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# Carbonylcyanometalates as building blocks: heterometallic complexes containing Mn(μ-C≡N)M (M = Cu, Au, Ni, Pd or Pt), Mn(μ-C≡N)Pd(μ-dppm)$_2$Mn and Mn(μ-C≡N)M(μ-dppm)$_2$Pd(μ-N≡C)-Mn (M = Pt or Pd) chains of atoms and crystal structure of the mixed-metal cluster [Ru$_3${(μ$_3$-NC)MnCp(CO)$_2$}(μ-AuPPh$_3$)(CO)$_{10}$] †

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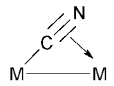
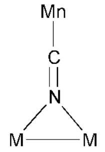
A comparison between the products obtained by reaction of the isosteric metalates [MoCp(CO)$_3$]$^-$ (Cp = η$^5$-C$_5$H$_5$) and [MnCp(or Cp′)(CN)(CO)$_2$]$^-$ (Cp′ = η$^5$-C$_5$H$_4$Me) with various mono- or poly-nuclear complexes of Cu, Au, Ni, Pd, Pt or Ru showed that the metal-centered basicity of the former leads to metal–metal bonding whereas the dominant σ-donor properties of the CN ligand in the latter preferentially lead to the formation of cyanide bridges between the metal centres. Only in the case of the unusual heterometallic octanuclear cluster [(OC)Pd(μ-NC)-MnCp′(CO)$_2$]$_4$ were direct metal–metal bonding *and* CN-bridge formation observed. The crystal structure of [Ru$_3${(μ$_3$-NC)MnCp(CO)$_2$}(μ-AuPPh$_3$)(CO)$_{10}$] was shown by X-ray diffraction to consist of a Ru$_3$Au butterfly whose Ru–Ru hinge is bridged by the *N*-bonded NCMnCp(CO)$_2$ fragment. Controlled thermolysis of the octanuclear cluster [(OC)Pd(μ-NC)MnCp′(CO)$_2$]$_4$ led to the formation of bimetallic particles.

## Introduction

Owing to their often unique structural, physical and chemical properties, cyanide-bridged polynuclear complexes currently arouse increasing interest in co-ordination and organometallic chemistry.[1] The ligands CN$^-$ and CO are isolobal and isoelectronic and generally bind to metals in a terminal manner, through the carbon atom. However, contrary to CO, the cyanide ligand readily forms bridges in M(μ-CN)M binuclear complexes or in M(μ-CN)M(μ-CN)M polynuclear complexes of linear to severely bent curvatures. The metalates [MoCp(CO)$_3$]$^-$ (Cp = η$^5$-C$_5$H$_5$) and [MnCp(CN)(CO)$_2$]$^-$ are isosteric and we became interested in comparing their reactivity towards metal complexes in order to characterize the resulting polymetallic or cluster complexes and evaluate the differences brought about by the cyano ligand.[2] We have recently extended this comparison and reported on new heteropolymetallic chain complexes prepared from the carbonylcyanometalate [Fe{η$^5$-PhBC$_4$H$_4$)(CN)(CO)$_2$]$^-$, which is also isoelectronic with [MnCp(CN)(CO)$_2$]$^-$.[3] The carbonylcyanometalates [Mn(η$^5$-C$_5$H$_4$R)(CN)(CO)$_2$]$^-$ (R = H **1a** or Me **1b**[4]) react with metal complexes such as [W(CO)$_5$(THF)] (THF = tetrahydrofuran) or [MnCp′(CO)$_2$(THF)] (Cp′ = η-C$_5$H$_4$Me) to produce dinuclear anions, [(OC)$_2$Cp′Mn(μ-CN)ML]$^-$ (M = W, L = (CO)$_5$ or M = Mn, L = Cp(CO)$_2$), in which the bridging cyanide ligand acts as an anionic 4 electron donor and the metalloligand [Mn(η$^5$-C$_5$H$_4$R)(CN)(CO)$_2$]$^-$ as a 2 electron donor, through the nitrogen atom. A rarer situation is encountered when the bridging cyanide ligand acts as a σ–π, 4 electron donor of type **A**, as in the homodinuclear complexes [Mo$_2$Cp$_2$(μ-η$^2$-CN)(CO)$_4$]$^-$,[5] [Mn$_2$H(CO)$_4$(μ-η$^2$-CN)(μ-dppm)$_2$],[6] and [Rh$_2$(μ-η$^2$-CN)(μ-CO)-(CO)$_2$(μ-dppm)$_2$]$^+$,[7] or, for the first time in cluster chemistry, in the double helix mixed-metal cluster [(OC)Pd(μ-NC)MnCp′-(CO)$_2$]$_4$ (see **19b** below) which was prepared by reaction of **1b** with [Pd$_4$(μ-CO)$_4$(μ-OAc)$_4$].[2]



(**A**)



(**B**)

The reaction of **1b** with [Ru$_3$(CO)$_{12}$] afforded complexes which display a novel bonding mode for the CN$^-$ ligand, μ$_3$-η$^2$ bonded between two ruthenium and the manganese atoms and thus acting as a 5 electron donor ligand (type **B**).[4b] In these molecules, [MnCp′(CN)(CO)$_2$]$^-$ behaves as an anionic 4 electron donor metalloligand, as in [(OC)Pd(μ-NC)MnCp′(CO)$_2$]$_4$ owing to a μ-CN bridge between the Mn and Pd atoms and a direct Mn–Pd bond.[2] This possible increase in electron donicity of the metalloligand [MnCp′(CN)(CO)$_2$]$^-$ parallels that observed with the isosteric carbonylmetalate [MoCp-(CO)$_3$]$^-$ when it interacts with one (2 electron donor), two (4 electron donor), or three (6 electron donor) metal centres.[8] In order to gain a better insight into the comparative bonding mode of organometallic cyanometalates and carbonylmetalates in polymetallic complexes and clusters, we have examined different systems and present here various heterometallic cyano complexes obtained from reactions between **1a** or **1b** and [Cu(or Au)Cl(PPh$_3$)], [NiCl$_2$(PR$_3$)$_2$] (R = Et or Ph),

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† Dedicated to Prof. S. Shore (Ohio State University) on the occasion of his 70th birthday, with our sincere congratulations and best wishes.

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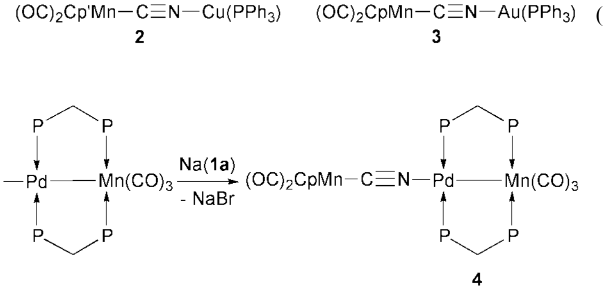
$[Pd(\text{or } Pt)Cl_2(PPh_3)_2]$, $[Pt(dppm\text{-}P,P')_2]Cl_2$, $[MCl_2(dppm\text{-}P,P')]$, $[PdMCl_2(\mu\text{-}dppm)_2]$ (M = Pd or Pt), $[Pd_2Cl_2(\mu\text{-}CO)(PPh_3)_3]$, $[Ru_3(CO)_{12}]$ and $[Pd_4(\mu\text{-}CO)_4(\mu\text{-}OAc)_4]\cdot 2AcOH$.

## Results and discussion

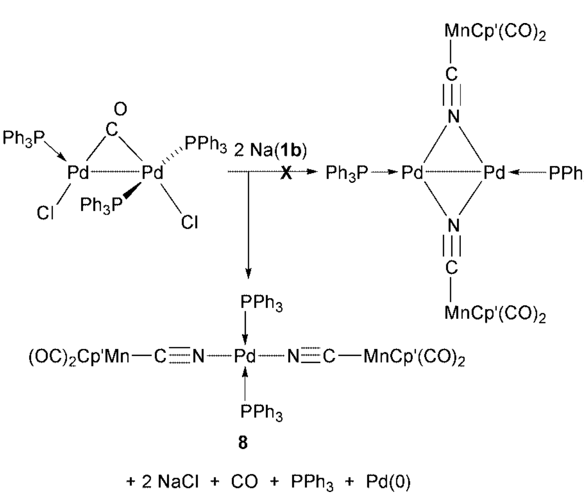
The reactions of 1 equivalent of **1a** or **1b** with $[MCl(PPh_3)]$ (M = Cu or Au) or $[Br\overline{Pd(\mu\text{-}dppm)_2}Mn(CO)_3]$ (dppm = $Ph_2PCH_2PPh_2$), eqn. (1), or of 2 equivalents of cyanometalate with $[MCl_2(PPh_3)_2]$ (M = Ni, Pd or Pt), $[NiCl_2(PEt_3)_2]$, $[MCl_2(dppm\text{-}P,P')]$ (M = Pd or Pt), or $[NiCl_2(dppe\text{-}P,P')]$ afforded quantitatively (eqn. 2) complexes in which the metalloligand is co-ordinated by the nitrogen atom to the metal center, leading to linear chains of 4, 5 or 7 atoms in complexes of type [Mn(μ-CN)M] (M = Cu **2** or Au **3**), [Mn(μ-CN)PdMn] **4** or [Mn(μ-CN)M(μ-NC)Mn] (M = Ni **5**–**7**; Pd **8**,**9**; Pt **10**,**11**), respectively. Complex **8** was also obtained (44% yield) in the reaction of $[Pd_2Cl_2(CO)(PPh_3)_3]$[9] with 2 equivalents of **1b**, eqn. (3), as a result of a disproportionation reaction ($2\,Pd^I \longrightarrow Pd^0 + Pd^{II}$) which leads to rupture of the $Pd^I$–$Pd^I$ bond.



$$[M]Cl_2 \xrightarrow[-\,2\,NaCl]{Na[Mn(\eta^5\text{-}C_5H_4R)(CN)(CO)_2]} \qquad (2)$$

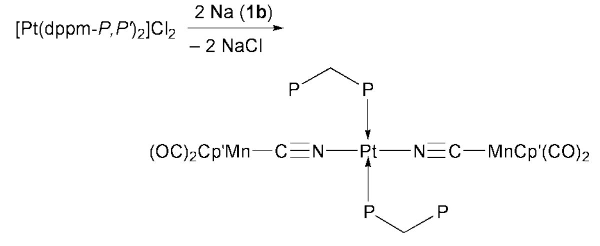
$$(OC)_2(\eta^5\text{-}C_5H_4R)Mn{-}C{\equiv}N{-}[M]{-}N{\equiv}C{-}Mn(\eta^5\text{-}C_5H_4R)(CO)_2$$

**5** $[M] = Ni(PEt_3)_2$; R = H
**6** $[M] = Ni(PPh_3)_2$; R = Me
**7** $[M] = Ni(dppe\text{-}P,P')$; R = Me
**8** $[M] = Pd(PPh_3)_2$; R = Me
**9** $[M] = Pd(dppm\text{-}P,P')$; R = Me
**10** $[M] = Pt(PPh_3)_2$; R = Me
**11** $[M] = Pt(dppm\text{-}P,P')$; R = Me

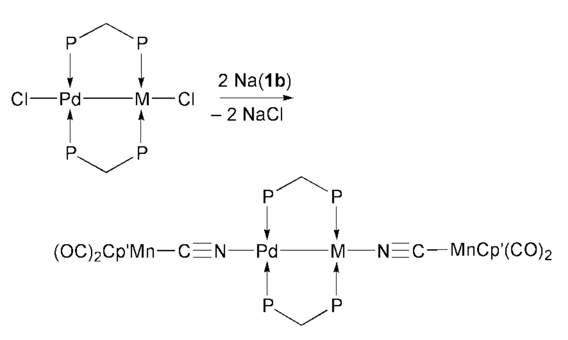


When a solution of **11** in $CH_2Cl_2$ was stirred with an excess of LiCl its $^{31}P\text{-}\{^1H\}$ NMR spectrum ($CH_2Cl_2$–$C_6D_6$) showed the presence of 3 compounds (spectroscopic yield): $[PtCl_2(dppm\text{-}P,P')]$ (27%), **11** (34%) and a complex that could not be isolated pure but was formulated as $[PtCl\{(\mu\text{-}NC)Mn(CO)_2Cp'\}(dppm\text{-}P,P')]$ (39%) (see Experimental section). The same complexes were also obtained, although in a different relative ratio, in the reaction of $[PtCl_2(dppm\text{-}P,P')]$ with 1 equivalent of **1b**. No ligand exchange reaction was observed when equimolar amounts of **11** and $[PtCl_2(dppm\text{-}P,P')]$ were stirred in $CH_2Cl_2$. The $^{31}P\text{-}\{^1H\}$ NMR data for $[PtCl\{(\mu\text{-}NC)MnCp'(CO)_2\}(dppm\text{-}P,P')]$ are consistent with those of *e.g.* $[PtCl\{Mn(CO)_5\}(dppm\text{-}P,P')]$, a platinum(II) chloro complex obtained previously by reaction of $[PtCl_2(dppm\text{-}P,P')]$ with 1 equivalent of $[Mn(CO)_5]^-$.[10] With the aim of generating higher nuclearity complexes, **11** was treated with $[Fe_2(CO)_9]$ but only the known triangular cluster $[Fe_2Pt(CO)_8(\mu\text{-}dppm)]$[11] was isolated after column chromatography. No reaction occurred at room temperature (12 h) between **11** and $[Pd(dba)_2]$ (dba = dibenzylideneacetone).

Reaction of 2 equivalents of **1b** with $[Pt(dppm\text{-}P,P')_2]Cl_2$ resulted in the displacement of two Pt–P bonds and afforded $[Pt\{(\mu\text{-}NC)MnCp'(CO)_2\}_2(dppm\text{-}P)_2]$ **12** in *ca.* 66% yield, eqn. (4). The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **12** at 186 K contains a low field doublet at $\delta$ 9.30 assigned to the phosphorus atoms bonded to platinum ($^1J(PtP)$ = 2367 Hz) and a doublet at $\delta$ −27, assigned to the unco-ordinated phosphorus atoms. At higher temperatures, broadening of the signals occurs owing to exchange between the co-ordinated and unco-ordinated phosphorus atoms. This dynamic intramolecular process occurs by rapid exchanges "end over end".[12] A related opening of chelating dppm was observed in the reaction of $[Pt(dppm\text{-}P,P')_2]^{2+}$ with $CN^-$ which yielded $[Pt(CN)_2(dppm\text{-}P)_2]$.[12a]

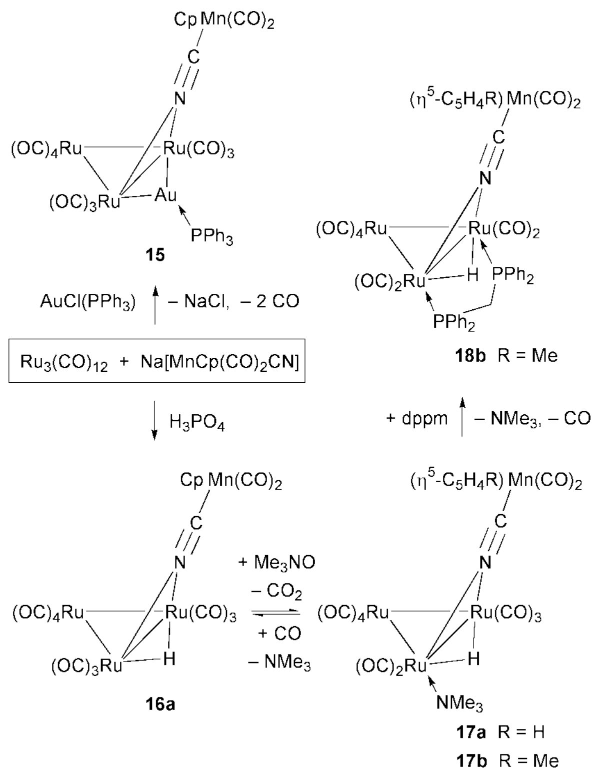


The reaction of $[PdMCl_2(\mu\text{-}dppm)_2]$ (M = Pt or Pd) with 2 equivalents of **1b** afforded quantitatively complexes in which the metalloligand $[MnCp'(CN)(CO)_2]^-$ is again co-ordinated to the metal centres through the nitrogen atom, thus generating linear 8 atom chains in Mn(μ-CN)PdM(μ-NC)Mn (M = Pd **13** or Pt **14**), eqn. (5). As expected, the infrared spectra of complexes **2**–**14** recorded as Nujol mulls or in $CH_2Cl_2$ solutions always contained three main absorptions around 2070 ($\nu$(CN)), 1920 and 1850 $cm^{-1}$ ($\nu$(CO)).



### Reactions with $[Ru_3(CO)_{12}]$ and molecular structure of $[Ru_3\{(\mu_3\text{-}NC)MnCp(CO)_2\}(\mu\text{-}AuPPh_3)(CO)_{10}]$ 15

When the anion $[Ru_3\{(\mu_3\text{-}NC)MnCp(CO)_2\}(CO)_{10}]^-$, generated *in situ* from **1a** and $[Ru_3(CO)_{12}]$,[4b] was treated with $[AuCl(PPh_3)]$ it afforded the cluster $[Ru_3\{(\mu_3\text{-NC})MnCp(CO)_2\}(\mu\text{-AuPPh}_3)(CO)_{10}]$ **15** (Scheme 1) in which the $AuPPh_3$ group bridges a Ru–Ru bond. This complex was characterized by elemental analysis and IR and $^1H$, $^{31}P\text{-}\{^1H\}$ NMR spectroscopic methods and its detailed structure was determined by single-crystal X-ray diffraction (Fig. 1). The $Au(PPh_3)$ group symmetrically bridges the Ru(1)–Ru(3) side of the almost equilateral Ru triangular cluster [Au–Ru(1) 2.756(1) and Au–Ru(3) 2.734(1) Å, Table 1]. These values are comparable to those found in related systems.[13] The Ru atoms of the cluster [Ru–Ru 2.820(1), 2.818(1) and 2.813(1) Å] are bound to ten terminal carbonyl groups. The $Ru_3Au$ metal core is in a butterfly arrangement with the two wings forming a dihedral angle of 121.8(1)°. The cyanocarbonylmetalate ligand is attached *via* the nitrogen atom, which bridges the Ru(1)–Ru(3) side, and acts as a four-electron donor. The Mn(1)C(11)N group is almost linear [Mn(1)–C(11)–N 177.5(7)°] indicating that this fragment is unsaturated; the C(11)–N and Mn–C(11) bond distances are 1.197(10) Å and 1.819(9) Å respectively, in agreement with other values of C–N or Mn–C bond distances. The nitrogen atom is approximately *trans* to two carbonyl groups [N–Ru(3)–C(9) 168.4(3) and N–Ru(1)–C(1) 168.3(3)°]. The nitrogen atom is equidistant from the bridged Ru atoms [N–Ru(1) 2.111(6) and N–Ru(3) = 2.132(6) Å, Ru(1)–N–Ru(3) 83.3(2)°]. These structural data are similar to those found in the structure of $[Ru_3\{(\mu_3\text{-NC})MnCp'(CO)_2\}(\mu\text{-H})(CO)_{10}]$ **16b**,[4b] showing that replacement of the μ-H ligand in the latter by the isolobal $\mu\text{-Au(PPh}_3)$ group is only of little structural consequence.



**Scheme 1**

The complex $[Ru_3\{(\mu_3\text{-NC})MnCp(CO)_2\}(\mu\text{-H})(CO)_{10}]$ **16a** reacts with 1 equivalent of $Me_3NO$ to give $[Ru_3\{(\mu_3\text{-NC})MnCp(CO)_2\}(\mu\text{-H})(CO)_9(NMe_3)]$ **17a**, identified by IR and $^1H$ NMR spectroscopic methods (Scheme 1). Bubbling of CO through its solution quantitatively regenerated **16a**, as shown by infrared spectroscopy. Reaction of **17b** with dppm produced $[Ru_3\{(\mu_3\text{-NC})MnCp'(CO)_2\}(\mu\text{-H})(CO)_8(\mu\text{-dppm})]$ **18b** in 87% yield, in which the dppm ligand and the fragment $(\mu\text{-NC})MnCp'(CO)_2$ bridge the same Ru–Ru bond. Its $^1H$ NMR spectrum showed a high-field triplet (relative intensity 1) at $\delta$ −12.24, assigned to the hydride bridging a metal–metal bond which is coupled with two equivalent P nuclei and two doublets of triplets at $\delta$ 3.71 and 2.99 for the $CH_2$ protons of the dppm ligand.

**Table 1** Selected bond lengths (Å) and angles (°) with esds in parentheses for complex **15**

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 2.820(1) | Mn–C(11) | 1.819(9) |
| Ru(1)–Ru(3) | 2.818(1) | Ru(1)–N | 2.111(6) |
| Ru(2)–Ru(3) | 2.813(1) | Ru(3)–N | 2.132(6) |
| Au–Ru(1) | 2.756(1) | Au–P | 2.304(2) |
| Au–Ru(3) | 2.734(1) | N–C(11) | 1.197(10) |
| Ru(2)–Ru(1)–Ru(3) | 59.85(2) | Au–Ru(3)–Ru(1) | 59.52(2) |
| Ru(1)–Ru(2)–Ru(3) | 60.04(2) | Mn–C(11)–N | 177.5(7) |
| Ru(1)–Ru(3)–Ru(2) | 60.11(2) | Ru(1)–N–Ru(3) | 83.3(2) |
| Ru(1)–Au–Ru(3) | 61.76(2) | C(11)–N–Ru(1) | 141.8(6) |
| Au–Ru(1)–Ru(3) | 58.73(2) | C(11)–N–Ru(3) | 135.0(6) |

## Reaction of complex 1a or 1b with $[Pd_4(CO)_4(OAc)_4]$

We have previously reported that complex **1b** reacts with the palladium(I) cluster $[Pd_4(CO)_4(OAc)_4]\cdot 2AcOH$ to give the blue octanuclear cluster $[(OC)Pd(\mu\text{-NC})MnCp'(CO)_2]_4$ **19b** in high yield whose core structure of $S_4$ symmetry has been shown by X-ray diffraction to consist of two orthogonal helices (see below).[2] A similar cluster was obtained with **1a**. No reaction was observed between **19b** and $PhC_2Ph$, $MeO_2CC{\equiv}CCO_2Me$, $[PtCl_2(NCPh)_2]$, CO, $[Fe_2(CO)_9]$, $[Fe(CO)_5]$ or $NaN_3$, whereas with $HBF_4$, $NaBH_4$, $[Au(PPh_3)]PF_6$ or $HgCl_2$ only decomposition occurred. In the reaction with the phosphines $PPh_3$ or dppm disproportionation of $Pd^I$ took place with formation of **8** or **9**, respectively.

Preliminary studies on the reactivity of $[MoCp(CN)(CO)(NO)]^-$ or $[Cr(CN)(CO)_5]^-$ with $[Pd_4(CO)_4(OAc)_4]\cdot 2AcOH$ were also performed. The reactions are rapid in THF at low temperature (−80 °C), and a nice, green solution is obtained in the former case. However, isolation of pure complexes was not possible, owing to rapid decomposition (even after extraction of the product in toluene). No reaction was observed between **1b** and $[Pt_4(OAc)_8]$.

## Compared reactivity of the isosteric anions $Na[MoCp(CO)_3]$ and $Na[MnCp(CN)(CO)_2]$

Depending on the nature of the metal complexes which were treated with the carbonylcyanometalate **1a** or **1b**, different behaviours and structures were observed which allow comparisons with the results obtained with the isoelectronic carbonylmetalate $[MoCp(CO)_3]^-$.

(*i*) Substitution of Cl in $[MCl(PPh_3)]$ (M = Cu or Au) by 1 equivalent of $[MnCp\ (\text{or}\ Cp')\ (CN)(CO)_2]^-$ yielded the cyanide-bridged complexes $[M\{(\mu\text{-CN})MnCp\ (\text{or}\ Cp')\ (CO)_2\}(PPh_3)]$ **2** and **3** whereas $[MoCp(CO)_3]^-$ afforded the metal–metal bonded complexes $[M\{MoCp(CO)_3\}(PPh_3)]$.[14]

$$(OC)_2CpMn\text{–}C{\equiv}N\text{–}M(PPh_3) \qquad (OC)_3CpMo\text{–}M(PPh_3)$$
$$M = Cu \text{ or } Au$$

(*ii*) Disubstitution of the Cl ligands in $[NiCl_2(PR_3)_2]$ by 2 equivalents of **1a** or **1b** yielded $[Ni\{(\mu\text{-NC})MnCp(\text{or}\ Cp')(CO)_2\}_2(PR_3)_2]$ (R = Et **5** or Ph **6**), respectively. In contrast, the metal–metal bonded heterodinuclear, paramagnetic complex $[Ni\{MoCp(CO)_3\}(PR_3)_2]$ (R = Et or Ph) and trinuclear complex $[Ni\{MoCp(CO)_3\}_2(PR_3)_2]$ were obtained with $[MoCp(CO)_3]^-$.[15]

(*iii*) Disubstitution of the Cl ligands in $[MCl_2(PPh_3)_2]$ (M = Pd or Pt) by 2 equivalents of $[MnCp'(CN)(CO)_2]^-$ afforded the square-planar complexes *trans*-$[M\{(\mu\text{-NC})MnCp'(CO)_2\}_2(PPh_3)_2]$ (M = Pd **8** or Pt **10**) which contain a linear chain of 7 atoms in which the cyano ligands form bridges between Mn and

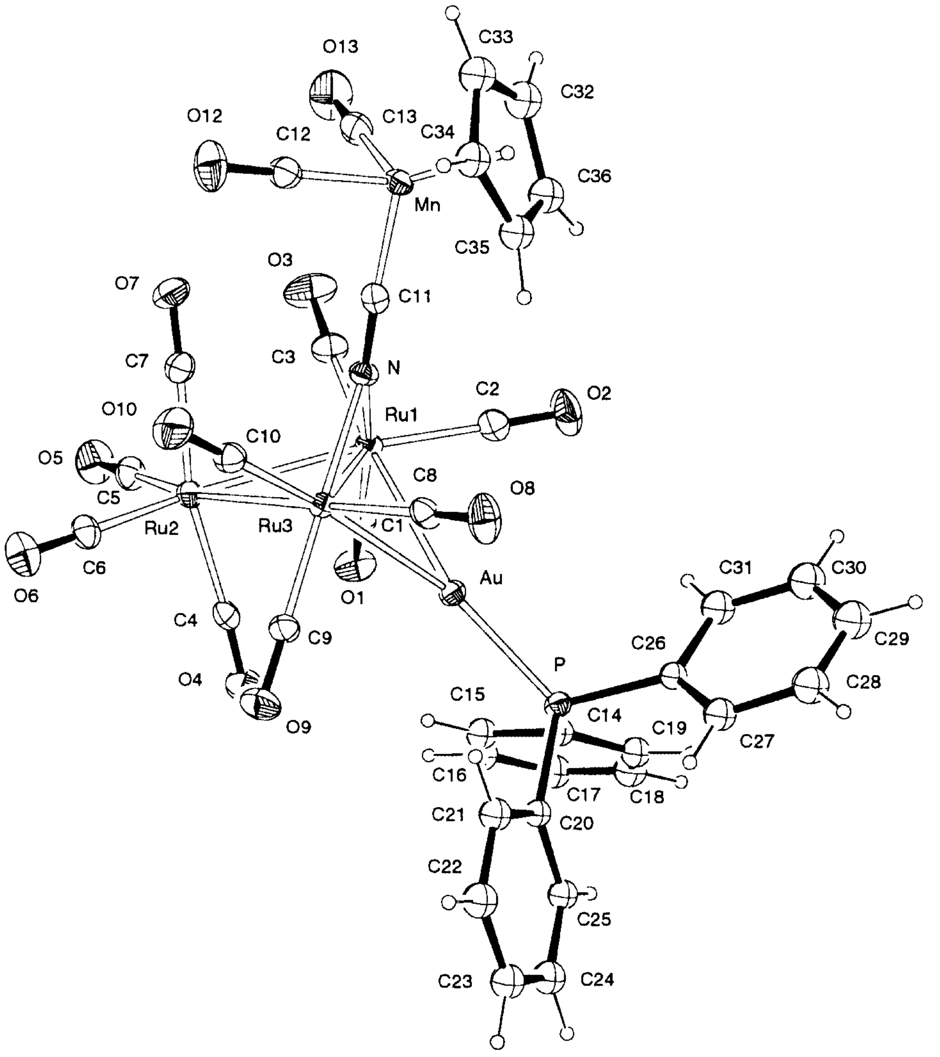
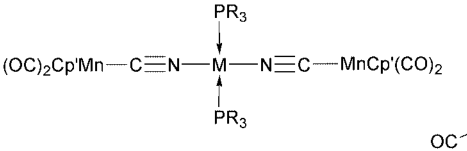


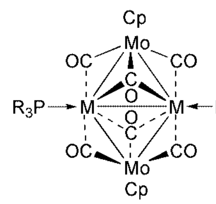
**Fig. 1** View of the molecular structure of $[Ru_3\{(\mu_3\text{-}NC)MnCp(CO)_2\}(\mu\text{-}AuPPh_3)(CO)_{10}]$ **15**.

Pd or Pt, respectively. In contrast, redox reactions between $[MoCp(CO)_3]^-$ and *trans*-$[MCl_2(PR_3)_2]$ (M = Pt or Pd; R = Et, Ph or Bu) resulted in the synthesis of the planar, triangulated, 56 electron clusters $[M_2Mo_2Cp_2(CO)_6(PR_3)_2]$.[16]

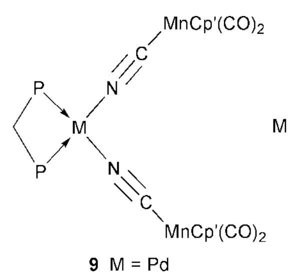


$$(OC)_2Cp'Mn{-}C{\equiv}N{-}\underset{\uparrow}{\overset{\downarrow}{M}}{-}N{\equiv}C{-}MnCp'(CO)_2 \quad (M: PR_3 \text{ above and below})$$

M = Pd, Pt

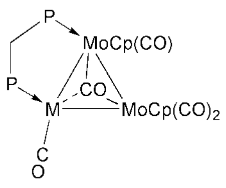


(*iv*) Reaction of $[MnCp'(CN)(CO)_2]^-$ with the $Pd^I$–$Pd^I$ dinuclear complex $[Pd_2Cl_2(\mu\text{-}CO)(PPh_3)_3]$ led to a disproportionation reaction and formation of the palladium(II) complex $[Pd\{(\mu\text{-}NC)MnCp'(CO)_2\}_2(PPh_3)_2]$ **8** and palladium metal, eqn. (3). In contrast, reaction of 2 equivalents of $[MoCp(CO)_3]^-$ yielded the planar cluster $[Pd_2Mo_2Cp_2(CO)_6(PPh_3)_2]$ (see (*iii*)) in which the metalloligands $[MoCp(CO)_3]^-$ bridge the Pd–Pd bond.[9]



**9** M = Pd

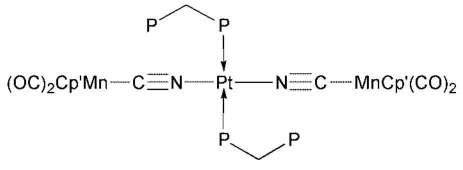
**11** M = Pt



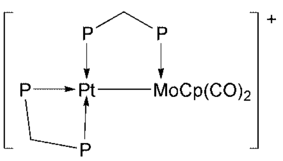
M = Pd, Pt

(*v*) Disubstitution of the Cl ligands in $[MCl_2(dppm\text{-}P,P')]$ (M = Pd or Pt) by 2 equivalents of $[MnCp'(CN)(CO)_2]^-$ afforded $[M\{(\mu\text{-}NC)MnCp'(CO)_2\}_2(dppm\text{-}P,P')]$ (M = Pd **9** or Pt **11**) in which the ligand dppm remains chelated to Pd or Pd. In contrast, the reaction of $[MoCp(CO)_3]^-$ with $[MCl_2(dppm\text{-}P,P')]$ led to triangular clusters $[MMo_2Cp_2(CO)_5(\mu\text{-}dppm)]$ in which the dppm ligand bridges a M–Mo bond.[10] That ring opening of the chelating dppm was not observed here is due to the large separation between the metal centres imposed by the cyano ligand, which releases the steric hindrance generated otherwise.

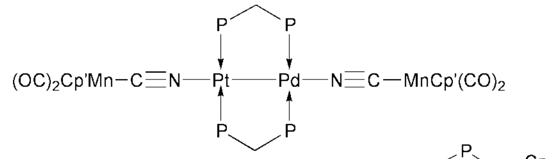
(*vi*) Rupture of two P–Pt bonds in $[Pt(dppm\text{-}P,P')_2]Cl_2$ occurred upon reaction with 2 equivalents of $[MnCp'(CN)(CO)_2]^-$ to afford the neutral complex $[Pt\{(\mu\text{-}NC)MnCp'(CO)_2\}_2(dppm\text{-}P)_2]$ **12**, eqn. (4), which has dangling P atoms. When the corresponding reaction was performed with 2 equivalents of $[MoCp(CO)_3]^-$ the bimetallic cation $[(OC)_2CpMo(\mu\text{-}dppm)Pt(dppm\text{-}P,P')]^+$ was obtained in which a dppm ligand bridges the Pt–Mo bond and the other chelates the Pt.[10b] In the latter case steric factors are again at work which prevent the formation of a stable trinuclear chain complex Mo–Pt–Mo when two sterically demanding ligands, such as tertiary phosphines, are also co-ordinated to Pt.



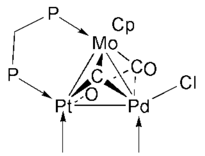
**12**



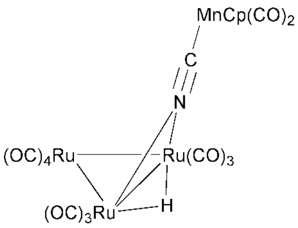
(*vii*) With the dinuclear complexes [$PdMCl_2(\mu\text{-dppm})_2$] (M = Pd or Pt) substitution of both chlorides by two metalloligands [$MnCp'(CN)(CO)_2$]$^-$ led to a linear 8 atoms chain complex MnCNPdPdNCMn **13** or MnCNPtPdNCMn **14**, eqn. (5). No metal insertion into a Pd–P bond with stabilization of a metal–metal bond by the dppm ligand was observed, in contrast to the reaction with 2 equivalents of [$MoCp(CO)_3$]$^-$ which resulted in the formation of the triangular cluster [$PdPtMoCpCl(CO)_2(\mu\text{-dppm})_2$] (see (*v*)).[17]



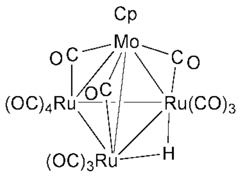
**13**



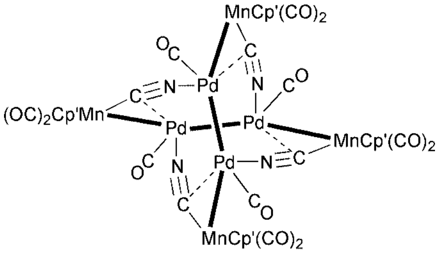
(*viii*) [$MnCp(CN)(CO)_2$]$^-$ reacted with [$Ru_3(CO)_{12}$] to give, after acidification with $H_3PO_4$, the neutral complex [$HRu_3\{(\mu\text{-NC})MnCp(CO)_2\}(CO)_{10}$] **16a** in which the metalloligand bridges a Ru–Ru bond through the cyano group.[4b] When this reaction was carried out with [$MoCp(CO)_3$]$^-$ instead the tetranuclear cluster [$HRu_3MoCp(CO)_{12}$] was isolated (also after acidification).[18]



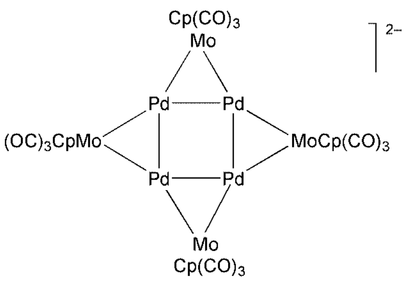
**16a**



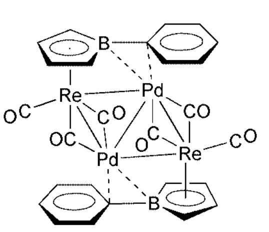
(*ix*) [$MnCp'(CN)(CO)_2$]$^-$ displaces the acetate ligands from the cluster [$Pd_4(OAc)_4(CO)_4$] to give the octanuclear cluster [$(OC)Pd(\mu\text{-NC})MnCp'(CO)_2]_4$ **19b**.[2] The four metalloligands [$MnCp'(CN)(CO)_2$]$^-$ are co-ordinated in an unexpected manner: two orthogonal, tetranuclear chains (Mn–Pd–Pd–Mn) are linked through 4 Pd–N bonds, giving rise to an unprecedented double-helix structure **19a**,**b**. The corresponding reaction of 4 equivalents [$MoCp(CO)_3$]$^-$ with [$Pd_4(OAc)_4(CO)_4$] has yielded in moderate yield the anionic, octanuclear cluster [$Pd_4Mo_4Cp_4(CO)_{12}$]$^{2-}$ **20** through a redox process.[19] A further comparison is available with the reaction of the isoelectronic borole-based metalate [$Re(CO)_3(\eta^5\text{-}C_4H_4BPh)$]$^-$ which afforded with the same palladium precursor the triangulated, 54 e cluster **21**.[20]



**19b**



**20**



**21**

In conclusion, the anions [$Mn(\eta^5\text{-}C_5H_4R)(CN)(CO)_2$]$^-$ (R = H **1a** or Me **2b**) preferentially bind to metals *via* the cyano ligand to give Mn($\mu$-CN)M linkages whereas direct metal–metal interactions M–Mo are favoured in the case of [$MoCp(CO)_3$]$^-$. This is consistent with the HOMO of the cyanometalate reagent being mostly centered on the nitrogen whereas it is metal-based in the latter reagent. Only in the case of the double helix cluster **19** CN-bridge formation and additional Mn–M bonding were observed. There is a parallel behaviour of these metalates towards electrophilic metal complexes and organic electrophiles since carbonylcyanometalates of the type [$M(CN)(CO)_nL_m$]$^{x-}$ undergo various electrophilic addition reactions at the nitrogen atom of the cyanide with formation of terminal isocyanide ligands,[1a] whereas usual carbonylmetalates are *e.g.* alkylated at the metal.

Finally, considering the potential of cluster-derived bimetallic particles in catalysis,[21] we performed preliminary experiments to examine the thermal decomposition of cluster **19b** under an inert atmosphere. This cluster was thermolysed in the bulk or in toluene solution and the resulting black powders were analysed by EDAX and ESCA. The samples contained a homogeneous dispersion of particles (*ca.* 40 Å) containing both palladium (mostly metallic) and Mn (in the form of oxides). The atomic ratios Pd : Mn were always superior to 1 : 1 and ranged from 1.56 to 1.85 (elemental analysis) or 1.34 to 2.10 : 1 (EDAX), which is due to the liberation of some [$MnCp'(CO)_3$] during thermal treatment (see Experimental section). Formation of manganese oxides is not surprising for finely divided particles. Thermogravimetric studies have shown that thermal decomposition of $Mn[Mn(C_2O_4)]\cdot 4H_2O$ under nitrogen affords pyrophoric MnO which transforms in contact with air into $Mn_2O_3$.[22] Further studies will be required to evaluate the properties of the bimetallic particles.

## Experimental

### Reagents and general techniques

All reactions were carried out under an atmosphere of dry nitrogen, in Schlenk-type flasks. Solvents were purified by conventional methods and were dried and distilled under nitrogen. Reagents were used as received, without further purification. Column chromatography was performed under nitrogen with use of silica gel (Kieselgel 60, Merck). Infrared spectra were recorded either as KBr pellets or solutions on a Perkin-Elmer 398 spectrophotometer in the region 4000–400 cm$^{-1}$, NMR spectra on a FT-Bruker WP 200 SY instrument at 200.13 ($^1$H) or 81.02 MHz ($^{31}$P). Proton chemical shifts were positive downfield relative to external SiMe$_4$, $^{31}$P chemical shifts externally referenced to 85% H$_3$PO$_4$ in water, with downfield chemical shifts reported as positive. Elemental analyses were performed by the Service Central de Microanalyses du CNRS. The EDX spectra were recorded on a TEM-STEM Philips EM 420 instrument equipped with EDAX detection; the quantitative calculations were performed by using the usual Cliff–Lorimer method without standard.[23]

### Syntheses

The following complexes were synthesized according to literature methods: Na[MnCp(CN)(CO)$_2$] **1a**,[4a] Na[MnCp′(CN)(CO)$_2$] **1b**,[4b] [MCl(PPh$_3$)] (M = Cu or Au),[24] [NiCl$_2$(PR$_3$)$_2$] (R = Et or Ph),[25] [NiCl$_2$(dppe-*P*,*P*′)],[25] [MCl$_2$(PPh$_3$)$_2$] (M = Pd or Pt),[26] [PtCl$_2$(NCPh)$_2$],[27] [PdCl$_2$(dppm-*P*,*P*′)],[28] [PtCl$_2$(dppm-*P*,*P*′)],[28] [Pt(dppm-*P*,*P*′)$_2$]Cl$_2$,[10b] [PdMCl$_2$(μ-dppm)$_2$] (M = Pt or Pd),[29] [Pd$_2$Cl$_2$(CO)(PPh$_3$)$_3$],[9] [BrPd(μ-dppm)$_2$Mn(CO)$_3$],[30] [Ru$_3$(CO)$_{12}$],[31] [Ru$_3${(μ-NC)MnCp(CO)$_2$}(μ-H)(CO)$_{10}$] **16a**,[4b] [Ru$_3${(μ-NC)MnCp′(CO)$_2$}(μ-H)(CO)$_{10}$] **16b**.[4b] Me$_3$NO was sublimed before use. For the preparation of [Pd$_4$(CO)$_4$(OAc)$_4$]·2AcOH[32] we found it beneficial to recycle the mother liquor, adding each time a quantity of [Pd(OAc)$_2$] equal to that converted into [Pd$_4$(CO)$_4$(OAc)$_4$]·2AcOH in the previous synthesis. The platinum complex [Pt$_4$(OAc)$_8$] was prepared according to the literature, but PtCl$_2$ was used in place of PtCl$_4$, affording similar yields.[33] The cyanometalates **1a** and **1b** have the same reactivity and may be used indifferently. Slight solubility differences are sometimes observed which may facilitate crystallization of the products.

**[Cu{(μ-NC)MnCp′(CO)$_2$}(PPh$_3$)] 2.** Solid [CuCl(PPh$_3$)] (0.360 g, 1.00 mmol) was added to a solution of complex **1b** (0.239 g, 1 mmol) in CH$_2$Cl$_2$ (10 mL). After the mixture was stirred for 0.2 h the solvent was evaporated under reduced pressure. It afforded a pale yellow oil which yielded a solid foam upon prolonged evaporation (0.46 g, 87%). Calc. for **2**·PhCH$_3$: C$_{34}$H$_{30}$CuMnNO$_2$P: C, 64.40; H, 4.77; N, 2.20. Found: C, 64.16; H, 4.32; N, 2.23%. $^{31}$P-{$^1$H} NMR (THF–C$_6$D$_6$): $\delta$ −1.61 (s, br). IR (KBr): $\nu$(CN) 2072m,s, $\nu$(CO) 1912s, 1860s cm$^{-1}$.

**[Au{(μ-NC)MnCp(CO)$_2$}(PPh$_3$)] 3.** The procedure described for the synthesis of complex **2** was applied to the reaction of **1a** (0.225 g, 1.00 mmol) with [AuCl(PPh$_3$)] (0.495 g, 1.00 mmol). The dry residue obtained after evaporation of the solvent was extracted with toluene. Concentration of the toluene solution to *ca.* 10 mL followed by addition of hexane (50 mL) yielded a yellow powder of **3** (0.61 g, 92%). Calc. for C$_{26}$H$_{20}$AuMnNO$_2$P: C, 47.22; H, 3.05; N, 2.12. Found: C, 47.43; H, 3.10; N, 2.15%. $^{31}$P-{$^1$H} NMR (CH$_2$Cl$_2$–CDCl$_3$): $\delta$ 31.35 (s). $^1$H NMR (C$_6$D$_6$): $\delta$ 6.93 (m, 15 H, C$_6$H$_5$) and 4.55 (s, 5 H, C$_5$H$_5$). IR (CH$_2$Cl$_2$): $\nu$(CN) 2064m,s, $\nu$(CO) 1923s, 1862s cm$^{-1}$. IR (Nujol): $\nu$(CN) 2058s, $\nu$(CO) 1927s, 1862s cm$^{-1}$.

**[(OC)$_2$CpMn(μ-CN)Pd(μ-dppm)$_2$Mn(CO)$_3$] 4.** A mixture of [BrPd(μ-dppm)$_2$Mn(CO)$_3$] (1.03 g, 1.00 mmol) and complex **1a** (0.225 g, 1.00 mmol ) in THF (20 mL) was allowed to react at room temperature for 12 h. The red solution was evaporated to dryness under reduced pressure. Extraction with toluene and addition of hexane yielded at −30 °C a red powder of **4** (1.05 g, 87% based on Pd). Calc. for C$_{61}$H$_{49}$Mn$_2$NO$_5$P$_4$Pd: C, 60.24; H, 4.06; N, 1.15. Found: C, 60.26; H, 4.16; N, 1.32%. $^1$H NMR (C$_6$D$_6$): $\delta$ 7.86–6.89 (m, 40 H, C$_6$H$_5$ ), 3.96 (s, 5 H, C$_5$H$_5$) and 3.61 (quint, 4 H, CH$_2$, $|^2J(\mathrm{PH}) + {}^4J(\mathrm{PH})| = 5$ Hz). $^{31}$P-{$^1$H} NMR (CDCl$_3$–CH$_2$Cl$_2$), AA′XX′ spin system: $\delta$ 75.9 (1 P, P–Mn, $N = 121$) and 22.1 (1 P, P–Pd, $N = 121$ Hz). IR (Nujol): 2085m, 1921s, 1860vs and 1828m cm$^{-1}$. IR (CH$_2$Cl$_2$): 2073mw, 1916s and 1851vs, br cm$^{-1}$.

**[Ni{(μ-NC)MnCp(CO)$_2$}$_2$(PEt$_3$)$_2$] 5.** A mixture of complex **1a** (0.585 g, 2.6 mmol) and [NiCl$_2$(PEt$_3$)$_2$] (0.731 g, 2.0 mmol) in toluene (50 mL) was allowed to react at room temperature for 1 h. It was then concentrated to *ca.* 10 mL, filtered through a Celite-padded filter funnel and addition of hexane (50 mL) yielded orange crystals of **5** (1.14 g, 85% yield based on Ni). Calc. for C$_{28}$H$_{40}$Mn$_2$NiO$_4$P$_2$: C, 48.10; H, 5.77; N, 4.01. Found: C, 48.32; H, 5.73; N, 4.08%. $^1$H NMR (C$_6$D$_6$): $\delta$ 4.37 (s, 10 H, C$_5$H$_5$), 1.45 (m, poorly resolved, 12 H, CH$_2$CH$_3$, $^3J$(HH) = 7.92) and 1.14 (dt, 18 H, CH$_2$CH$_3$, $^3J$(HH) = 7.92, $^3J$(PH) = 15.8 Hz). $^{31}$P-{$^1$H} NMR (THF–C$_6$D$_6$): $\delta$ 17.6 (s). IR (CH$_2$Cl$_2$): $\nu$(CN) 2073s, $\nu$(CO) 1926vs, 1862vs cm$^{-1}$. IR (Nujol): $\nu$(CN) 2080m, $\nu$(CO) 1918s, 1860s cm$^{-1}$.

**[Ni{(μ-NC)MnCp′(CO)$_2$}$_2$(PPh$_3$)$_2$] 6.** A mixture of complex **1b** (0.621 g, 2.6 mmol) and [NiCl$_2$(PPh$_3$)$_2$] (0.653 g, 1.0 mmol) in toluene (50 mL) was allowed to react at room temperature for 3 h. It was then concentrated to *ca.* 10 mL, filtered through a Celite-padded filter funnel and addition of hexane (50 mL) yielded violet crystals of **6** (0.88 g, 87% yield based on Ni). Calc. for C$_{54}$H$_{44}$Mn$_2$N$_2$NiO$_4$P$_2$: C, 63.87; H, 4.37; N, 2.76. Found: C, 63.95; H, 4.38; N, 2.85%. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 7.77–7.40 (m, 30 H, C$_6$H$_5$), 3.45 (m, 8 H, MeC$_5$H$_4$) and 1.38 (s, 6 H, MeC$_5$H$_4$). $^{31}$P-{$^1$H} NMR (THF–C$_6$D$_6$): $\delta$ −2.95 (s, br). IR (CH$_2$Cl$_2$): $\nu$(CN) 2063m, $\nu$(CO) 1919vs, 1859vs cm$^{-1}$. IR (Nujol): $\nu$(CN) 2054s, $\nu$(CO) 1918s, 1853s cm$^{-1}$.

**[Ni{(μ-NC)MnCp′(CO)$_2$}$_2$(dppe-*P*,*P*′)] 7.** A mixture of complex **1b** (0.550 g, 2.3 mmol) and [NiCl$_2$(dppe-*P*,*P*′)] (0.529 g, 1.00 mmol) in THF (50 mL) was allowed to react at room temperature for 5 h. It was then evaporated to dryness under reduced pressure. Extraction was performed with toluene, until the solution was nearly colorless, and the violet solution was concentrated and stored at −30 °C where it yielded deep violet crystals of **7** (0.65 g, 73% yield based on Ni). Calc. for C$_{44}$H$_{38}$Mn$_2$N$_2$NiO$_4$P$_2$: C, 59.42; H, 4.31; N, 3.15. Found: C, 59.21; H, 4.19; N, 3.24%. $^1$H NMR (CDCl$_3$): $\delta$ 7.85–7.58 (m, 20 H, C$_6$H$_5$), 4.12 (m, 8 H, C$_5$*H*$_4$Me), 2.20 (m, 4 H, PCH$_2$) and 1.77 (s, 6 H, C$_5$H$_4$*Me*). $^{31}$P-{$^1$H} NMR (THF–C$_6$D$_6$): $\delta$ 57.8 (s). IR (CH$_2$Cl$_2$): $\nu$(CN) 2073s, $\nu$(CO) 1918vs, 1856vs cm$^{-1}$. IR (Nujol): $\nu$(CN) 2077 (sh), 2063vs, $\nu$(CO) 1910vs, 1844vs cm$^{-1}$.

**[Pd{(μ-NC)MnCp′(CO)$_2$}$_2$(PPh$_3$)$_2$] 8.** A mixture of complex **1b** (0.621 g, 2.6 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (0.700 g, 1.00 mmol) in THF (50 mL) was allowed to react at room temperature for 8 h. The solvent was evaporated to dryness under reduced pressure. Extraction with toluene (100 mL) and addition of hexane yielded a red powder of **8** (0.95 g, 89% based on Pd). Calc. for C$_{54}$H$_{44}$Mn$_2$N$_2$O$_4$P$_2$Pd: C, 61.00; H, 4.17; N, 2.63. Found: C, 61.23; H, 4.21; N, 2.64%. $^1$H NMR (C$_6$D$_6$): $\delta$ 7.83–7.11 (m, 30 H, C$_6$H$_5$), 3.71–3.66 (m, 8 H, C$_5$*H*$_4$Me) and 1.54 (s, 6 H, C$_5$H$_4$*Me*). $^{31}$P-{$^1$H} NMR (THF–C$_6$D$_6$): $\delta$ 19.2 (s). IR (CH$_2$Cl$_2$): $\nu$(CN) 2074s, $\nu$(CO) 1918vs, 1865vs cm$^{-1}$. IR (Nujol): $\nu$(CN) 2070vs, $\nu$(CO) 1918vs, 1909vs, 1849vs, br cm$^{-1}$.

**Reaction of [Pd$_2$Cl$_2$(CO)(PPh$_3$)$_3$] with complex 1b.** Toluene (15 mL) was added to a solid mixture of complex **1b** (0.239 g, 1.00 mmol) and [Pd$_2$Cl$_2$(CO)(PPh$_3$)$_3$] (0.548 g, 0.5 mmol) at −80 °C. The solution slowly turned from yellow to deep violet at 0 °C. The reaction temperature was progressively raised to 25 °C (5 h). The mixture was filtered through a Celite-padded filter funnel, and the volume of the filtrate reduced to *ca.* 5 mL by evaporation under vacuum. Addition of hexane (25 mL) yielded a violet powder of **8** (0.24 g, 44% yield based on Pd). When THF was used in place of toluene similar results were observed but **8** was obtained in 39% yield only.

**[Pd{(μ-NC)MnCp′(CO)$_2$}$_2$(dppm-*P*,*P*′)] 9.** A mixture of complex **1b** (0.621 g, 2.6 mmol) and [PdCl$_2$(dppm-*P*,*P*′)] (0.562 g, 1.00 mmol) in THF (50 mL) was allowed to react at room temperature for 12 h then evaporated to dryness under reduced pressure. Extraction with toluene (100 mL) and addition of hexane yielded a red powder of **9** (1.64 g, 90% yield based on Pd). Calc. for $C_{41}H_{32}Mn_2N_2O_4P_2Pd$: C, 56.20; H, 3.51; N, 3.05. Found: C, 55.99; H, 3.74; N, 3.04%. $^1$H NMR ($C_6D_6$): $\delta$ 7.64–6.92 (m, 20 H, $C_6H_5$), 4.44–4.38 (m, 8 H, C$_5$*H*$_4$Me), 3.12 (t, 2H, CH$_2$, $^2J$(PH) = 10.8 Hz) and 2.03 (s, 6 H, C$_5$H$_4$*Me*). $^{31}$P-{$^1$H} NMR (THF–$C_6D_6$): $\delta$ −56.7 (s). IR ($CH_2Cl_2$): *ν*(CN) 2088m, *ν*(CO) 1918vs, 1854vs cm$^{-1}$. IR (Nujol): *ν*(CN) 2063vs, *ν*(CO) 1909vs, 1844vs cm$^{-1}$.

**[Pt{(μ-NC)MnCp′(CO)$_2$}$_2$(PPh$_3$)$_2$] 10.** The same procedure as described for the synthesis of complex **9** was used but starting from [PtCl$_2$(PPh$_3$)$_2$] (1.18 g, 1.5 mmol) and **1b** (1.08 g, 4.5 mmol). It afforded **10** as a yellow powder after precipitation from a toluene solution using hexane (1.43 g, 83% yield based on Pt). Calc. for $C_{54}H_{44}Mn_2N_2O_4P_2Pt$: C, 56.23; H, 3.85; N, 2.43. Found: C, 56.44; H, 3.94; N, 2.60%. $^1$H NMR ($C_6D_6$): $\delta$ 7.80–7.01 (m, 30 H, $C_6H_5$), 3.68–3.56 (m, 8 H, C$_5$*H*$_4$Me) and 1.53 (s, 6 H, C$_5$H$_4$*Me*). $^{31}$P-{$^1$H} NMR (THF–$C_6D_6$): $\delta$ 14.9 (s, with platinum satellites, $^1J$(PtP) = 2508 Hz). IR ($CH_2Cl_2$): *ν*(CN) 2071s, *ν*(CO) 1920vs, 1858vs cm$^{-1}$. IR (Nujol): *ν*(CN) 2071vs, *ν*(CO) 1911vs, 1847vs cm$^{-1}$.

**[Pt{(μ-NC)MnCp′(CO)$_2$}$_2$(dppm-*P*,*P*′)] 11.** A mixture of complex **1b** (0.621 g, 2.6 mmol) and [PtCl$_2$(dppm-*P*,*P*′)] (0.651 g, 1.00 mmol) in THF (50 mL) was allowed to react at room temperature for 12 h, after which time a white precipitate of NaCl formed. The yellow suspension was evaporated to dryness under reduced pressure. Extraction with toluene, followed by filtration of the solution through a Celite-padded filter funnel, concentration of this solution and addition of *n*-hexane yielded a yellow powder of **11** (0.79 g, 78% based on Pt). Calc. for $C_{43}H_{36}Mn_2O_4P_2Pt$: C, 51.05; H, 3.59; N, 2.77. Found: C, 50.43; H, 3.50; N, 2.81%. $^1$H NMR ($C_6D_6$): $\delta$ 7.61–6.94 (m, 20 H, $C_6H_5$), 4.39–4.35 (m, 8 H, C$_5$*H*$_4$Me), 3.48 (t, 2 H, CH$_2$, $^2J$(PH) = 10.7 Hz) and 2.00 (s, 6 H, C$_5$H$_4$*Me*). $^{31}$P-{$^1$H} NMR (THF–$C_6D_6$): $\delta$ −70.8 (s, with platinum satellites, $^1J$(PtP) = 2893 Hz). Signals due to THF were always detected. IR ($CH_2Cl_2$): *ν*(CN) 2071s, *ν*(CO) 1920vs, 1858vs cm$^{-1}$. IR (Nujol): *ν*(CN) 2073s, *ν*(CO) 1921s, 1852s cm$^{-1}$.

**Reaction of complex 11 with an excess of LiCl.** Solid LiCl (0.011 g, tenfold excess) was added to a stirred solution of complex **11** (0.252 g, 0.25 mmol) in $CH_2Cl_2$ (20 mL). The solution was stirred for 5 h and evaporated to dryness under reduced pressure. The $^{31}$P-{$^1$H} NMR ($CH_2Cl_2$–$C_6D_6$) showed the presence of 3 compounds with the following spectroscopic yields: [PtCl$_2$(dppm-*P*,*P*′)] (27%), **11** (34%) and [PtCl{(μ-NC)MnCp′(CO)$_2$}(dppm-*P*,*P*′)] (39%) [$\delta$ −63.8 (d with platinum satellites, $^2J$(PP) = 70, $^1J$(PtP) = 3013, 1P, PtP *trans* to Cl) and −71.5 (d with platinum satellites, $^2J$(PP) = 70, $^1J$(PtP) = 2938 Hz, 1P, PtP *trans* to MnCp′(CN)(CO)$_2$].

**Reaction of [PtCl$_2$(dppm-*P*,*P*′)] with one equivalent of complex 1b.** To a stirred solution of [PtCl$_2$(dppm-*P*,*P*′)] (0.651 g, 1.00 mmol) in $CH_2Cl_2$ (50 mL) was added very slowly (10 h) at room temperature a solution of complex **1b** (0.239 g, 1.00 mmol) in THF (20 mL). The pale yellow suspension was then evaporated to dryness under reduced pressure. The $^{31}$P-{$^1$H} NMR spectrum ($CH_2Cl_2$–$C_6D_6$) of this mixture showed the presence of 3 compounds: [PtCl$_2$(dppm-*P*,*P*′)] (48%), **11** (26%) and [PtCl{(μ-NC)MnCp′(CO)$_2$}(dppm-*P*,*P*′)] (26%) (spectroscopic yields).

**Reaction of complex 11 with [Fe$_2$(CO)$_9$].** A mixture of complex **11** (1.50 g, 1.48 mmol) and [Fe$_2$(CO)$_9$] (0.73 g, 2.00 mmol) in THF (20 mL) was stirred for 5 h. The red solution was evaporated to dryness under reduced pressure. The residue was chromatographed on a silica gel column. Elution with $CH_2Cl_2$–hexane (1 : 3) gave a red band of [PtFe$_2$(μ-dppm)(CO)$_8$], characterized by IR and $^{31}$P-{$^1$H} NMR spectroscopy and comparison with the literature values.[11]

**[Pt{(μ-NC)MnCp′(CO)$_2$}$_2$(dppm-*P*)$_2$] 12.** A mixture of [Pt(dppm-*P*,*P*′)$_2$]Cl$_2$ (0.517 g, 0.5 mmol) and complex **1b** (0.239 g, 1.00 mmol) was suspended in THF (20 mL) and stirred for 12 h at room temperature. The yellow suspension was then evaporated to dryness under reduced pressure. Extraction with toluene followed by filtration through a Celite-padded filter funnel, concentration and addition of hexane yielded at −30 °C a yellow powder of **12** (0.46 g, 66.5% based on Pt). Calc. for $C_{68}H_{58}Mn_2N_2O_4P_4Pt$: C, 58.50; H, 4.19; N, 2.00. Found: C, 58.63; H, 4.16; N, 2.27%. $^1$H NMR ($C_6D_6$): $\delta$ 7.65–6.76 (m, 40 H, $C_6H_5$), 3.81 (m, 12 H, C$_5$*H*$_4$Me and PCH$_2$P) and 1.62 (s, 6 H, C$_5$H$_4$*Me*). $^{31}$P-{$^1$H} NMR (THF–$C_6D_6$, 186 K): $\delta$ 9.30 (1 P, P–Pt, $^1J$(PtP) = 2367 Hz) and −27.0 (1 P, uncoordinated P) with $N = |^2J(P_AP_B) + {}^4J(P_AP_{B'})| = 76.2$ Hz. IR ($CH_2Cl_2$): *ν*(CN) 2083s, *ν*(CO) 1922vs, 1857vs cm$^{-1}$. IR (Nujol): *ν*(CN) 2070vs, *ν*(CO) 1920vs, 1858vs cm$^{-1}$.

**[Pd$_2${(μ-NC)MnCp′(CO)$_2$}$_2$(μ-dppm)$_2$] 13.** A mixture of complex **1b** (0.621 g, 2.6 mmol) and [Pd$_2$Cl$_2$(μ-dppm)$_2$] (1.05 g, 1.00 mmol) in THF (50 mL) was allowed to react at room temperature for 1 h. After evaporation to dryness under reduced pressure, extraction with toluene and addition of hexane yielded a red powder of **13** (1.29 g, 91% yield based on Pd). Calc. for $C_{68}H_{58}Mn_2N_2O_4P_4Pd_2$: C, 57.76; H, 4.42; N, 1.98. Found: C, 57.63; H, 4.34; N, 2.09%. $^1$H NMR ($C_6D_6$): $\delta$ 7.43–7.07 (m, 40 H, $C_6H_5$), 4.26–3.66 (m, 8 H, C$_5$*H*$_4$Me), 3.68 (m, 4 H, $^2J$(PH) = 5 Hz, PCH$_2$P) and 1.71 (s, 6 H, C$_5$H$_4$*Me*). $^{31}$P-{$^1$H} (THF–$C_6H_6$): $\delta$ −5.9 (s). IR ($CH_2Cl_2$): *ν*(CN) 2067s, *ν*(CO) 1913vs, 1846vs cm$^{-1}$. IR (Nujol): *ν*(CN) 2075vs, *ν*(CO) 1916vs, 1905vs, 1834vs cm$^{-1}$.

**[PdPt{(μ-NC)MnCp′(CO)$_2$}$_2$(μ-dppm)$_2$] 14.** A mixture of complex **1b** (0.621 g, 2.6 mmol) and [PdPtCl$_2$(μ-dppm)$_2$] (1.14 g, 1.00 mmol) in THF (20 mL) was allowed to react at room temperature for 3 h then evaporated to dryness under reduced pressure. Extraction with toluene and addition of hexane yielded an orange powder of **14** (1.38 g, 92% based on Pd). Calc. for $C_{68}H_{58}Mn_2N_2O_4P_4PdPt$: C, 54.36; H, 3.89; N, 1.86. Found: C, 54.64; H, 3.89; N, 1.90%. $^1$H NMR ($C_6D_6$): $\delta$ 7.43–7.03 (m, 40 H, $C_6H_5$), 3.91–3.79 (m, 12 H, C$_5$*H*$_4$Me and PCH$_2$P), 1.69 (s, 3 H, C$_5$H$_4$*Me*) and 1.68 (s, 3 H, C$_5$H$_4$*Me*). $^{31}$P-{$^1$H} NMR (THF–$C_6D_6$): $\delta$ 6.5 (d with Pt satellites, $^{2+3}J$(PP) = 43, $^2J$(PtP) = 151; P–Pd) and 0.6 (d with Pt satellites, $^{2+3}J$(PP) = 43, $^1J$(PtP) = 2878 Hz; Pt–P). IR ($CH_2Cl_2$): *ν*(CN) 2070s, *ν*(CO) 1915vs, 1847vs, br cm$^{-1}$. IR (Nujol): *ν*(CN) 2075s, *ν*(CO) 1918s, 1904s, 1833s, br cm$^{-1}$.

**[Ru$_3${(μ-NC)MnCp(CO)$_2$}(μ-AuPPh$_3$)(CO)$_{10}$] 15.** Solid [Ru$_3$(CO)$_{12}$] (0.50 g, 0.78 mmol) was added to a solution of complex **1a** (0.19 g, 0.8 mmol) in THF (25 mL). The mixture was stirred for 12 h and the resulting solution evaporated to dryness. The red residue was dissolved in $CH_2Cl_2$ (25 mL) and solid [AuCl(PPh$_3$)] (0.39 g, 0.80 mmol) added. The red mixture was stirred for 0.2 h and the solvent removed under vacuum. The residue was chromatographed on a silica gel column with hexane–benzene (5 : 1), affording a yellow band of [Ru$_3$(CO)$_{12}$] (0.047 g), followed by a deep red solution of [H$_3$Ru$_4$Au-

$(PPh_3)(CO)_{12}]$ (0.115 g), identified by comparison of its spectroscopic data [$^1$H NMR ($CD_2Cl_2$): $\delta$ 6.8 (m, $C_6H_5$) and −17.61 (s, RuHRu); IR (hexane) $\nu$(CO) 2095m, 2064vs, 2054vs, 2033s, 2015vs, 1978w, 1957w cm$^{-1}$] with those of the literature.[34] Further elution afforded a red solution of **15** (0.60 g, 62%). Calc. for $C_{36}H_{20}AuMnNO_{12}PRu_3$: C, 34.74; H, 1.62; N, 1.12. Found: C, 35.16; H 1.68; N, 1.12%. $^1$H NMR ($C_6D_6$): $\delta$ 7.56–7.02 (m, $C_6H_5$) and 4.30 (s, $C_5H_5$). $^{31}$P-{$^1$H} NMR (THF–$C_6D_6$): $\delta$ 69.9 (s). IR (hexane): 2084w, 2040vs, 2005s, 1969w, 1947w, 1925w and 1846s cm$^{-1}$. IR (KBr): 2094s, 2043vs, 2009vs, 1889s, 1975s, 1954s, 1913s and 1840vs, br cm$^{-1}$.

**[Ru$_3${(μ-NC)MnCp(CO)$_2$}(μ-H)(CO)$_9$(NMe$_3$)] 17a.** A solution of $Me_3NO$ (0.017 g, 0.24 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise to a stirred solution of complex **16a** (0.127 g, 0.16 mmol) in hexane (50 mL) at 0 °C. The IR spectrum showed quantitative conversion into **17**. Owing to its lability, this complex could not be isolated pure in the solid state and was identified by IR and $^1$H NMR spectroscopy. $^1$H NMR ($C_6D_6$): $\delta$ 4.28 (s, 5 H, $C_5H_5$), 2.11 (s, 9 H, $(CH_3)_3N$) and −11.73 (s, 1 H, RuHRu). IR (hexane): 2105w, 2065s, 2025vs, 2002s, 1995m, 1977w, 1940m, 1910m and 1850s cm$^{-1}$. IR (Nujol): 2100w, 2065vs, 2025vs, 2020vs, 2005vs, 1940m and 1847s cm$^{-1}$. When CO was bubbled through a hexane solution of **17a** the solution immediately changed from orange to red. The infrared spectra showed quantitative conversion into **16a**.

**[Ru$_3${(μ-NC)MnCp′(CO)$_2$}(μ-H)(CO)$_8$(μ-dppm)] 18b.** A solution of dppm (0.123 g, 0.320 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise with stirring to a red solution of complex **17b** (0.251 g, 0.320 mmol) in hexane (25 mL) at 0 °C. After the mixture was stirred for 0.2 h, the solvent was removed under vacuum and the orange residue chromatographed on a silica gel column. Elution with hexane–benzene (1 : 1) gave a yellow solution of $[Ru_3(CO)_{12}]$, followed by an orange fraction of **18b** (0.31 g, 87%). Calc. for $C_{42}H_{30}MnNO_{10}P_2Ru_3\cdot 0.5C_6H_6$: C, 46.28; H, 2.84; N, 1.19. Found: C, 46.71; H, 2.95; N, 1.15%. $^1$H NMR ($C_6D_6$): $\delta$ 7.70 (m, $C_6H_5$), 4.23 (m, 4 H, $C_5\mathit{H}_4$Me), 3.71 (dt, 1 H, $^2J$(PH) = 10, $^2J$(HH) = 13.8, PCH$^A$P), 2.99 (dt, 1 H, $^2J$(PH) = 12.1, $^2J$(HH) = 13.8, PCH$^B$P), 1.40 (s, 3 H, $C_5H_4\mathit{Me}$) and −12.24 (t, 1 H, $^2J$(PH) = 13.8 Hz, RuHRu). $^{31}$P-{$^1$H} NMR (THF–$C_6D_6$): $\delta$ 14.85 (s), 10.77 (s). IR (hexane): 2060s, 2010s, 1995s, 1970 (sh), 1955 (sh), 1890w and 1853w cm$^{-1}$. IR (Nujol): 2080m, 2072m, 2020vs, 2007vs, 1990vs, 1982vs, 1970vs, 1943w, 1890m, 1875m, 1865m and 1845m cm$^{-1}$.

**[(OC)Pd(μ-NC)MnCp(CO)$_2$]$_4$ 19a.** The procedure was similar to that detailed below for complex **19b**. Deep violet **19a** was isolated in 85% yield from the reaction of Na[MnCp(CN)(CO)$_2$] (0.450 g, 2.00 mmol) with $[Pd_4(CO)_4(OAc)_4]\cdot 2AcOH$ (0.45 g, 0.5 mmol). $^1$H NMR (toluene-$d_8$): $\delta$ 4.16 (s, Cp). IR (KBr): 2060m, 2050m, 1922vs, 1868m and 1860m cm$^{-1}$.

**[(OC)Pd(μ-NC)MnCp′(CO)$_2$]$_4$ 19b.** A mixture of complex **1b** (0.956 g, 4.0 mmol) and $[Pd_4(CO)_4(OAc)_4]\cdot 2AcOH$ (0.894 g, 1.00 mmol) in toluene (50 mL) was allowed to react at −40 °C. The temperature was progressively raised to 25 °C (4 h) at which the mixture was deep violet. It was filtered through a Celite-padded filter funnel, concentrated to *ca.* 5 mL under reduced pressure and addition of diethyl ether (50 mL) yielded at −30 °C deep violet crystals of **19b** (1.08 g, 78% yield based on Pd). Calc. for $C_{40}H_{28}Mn_4N_4O_{12}Pd_4$: C, 34.27; H, 2.01; Mn, 15.67; N, 4.00; Pd, 30.36. Found: C, 34.45; H, 1.98; Mn, 14.93; N, 3.99; Pd, 29.62%. $^1$H NMR ($C_6D_6$): $\delta$ 4.37–4.15 (m, 4 H, $C_5\mathit{H}_4$Me) and 1.65 (s, 3 H, $C_5H_4\mathit{Me}$). IR (Nujol): 2061m, 2048m, 2023w, 1938vs, 1925vs, 1870m and 1855m, br cm$^{-1}$. IR (THF): 2051w, 2022s, 1930vs, 1885w and 1865m cm$^{-1}$. FT IR (polyethylene): 227m, 193s and 170vs. Mass spectrum (FAB), *m*/*z* (relative intensity, ion): 1401.5 (3, *M*), 1205.5 (5, *M* − 7 CO) and 213 (100%, Mn(Cp′)$_2$).

**Reaction of complex 19b with PPh$_3$.** Solid $PPh_3$ (0.225 g, 0.86 mmol) was added in small portions to a toluene (25 mL) solution of complex **19b** (0.300 g, 0.215 mmol) at 0 °C. Thin-layer chromatography (TLC) monitoring showed that a red compound immediately formed and the reaction mixture slowly turned from deep violet to red. The red solution was filtered through a Celite-padded filter funnel and concentrated to *ca.* 10 mL. Addition of diethyl ether (50 mL) yielded at −30 °C red crystals of **8** (0.173 g, 38% yield based on Pd). When only 1 equivalent of $PPh_3$ was used similar results were observed but only *ca.* 25% of **19b** was converted into **8**.

**Reaction of complex 19b with Ph$_2$PCH$_2$PPh$_2$ (dppm).** A solution of dppm (0.0345 g, 0.09 mmol) in toluene (10 mL) was added dropwise to a stirred solution of complex **19b** (0.063 g, 0.045 mmol) in toluene (25 mL) at 0 °C. The mixture turned from deep violet to red. The $^{31}$P-{$^1$H} NMR (THF–$C_6D_6$) spectrum of this solution showed the presence of **9** together with unidentified species.

**Reaction of [Pt$_4$(OAc)$_8$] with complex 1b.** A mixture of $[Pt_4(OAc)_8]$ (0.100 g, 0.080 mmol) and complex **1b** (0.153 g, 0.64 mmol) in THF (25 mL) was allowed to react at room temperature. After 12 h the IR spectrum of the solution showed only the presence of **1b**. The mixture was then heated under reflux for 12 h, but no reaction was observed. Repeating this experiment under a CO atmosphere for 12 h led to the same results.

### Thermal decomposition of complex 19b

A solution of complex **19b** (0.100 g, 0.049 mmol) in toluene (20 mL) was refluxed for 4 h. After this time the IR spectrum of the solution showed no $\nu$(CO) absorption and the black powder formed (0.075 g) was filtered off, washed with hexane and dried under vacuum for 12 h (Sample 1). Found: Pd, 45.40; Mn, 12.65% (Pd : Mn = 1.85 : 1). A second sample was prepared by thermal decomposition of **19b** (0.100 g , 0.049 mmol) in toluene and 0.080 g of a black powder was obtained (Sample 2). Found: Pd, 42.60; Mn, 11.90% (Pd : Mn = 1.85 : 1). Finally, thermal decomposition of **19b** (0.100 g, 0.049 mmol) in benzene at 80 °C yielded 0.083 g of a black powder (Sample 3). Found: Pd, 40.20; Mn, 13.25% (Pd : Mn = 1.56 : 1).

**Solid 19b.** Solid complex **19b** (0.200 g, 0.098 mmol) was introduced in a Schlenk tube which was then evacuated under reduced pressure and closed. The sample was heated to 100 °C for 5 h. After this time it was cooled and fine droplets of [MnCp′(CO)$_3$] formed on the walls of the Schlenk tube (identified by the $\nu$(CO) absorptions in hexane (2021s, 1939vs cm$^{-1}$)). The black powder was washed with hexane and dried under reduced pressure for 12 h (0.170 g) (Sample 4).

**EDAX analysis.** A drop of a highly diluted dispersion in hexane of the black powder obtained by thermal decomposition of complex **19b** (Samples 1–4) was deposited onto a holey carbon layer mounted on a copper grid (thickness 150 Å). After solvent evaporation, agglomerates of small particules were observed on the carbon layer. The analyses were performed on a 1 μm diameter zone encompassing many aggregates. The composition of the aggregates appeared to be very homogeneous and the relative compositions in palladium and manganese (average % atomic over at least four determinations) were: Sample 1; Pd, 67.75; Mn, 32.35 (Pd : Mn = 2.10 : 1); Sample 2; Pd, 70.00; Mn, 30.00 (Pd : Mn = 2.33 : 1); Sample 3; Pd, 63.55; Mn, 36.45 (Pd : Mn = 1.74 : 1); Sample 4; Pd, 57.15; Mn, 42.85 (Pd : Mn = 1.34 : 1).

### X-Ray crystallography for complex 15

Crystal data, details of the data collection and structure refinement are given in Table 2. Data were corrected for Lorentz

**Table 2** Summary of crystallographic data of complex **15**

| | |
|---|---|
| Formula | $C_{36}H_{20}AuMnNO_{12}PRu_3$ |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $T$/K | 295 |
| $a$/Å | 9.339(3) |
| $b$/Å | 12.966(5) |
| $c$/Å | 17.725(5) |
| $\alpha$/° | 69.56(2) |
| $\beta$/° | 80.73(2) |
| $\gamma$/° | 81.07(2) |
| $V$/Å$^3$ | 1974(1) |
| $Z$ | 2 |
| $\mu$(Mo-Kα)/mm$^{-1}$ | 5.24 |
| Reflections collected | 5624 |
| Independent reflections | 5418 ($R_{int}$ = 0.0325) |
| Reflections with $F_o > 4\sigma(F_o)$ | 4478 |
| Final $R$ indices | $R1 = 0.0277$, $wR2 = 0.0625$ |

and polarization effects. Absorption correction was applied at the last stage of the isotropic refinement.[35] The structure was solved by Patterson methods using SHELXS 86.[36] The structure was refined on $F_o$ by SHELXL 97[37] using anisotropic displacement parameters for all non-hydrogen atoms excluding the carbon atoms of the aromatic rings. The hydrogen atoms were calculated and refined "riding" on their parent atoms with the geometrical constraint C–H 0.96 Å.

CCDC reference number 186/1969.

See http://www.rsc.org/suppdata/dt/b0/b002292f/ for crystallographic files in .cif format.

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