 ml) gave a red solution of **4a** and **4b**, contaminated with a little [Cr(CO)₆]. Recrystallization from CH₂Cl₂/hexane afforded pure **4** [8].

Reaction of [PdPt(μ-dppm)₂Cl₂] with [Et₄N][HCr(CO)₅]. THF (50 ml) was added at -40 °C to a solid mixture of **3** (1.14 g, 1 mmol) and [Et₄N][HCr(CO)₅] (0.65 g, 2 mmol). When the mixture was warmed to room temperature the yellow solution began to turn orange-red. The mixture was stirred for 2 h, then the orange suspension was removed by decantation and the supernatant liquor examined by ³¹P{¹H} NMR (THF, acetone-*d*₆) spectroscopy. This revealed the presence of unchanged **3** and [Pt(dppm)₂]²⁺ (singlet with Pt satellites, δ -43.2 ppm, ¹J(PtP) 1886 Hz, consistent with literature values [35]).

Reaction of [Pd₂(μ-dppm)₂Cl₂] with [Et₄N][HCr(CO)₅]. The reaction was carried out as above, but with [Pd₂(μ-dppm)₂Cl₂] in place of **3**. The mixture darkened progressively and after 4 h stirring it was evaporated to dryness. Extraction with toluene and filtration of the extract through Celite on a glass frit gave a yellow solution containing [Cr(CO)₄(dppm)] (and traces of [Cr(CO)₆]), identified by comparison of their IR (ν(CO)) and ³¹P{¹H} NMR spectra with those in the literature [17].

Reaction of $[Pd_2(\mu-dppm)_2Cl_2]$ with $Na_2[Cr_2(CO)_{10}]$. The reaction was carried out as above, using $Na_2[Cr_2(CO)_{10}]$ in a 1/1 ratio in place of $[Et_4N][HCr(CO)_5]$. The mixture was stirred for 2 h at room temperature, during which the initially orange-red suspension was replaced by a red suspension of $[Pd_2(\mu-CO)(\mu-dppm)_2Cl_2]$ (0.59 g, 55%). The orange solution contained $[Cr(CO)_4(dppm)]$ [17] and $[Et_4N][Cr_2(\mu-H)(CO)_{10}]$ [33], identified by comparison of their IR and $^{31}P\{^1H\}$ and 1H NMR spectra, respectively, with those in the literature.

Reaction of $[PtCl_2(dppm)]$ with $[Et_4N][HM(CO)_5]$ ($M = Cr, W$). THF (50 ml) was added at $-78^\circ C$ to a solid mixture of $[PtCl_2(dppm)]$ (0.65 g, 1 mmol) and $[Et_4N][HCr(CO)_5]$ (0.65 g, 2 mmol). The solution immediately turned red. It was stirred for 1 h as the temperature was raised to $0^\circ C$, then concentrated to ca. 10 ml. Cold hexane (50 ml) was added, to produce, at $0^\circ C$, a yellow precipitate which was filtered off and recrystallized twice from acetone/hexane (to remove traces of $[Et_4N][Cr_2(\mu-H)(CO)_{10}]$), to give $[Pt_2(\mu-H)(\mu-dppm)_2H_2][CrCl(CO)_5]$ (**5**) (0.61 g, 88% yield). Anal. Found: C, 43.8; H, 4.6. $C_{55}H_{47}ClCrO_5P_4Pt_2$ calcd.: C, 47.54; H, 3.41%. IR $\nu(CO)$ (THF): 2060 w, 1920 vs, 1857 s cm^{-1} ; 1H NMR (253 K, acetone- d_6) δ -7.5 (pseudo d of quint. with Pt satellites, 2H, PtH_{term} , $^1J(PtH)$ 1120 Hz, $^2J(PtH)$ 115 Hz, $^2J(HH)$ 15.8 Hz, $^{12+41}J(PH)$ 12 Hz), -5.72 (m with Pt satellites, 1H, $PtHPt$, $^1J(PtH)$ 534 Hz); $^{31}P\{^1H\}$ NMR (273 K, C_6D_6) δ 22.0 (s with Pt satellites, $^1J(PtP)$ 2756 Hz, $^2J(PtP)$ 17 Hz, $^2J(PP)$ 57 Hz, $^3J(PP)$ 19 Hz).

A similar experiment was carried out starting from $[Et_4N][HW(CO)_5]$ and gave (slightly less selectively than for the corresponding reaction with $M = Cr$) $[Pt_2(\mu-H)(\mu-dppm)_2H_2][WCl(CO)_5]$ (**6**) (48% spectroscopic yield). Its spectroscopic properties are analogous to those of **5**, with $\nu(CO)$ (THF): 2062 w, 1917 vs, 1858 s cm^{-1} . An authentic sample of $[Et_4N][WCl(CO)_5]$, prepared by a published procedure [20] displayed $\nu(CO)$ (THF) absorptions at 2062 w, 1913 vs, 1852 s cm^{-1} .

Reaction of $trans-[PtCl_2(PEt_3)_2]$ with $[Et_4N][HCr(CO)_5]$. THF (50 ml) was added at $25^\circ C$ to a solid mixture of $trans-[PtCl_2(PEt_3)_2]$ (0.50 g, 1 mmol) and $[Et_4N][HCr(CO)_5]$ (0.65 g, 2 mmol). The mixture was stirred for 12 h and the red solution then concentrated under vacuum to ca. 10 ml and filtered. Addition of hexane led to precipitation of yellow $[Cr(CO)_5(PEt_3)]$ (0.390 g, 63%). Further addition of hexane and cooling at $-40^\circ C$ afforded red $[Pt_4(\mu-CO)_5(PEt_3)_4]$ (0.27 g, 79% yield), identified by comparison of its IR ($\nu(CO)$) and $^{31}P\{^1H\}$ NMR spectra with those previously reported [21].

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