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High Nuclearity Heterometallic Gold(I)-Containing Derivatives from Manganese(I) and Ruthenium(II) dppm Complexes via Diphosphinomethanide Intermediates

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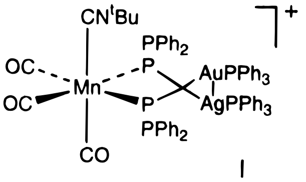
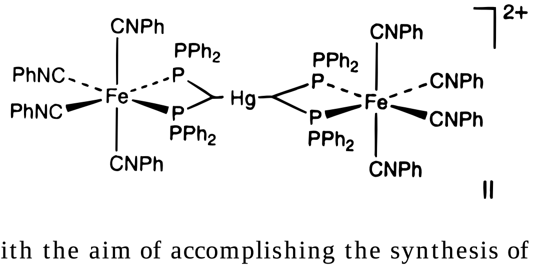
The cationic complexes *trans*-$[RuCl(L)(dppm)_2]^+$ (**1a**, L = CO; **1b**, L = CN^tBu; **1c**, L = CNPh), *trans*-$[Ru(CNR)_2(dppm)_2]^{2+}$ (**1d**, R = ^tBu; **1e**, R = Ph), and *trans*-$[Mn(CO)_2(dppm)_2]^+$ (**1f**) are selectively deprotonated with KOH or NaMeO affording the mixed ligand dppm/dppm-H complexes (dppm-H = $[(PPh_2)_2CH]^-$) *trans*-[RuCl(L)(dppm)(dppm-H)] (**2a**−**c**), *trans*-$[Ru(CNR)_2(dppm)(dppm\text{-}H)]^+$ (**2d**,**e**), and *trans*-$[Mn(CO)_2(dppm)(dppm\text{-}H)]$ (**2f**), respectively. Under more forcing conditions, **2d** and **2e** undergo a second deprotonation reaction to give *trans*-$[Ru(CNR)_2(dppm\text{-}H)_2]$ (**3d**,**e**). The treatment of **1f** with $[AuCl(PPh_3)]$ in the adequate stoichiometric ratio, in the presence of an excess of KOH, affords the heterometallic complexes *trans*-$[Mn(CO)_2(dppm)\{(PPh_2)_2CH(AuPPh_3)\}]^+$ (**4f**), *trans*-$[Mn(CO)_2\{(PPh_2)_2CH(AuPPh_3)\}_2]^+$ (**5f**), *trans*-$[Mn(CO)_2\{(PPh_2)_2CH(AuPPh_3)\}\{(PPh_2)_2C(AuPPh_3)_2\}]^+$ (**6f**), and *trans*-$[Mn(CO)_2\{(PPh_2)_2C(AuPPh_3)_2\}_2]^+$ (**7f**) as a result of the stepwise double metalation of the two dppm ligands. **4f** is more conveniently prepared by reaction of **2f** with an excess of $[AuCl(PPh_3)]$, although a good purification of the complex is not achieved. For **5f**, two isomers are present, in the same proportion, corresponding to the mutually *syn* or *anti* disposition of the two $Au(PPh_3)$ fragments. By contrast, in the treatment of the ruthenium derivatives **1d** and **1e** with $[AuCl(PPh_3)]$ in the presence of KOH, the products of partial metalation of the dppm ligands were not obtained and only the fully metalated pentametallic species *trans*-$[Ru(CNR)_2\{(PPh_2)_2C(AuPPh_3)_2\}_2]^{2+}$ (**7d** and **7e**) were isolated. For **2a** and **7e**, an X-ray diffraction study was undertaken.

Introduction

In the course of our investigations and those of others on the chemistry of transition metal diphosphinomethanide complexes, a general way to obtain heterometallic species containing the dppm-derived anionic ligands bis(diphenylphosphino)methanide $[(PPh_2)_2CH]^-$ or bis(diphenylphosphino)methanediide $[(PPh_2)_2C]^{2-}$ as building blocks has been found.[1,2] The doubly-deprotonated form of dppm is especially attractive owing to its high coordination ability, being a potential eight-electron donor ligand which may allow the synthesis of new structural forms of heterometallic complexes. Some remarkable examples already published by us are the trimetallic species *fac*-$[Mn(CN^tBu)(CO)_3\{(PPh_2)_2C(AuPPh_3)(AgPPh_3)\}]^+$(**I**)[1b] and $[\{Fe(CNPh)_4((PPh_2)_2C)\}_2Hg]^{2+}$ (**II**).[1c]



I



II

With the aim of accomplishing the synthesis of high nuclearity heterometallic species (lastly polymers) in a controlled manner, via methanide intermediates, we have now explored the chemistry of the bis(dppm) derivatives *trans*-$[RuCl(L)(dppm)_2]^+$ (**1a**−**c**, L = CO, CNR; R = ^tBu and Ph),[3,4] *trans*-$[Ru(CNR)_2(dppm)_2]^{2+}$ (**1d**,**e**)[4] and *trans*-$[Mn(CO)_2(dppm)_2]^+$ (**1f**).[5] Notably, we

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[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

[1] (a) Ruiz, J.; Riera, V.; Solans, X.; Tauler, E. *J. Chem. Soc., Dalton Trans.* **1990**, 1607. (b) Ruiz, J.; Riera, V.; Vivanco, M.; García-Granda, S.; García-Fernández, A. *Organometallics* **1992**, *11*, 4077. (c) Ruiz, J.; Arauz, R.; Riera, V.; Vivanco, M.; García-Granda, S.; Pérez-Carreño, E. *J. Chem. Soc., Chem. Commun.* **1993**, *9*, 740.

[2] Other selected articles about heterometallic and polymetallic complexes containing diphosphinomethanide ligands, see: Lusser, M.; Peringer, P. *Organometallics* **1984**, *3*, 1916. Al-Resayes, S. I.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1986**, 1710. Laguna, A.; Laguna, M. *J. Organomet. Chem.* **1990**, *394*, 743. Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; López-de-Luzuriaga, J. M. *J. Chem. Soc., Dalton Trans.* **1992**, 3365. Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; López-de-Luzuriaga, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 87. Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; López-de-Luzuriaga, J. M. *Organometallics* **1995**, *14*, 2918. Hutton, A. T.; Wewers, F. P. *J. Organomet. Chem.* **1995**, *492,* C14.

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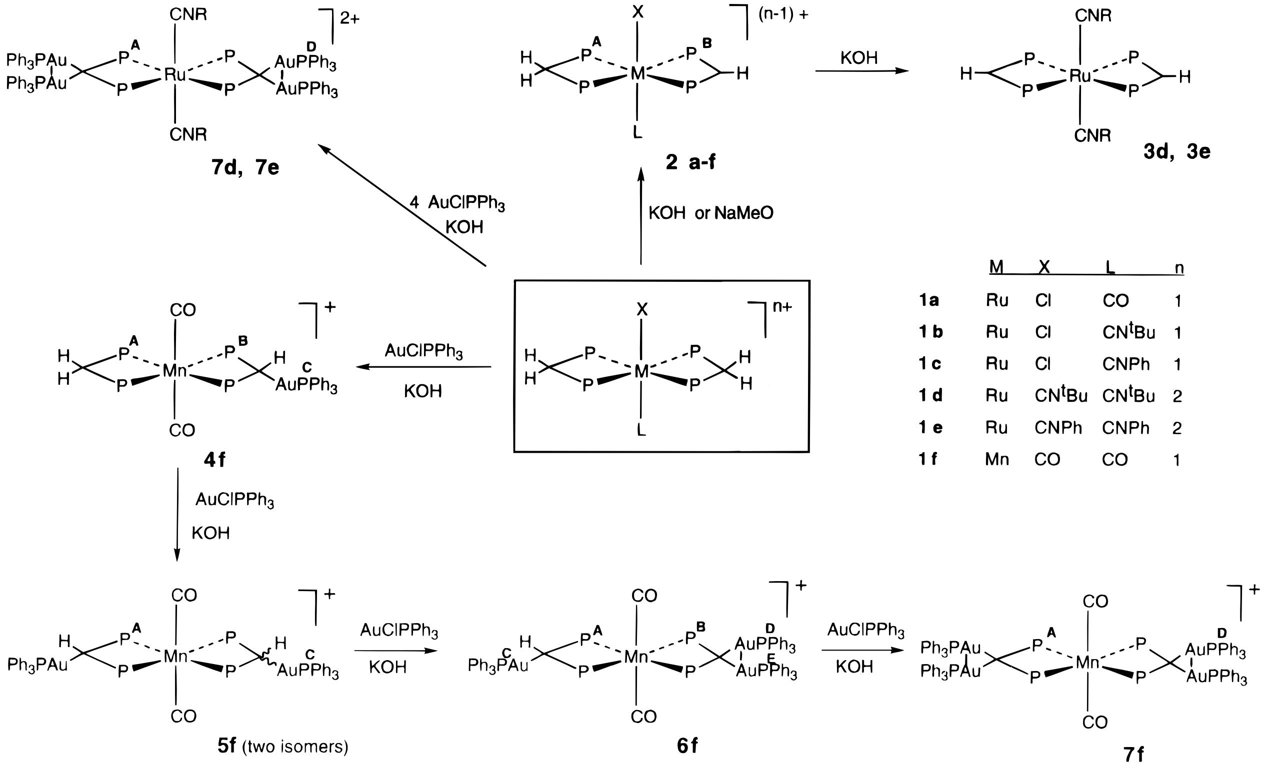
Scheme 1



	M	X	L	n
1a	Ru	Cl	CO	1
1b	Ru	Cl	CN^{t}Bu	1
1c	Ru	Cl	CNPh	1
1d	Ru	CN^{t}Bu	CN^{t}Bu	2
1e	Ru	CNPh	CNPh	2
1f	Mn	CO	CO	1

have been able to obtain di-, tri-, tetra-, and pentametallic species by stepwise double metalation of the two coordinated dppm ligands. These results are described throughout this paper.

Results and Discussion

Mixed Ligand dppm/dppm-H Complexes (dppm-H = [(PPh$_2$)$_2$CH]$^-$). The treatment of dichloromethane solutions of *trans*-[RuCl(L)(dppm)$_2$]$^+$ (**1a**, L = CO; **1b**, L = CN^{t}Bu; **1c**, L = CNPh), *trans*-[Ru(CNR)$_2$(dppm)$_2$]$^{2+}$ (**1d**, R = ^{t}Bu; **1e**, R = Ph), and *trans*-[Mn(CO)$_2$(dppm)$_2$]$^+$ (**1f**) with bases (KOH or NaMeO) affords *trans*-[RuCl(L)(dppm)(dppm-H)] (**2a**–**c**), *trans*-[Ru(CNR)$_2$(dppm)(dppm-H)]$^+$ (**2d**,**e**), and *trans*-[Mn(CO)$_2$(dppm)(dppm-H)] (**2f**), respectively, as a result of the selective deprotonation of the methylene group of only one chelating dppm ligand (Scheme 1). For the dicationic complexes **1d** and **1e**, a strict control of the reaction time is needed in order to avoid the formation of appreciable amounts of the bis(dppm-H) derivatives *trans*-[Ru(CNR)$_2$(dppm-H)$_2$] (**3d**,**e**), which will be described in detail below. All reactions were monitored by IR spectroscopy in solution in the region of 2200–1800 cm^{-1}, where the ν_{CO} and ν_{CN} bands of terminal carbonyl and isocyanide ligands normally appear. The IR spectra of **2a**–**f** (Table 1) show changes toward low frequencies in these bands (between 14 and 28 cm^{-1}) with respect to the corresponding starting compounds **1a**–**f**, a result of the increase of electron density in the complex. Complexes of type **2** show an interesting pattern in their NMR spectra (Table 1). Thus, the ^{31}P{^{1}H} NMR spectra are typical of second order AA′BB′ spin systems (Figure 1). The spin simulation parameters used for obtaining a best fit to the measured spectrum are listed in Table 1. The ^{1}H NMR spectra show highly coupled signals for the methylene hydrogens (P$_2$CH$_2$) at about δ 5 and for the methyne hydrogens (P$_2$CH) at about δ 2.5. Figure 2 shows the proton spectrum of **2a**. It consists of a triplet of triplets for the P$_2$CH hydrogen, whereas the two inequivalent P$_2$CH$_2$ protons gave resonances which are the part MN of an MNA$_2$B$_2$ spin system (M

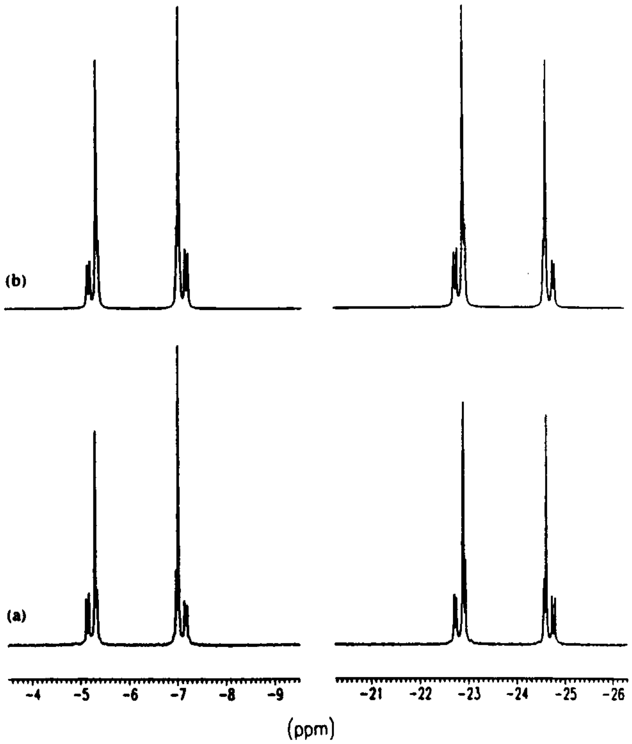


Figure 1. (a) Observed and (b) simulated ^{31}P{^{1}H} NMR spectrum of complex **2e**.

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(3) Mague, J. T.; Mitchener, J. P. *Inorg. Chem.* **1972**, *11*, 2714.

(4) Ruiz, J.; Mosquera, M. E. G.; Riera, V. *J. Organomet. Chem.* **1997**, *527*, 35.

(5) Carriedo, G. A.; Riera, V.; Santamaría, J. *J. Organomet. Chem.* **1982**, *234*, 175.

Table 1. IR and NMR Data for Compounds 1−7[a,b]

compd	ν(CN)/ν(CO) (cm^{-1})[c]	$^{31}P\{^1H\}$ NMR, δ (J, Hz)[d,e]			^1H NMR, δ (J, Hz)[f]	^{13}C NMR, δ (J, Hz)
2a	1961	δ_A −8.8	$J_{AA'} = 15$	$J_{AB'} = 294$	5.0 (ABM_2X_2, P_2CH_2, $^2J_{HH} = 15$, $^2J_{PH_A} = 11$, $^2J_{PH_B} = 10$, $^4J_{PH_B} = 2$)	200.4 (b, CO)
		δ_B −20.5	$J_{AB} = -7$	$J_{BB'} = 3$	2.7 (CM_2X_2, P_2CH, $^2J_{PH} = 6$, $^4J_{PH} = 3.5$)	49.4 (t, P_2CH_2, $^1J_{PC} = 20$) 23.4 (t, P_2CH, $^1J_{PC} = 61$)
2b	2117	δ_A −4.8	$J_{AA'} = 21$	$J_{AB'} = 294$	5.0 (ABM_2X_2, P_2CH_2, $^2J_{HH} = 15$, $^2J_{PH_A} = 11$, $^2J_{PH_B} = 9$, $^4J_{PH_B} = 2$)	50.86 (t, P_2CH_2, $^1J_{PC} = 18$) 29.5 (s, CH_3, ^tBu)
		δ_B −16.1	$J_{AB} = -12$	$J_{BB'} = -1$	2.7 (CM_2X_2, P_2CH, $^2J_{PH} = 6$, $^4J_{PH} = 4$), 0.15 (s, 9 H, ^tBu)	22.8 (t, P_2CH, $^1J_{PC} = 56$)
2c	2083	δ_A −6.2	$J_{AA'} = 17$	$J_{AB'} = 297$	5.1 (ABM_2X_2, m, P_2CH_2)	
		δ_B −17.5	$J_{AB} = -9$	$J_{BB'} = 2$	2.7 (CM_2X_2, P_2CH, $^2J_{PH} = 6$, $^4J_{PH} = 3$)	
2d	2141	δ_A −6.3	$J_{AA'} = 21$	$J_{AB'} = 227$	5.0 (t, P_2CH_2, $^2J_{PH} = 10$)	29.1 (s, CH_3, ^tBu)
		δ_B −23.3	$J_{AB} = -10$	$J_{BB'} = 11$	2.7 (CM_2X_2, P_2CH, $^2J_{PH} = 5$, $^4J_{PH} = 4.0$), 0.39 (s, 18 H, ^tBu)	21.4 (t, P_2CH, $^1J_{PC} = 63$)
2e	2123	δ_A −6.2	$J_{AA'} = 22$	$J_{AB'} = 216$	5.1 (t, P_2CH_2, $^2J_{PH} = 10$)	
		δ_B −23.7	$J_{AB} = -8$	$J_{BB'} = 6$	2.7 (CM_2X_2, P_2CH, $^2J_{PH} = 5$, $^4J_{PH} = 3.5$)	
2f	1887	δ_A 44.9 (m)			4.8 (m, P_2CH_2)	
		δ_B 15.4 (m)			2.3 (m, P_2CH)	
3d	2122	−15.1 (s)			3.1 (b, P_2CH)	29.1 (s, CH_3, ^tBu)
					0.3 (s, CH_3, ^tBu)	21.4 (t, P_2CH, $^1J_{PC} = 64$)
3e	2099[g]	−15.6 (s)				
4f	1902	δ_B 49.8 (m)			5.2 (q, P_2CH, $^2J_{PH} = {}^3J_{PH} = 10$)	
		δ_C 40.1 (t, $^3J_{P^CP^B} = 9$)			4.8 (t, P_2CH_2, $^2J_{PH} = 10$)	
		δ_A 38.8 (m)				
5f	1890	δ_C 40.3 (s)			5.1 (m, P_2CH)	
		δ_A 52.9 and 53.3 (s, two isomers)				
6f	1880	δ_B 66.6 (m)			5.1 (q, P_2CH, $^2J_{PH} = {}^3J_{PH} = 10$)	
		δ_A 55.8 (m)				
		δ_C 40.3 (t, $^3J_{P^CP^A} = 9$)				
		δ_D, δ_E 36.1 (nonresolved)				
7d	2132	δ_D 34.6 (aq, $J_{PP_a} = 3$)			0.27 (s, CH_3, ^tBu)	146.1 (b, P_2C)
		δ_A 18.9 (aqu, $J_{PP_a} = 3$)				29.8 (s, CH_3, ^tBu)
7e	2108	δ_D 35.6 (aqu, $J_{PP_a} = 3$)				144.1 (b, P_2C)
		δ_A 18.4 (aqu, $J_{PP_a} = 3$)				
7f	1868	δ_A 70.5 (s)				147.5 (b, P_2C)
		δ_D 36.3 (s)				

[a] In CD_2Cl_2 solutions. [b] Abbreviations: s = singlet, t = triplet, q = quartet, qu = quintet, a = apparent, b = broad. [c] Measured in CH_2Cl_2. [d] The notation of the phosphorus are those of Scheme 1. [e] AA′BB′ spin system for compunds **2a**−**e**, δ and J values obtained by computer simulation of the experimental spectra. [f] Spin system in parenthesis. [g] Measured in toluene.

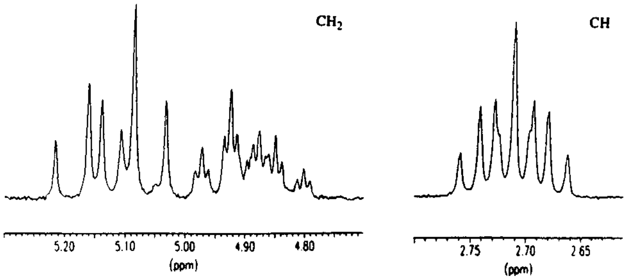

Figure 2. ^1H NMR spectrum of **2a** showing the signals of the P_2CH_2 and P_2CH protons.

and N being protons and A and B phosphorus). Interestingly, $^4J_{H_MP_B} = 2$ Hz whereas $^4J_{H_NP_B} = 0$ Hz, and this generates the curious appearance of the spectrum as a pseudodoublet of triplets of triplets (H_M) plus a pseudodoublet of triplets (H_N). The $^{13}C\{^1H\}$ NMR spectra of complexes **2** show triplets for both the P_2CH_2 and P_2CH carbon atoms. Of note is the considerably higher value of $^1J_{PC(methyne)}$ (about 60 Hz) than $^1J_{PC(methylene)}$ (about 20 Hz); this can be rationalized by taking into account the higher degree of s character in the methyne carbon atom (sp^2) than in the methylene carbon atom (sp^3).[6]

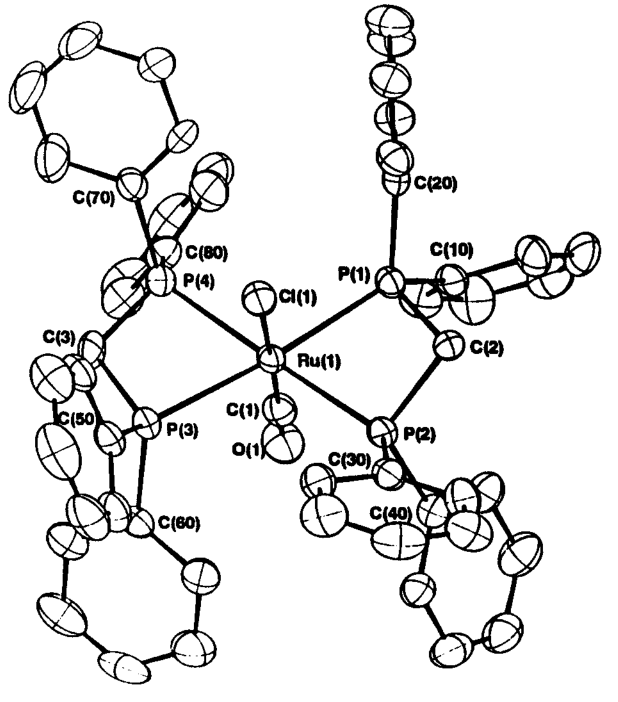

Figure 3. View of the molecular structure of the complex [RuCl(CO)(dppm)(dppm-H)] (**2a**).

For complex **2a**, an X-ray diffraction study was undertaken, allowing a direct comparison between the structural parameters of dppm and dppm-H (Figure 3). Thus, the P(3)C(3)P(4) skeleton of the dppm-H ligand is coplanar to the metal, while in the case of dppm, the carbon atom of the P(1)C(2)P(2) skeleton is 0.415 Å,

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(6) *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: New York, 1987; p 398.

Table 2. Crystallographic Data for Compounds 2a and 7e

	2a	7e
emp formula	$C_{51}H_{43}ClOP_4Ru\cdot 0.5CH_2Cl_2$	$C_{136}H_{110}Au_4F_{12}N_2P_{10}Ru\cdot 2CH_2Cl_2$
fw	974.79	3368.90
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a (Å)	10.448(2)	13.390(5)
b (Å)	24.772(6)	15.372(6)
c (Å)	17.958(3)	18.025(3)
α (deg)		108.87(3)
β (deg)	92.03(2)	100.37(2)
γ (deg)		98.79(3)
V (Å^3)	4645(3)	3363(49)
Z	4	1
d(calcd) (g/cm^3)	1.39	1.66
μ (cm^{-1})	6.18	47.08
diffractometer	CAD4 Enraf-Nonius	CAD4 Enraf-Nonius
T, K	298	298
radiation (λ, Å)	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
scan type	$\omega/2\theta$	$\omega/2\theta$
scan range (deg)	$0.8 + 0.345 \tan\theta$	$0.8 + 0.345 \tan\theta$
θ limits (deg)	$1 < \theta < 25$	$1 < \theta < 25$
residuals:R^a; R_w^b	0.062; 0.073	0.102; 0.122
goodness of fit	0.98	0.82
Δ/σ min (e Å^{-3})	−1.19	−4.5
Δ/σ max (e Å^{-3})	0.99	5.1

[a] $R = \Sigma|\Delta F|/\Sigma|F_o|$. [b] $R_w = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{1/2}$

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 2a

	Bond Lengths		
P(1)−C(2)	1.824(8)	P(3)−C(3)	1.696(8)
P(2)−C(2)	1.844(8)	P(4)−C(3)	1.692(9)
Ru(1)−P(1)	2.391(2)	Ru(1)−P(3)	2.390(2)
Ru(1)−P(2)	2.384(2)	Ru(1)−P(4)	2.373(2)
Ru(1)−Cl(1)	2.440(2)	Ru(1)−C(1)	1.851(8)
P(1)−C(10)	1.820(8)	P(1)−C(20)	1.814(8)
P(2)−C(30)	1.824(8)	P(2)−C(40)	1.840(8)
P(3)−C(50)	1.832(8)	P(3)−C(60)	1.826(8)
P(4)−C(70)	1.821(8)	P(4)−C(80)	1.830(8)
C(1)−O(1)	1.115(9)		
	Bond Angles		
P(1)−C(2)−P(2)	98.2(4)	P(3)−C(3)−P(4)	103.3(4)
P(1)−Ru(1)−P(2)	71.00(7)	P(1)−Ru(1)−P(3)	174.45(7)
P(2)−Ru(1)−P(3)	112.48(7)	P(1)−Ru(1)−P(4)	108.44(7)
P(2)−Ru(1)−P(4)	176.66(8)	P(3)−Ru(1)−P(4)	67.82(7)
P(1)−Ru(1)−Cl(1)	85.28(7)	P(2)−Ru(1)−Cl(1)	84.20(7)
P(3)−Ru(1)−Cl(1)	90.73(7)	P(4)−Ru(1)−Cl(1)	92.47(7)
P(1)−Ru(1)−C(1)	96.9(3)	P(2)−Ru(1)−C(1)	94.1(3)
P(3)−Ru(1)−C(1)	87.3(3)	P(4)−Ru(1)−C(1)	89.3(3)
Ru(1)−P(1)−C(2)	93.7(3)	Ru(1)−P(1)−C(10)	123.2(3)
C(2)−P(1)−C(10)	104.8(4)	Ru(1)−P(1)−C(20)	123.2(3)
C(2)−P(1)−C(20)	107.8(4)	C(10)−P(1)−C(20)	101.6(4)
Ru(1)−P(2)−C(2)	93.4(2)	Ru(1)−P(2)−C(30)	127.4(3)
C(2)−P(2)−C(30)	105.6(4)	Ru(1)−P(2)−C(40)	119.1(3)
C(2)−P(2)−C(40)	106.9(4)	C(30)−P(2)−C(40)	101.7(4)
Ru(1)−P(3)−C(3)	94.0(3)	Ru(1)−P(3)−C(50)	118.7(3)
C(3)−P(3)−C(50)	110.6(4)	Ru(1)−P(3)−C(60)	117.0(3)
C(3)−P(3)−C(60)	114.1(4)	C(50)−P(3)−C(60)	102.8(4)
Ru(1)−P(4)−C(3)	94.7(3)	Ru(1)−P(4)−C(70)	120.8(3)
C(3)−P(4)−C(70)	110.6(4)	Ru(1)−P(4)−C(80)	116.8(3)
C(3)−P(4)−C(80)	113.0(4)	C(70)−P(4)−C(80)	101.3(4)
Ru(1)−C(1)−O(1)	177.8(8)	Cl(1)−Ru(1)−C(1)	176.6(3)

Table 3, out of the plane Ru(1)P(1)P(2) directed toward the chlorine atom, as can be seen in the schematic view of the molecule depicted in Figure 4. Furthermore, the endocyclic P−C distances are slightly shorter in the methanide ligand (average value 1.694(8) Å) than in the dppm ligand (average value 1.834(8) Å). Naturally this shortening is due to the multiple bond character of the P−C(methanide) bonds, and this result is in agreement with the above-mentioned values of $^1J_{PC}$. Both dppm and dppm-H form highly strained four-membered chelate rings because of the restricted bite angles P−Ru−P of these bidentate ligands; the data show that the strain is appreciably higher in dppm-H owing to the planarity of the P(3)C(3)P(4)Ru(1) skeleton. The "RuClCO(dppm)" half of the molecule has very similar structural parameters to those already found for the starting compound **1a**.[7]

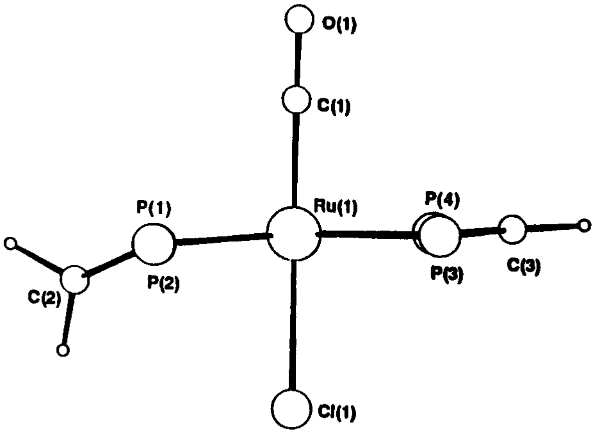

Figure 4. A schematic view of the structure of **2a** in which phenyl groups have been omitted for clarity.

Bis(dppm-H) Derivatives. The prolonged treatment of the cationic complexes **2d,e** with KOH in dichloromethane produces the deprotonation of the remaining dppm ligand, giving rise to the formation of the neutral bis(diphosphinomethanide) derivatives *trans*-[Ru(CNR)$_2$(dppm-H)$_2$] (**3d**, R = ^{t}Bu; **3e**, R = Ph), which were isolated as yellow solids. Following a similar behavior as their precursors, a new lowering in the frequency of the ν_{CN} bands of the isocyanide ligands is observed in the IR spectra of **3d** and **3e** (19 and 23 cm^{-1}, respectively). As shown in Table 1, complexes **3** give much more simple NMR spectra than **2** due to the chemical equivalence of the two dppm-H ligands. Surprisingly, **3e** is only slightly soluble in most common organic solvents, precluding its full spectroscopic characterization. By contrast, **3d** is very soluble in solvents such as dichloromethane, tetrahydrofuran or toluene. This complex shows a curious behavior in protic solvents. Thus, **3d** (a yellow solid) forms a colorless solution in methanol, which shows the same spectroscopic data (IR and ^{31}P NMR, Table 1) as those of **1d**, indicating that both methanide ligands have been protonated by methanol. But this process is reversible, and by taking the solution to dryness, a yellow residue of **3d** was recovered completely unchanged (verified by IR and NMR spectroscopy). Bis(diphosphinomethanide) derivatives are not very common in the literature; two examples closely related to **3d,e** are the neutral complexes [Pt(dppm-H)$_2$][8] and [ZrCl$_2$((PMe$_2$)$_2$CSiMe$_3$)$_2$].[9]

Heterometallic Mn/Au and Ru/Au Complexes. The diphosphinomethanide complexes **2** and **3** can be considered as metallo-ligands with C-methanide donor atoms, so they are promising substrates for the synthesis of heterometallic species by treatment with the

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adequate metallic fragments. In practice, we have obtained several heterometallic Mn/Au and Ru/Au complexes directly treating type **1** complexes with the appropriate amount of [AuCl(PPh$_3$)] (a source of the [Au(PPh$_3$)]$^+$ fragment) in the presence of KOH. As summarized in Scheme 1, in this way we have incorporated up to four gold fragments into the original manganese and ruthenium complexes.

The treatment of a dichloromethane solution of **1f** with 1 equiv of [AuCl(PPh$_3$)] and an excess of KOH gives a mixture of *trans*-[Mn(CO)$_2$(dppm){(PPh$_2$)$_2$CH(AuPPh$_3$)}]$^+$ (**4f**) and *trans*-[Mn(CO)$_2${(PPh$_2$)$_2$CH(AuPPh$_3$)}$_2$]$^+$ (**5f**) in a molar ratio of approximately 6:4 (by ^{31}P NMR), together with some amount of the starting material **1f** which remains unchanged. The selectivity in the attainment of **4f** can be considerably improved by dropwise addition of a dichloromethane solution of the methanide derivative **2f** to an stirred solution containing a 3-fold excess of [AuCl(PPh$_3$)] in the same solvent. Even in this case, little amounts of **5f** and **1f** are formed due to a proton transfer process from **4f** to **2f**. Only when a really large excess of [AuCl(PPh$_3$)] was employed (1/10), samples of **4f** essentially free of **5f** and **1f** were obtained. However, in this case, the presence of such an excess of [AuCl(PPh$_3$)] precludes a good purification of **4f**, so the attainment of analytically pure samples of this complex is difficult. Despite this, the spectroscopic characterization of **4f** was carried out. In the phosphorus spectrum, the signals of P$_A$ and P$_B$ appear as two unresolved broad doublets due to the quadrupolar moment effect of manganese and to the inherent multiplicity of the complex AA′BB′X spin system while the phosphorus of the PPh$_3$ group appears as a well-defined triplet. In the ^{1}H NMR spectrum, the P$_2$CH$_2$ protons give a triplet at δ 4.81 whereas the methyne P$_2$CHAu proton appears as an apparent quartet at δ 5.18 due to a similar value of $^2J_{\mathrm{P_BH}}$ and $^3J_{\mathrm{P_CH}}$.

Unlike **4f**, the heterometallic species *trans*-[Mn(CO)$_2${(PPh$_2$)$_2$CH(AuPPh$_3$)}$_2$]$^+$ (**5f**), *trans*-[Mn(CO)$_2${(PPh$_2$)$_2$CH(AuPPh$_3$)}{(PPh$_2$)$_2$C(AuPPh$_3$)$_2$}]$^+$ (**6f**), and *trans*-[Mn(CO)$_2${(PPh$_2$)$_2$C(AuPPh$_3$)$_2$}$_2$]$^+$ (**7f**) were selectively obtained by treating **1f** with 2, 3, and 4 equiv of [AuCl(PPh$_3$)], respectively, in the presence of KOH. The IR spectra of these complexes show a gradual change toward low frequencies in the ν_{CO} band of the carbonyl ligands on going from **1f** to **7f** (about 10 cm^{-1} of decrease for each new AuPPh$_3$ fragment). This indicates that each metalation of dppm makes the complex electronically richer. As a result, the remaining methyne hydrogens are less acidic, making each new deprotonation and metalation process more and more difficult. This is in agreement with the observed reaction times, which are progressively longer.

The NMR spectroscopy proved to be very useful to elucidate the structure of these complexes. Thus, for **5f**, three isomers are possible depending on the position of the two AuPPh$_3$ fragments. The ^{31}P spectrum shows the presence of two of these isomers in an approximate 1/1 ratio, which are those corresponding to the simultaneous metalation of the two dppm ligands either with the two AuPPh$_3$ fragments located mutually *syn* or *anti* (Scheme 1). The third isomer, corresponding to a double metalation of only one dppm ligand, was not observed, although the presence of two close gold atoms should be favored by the aurophilicity phenomenon.[10] As the first step in the formation of these complexes is a deprotonation process, the absence of this last isomer may be due to the less acidic character of the P$_2$CHAu proton compared with the P$_2$CH$_2$ protons in **4f** (see above).

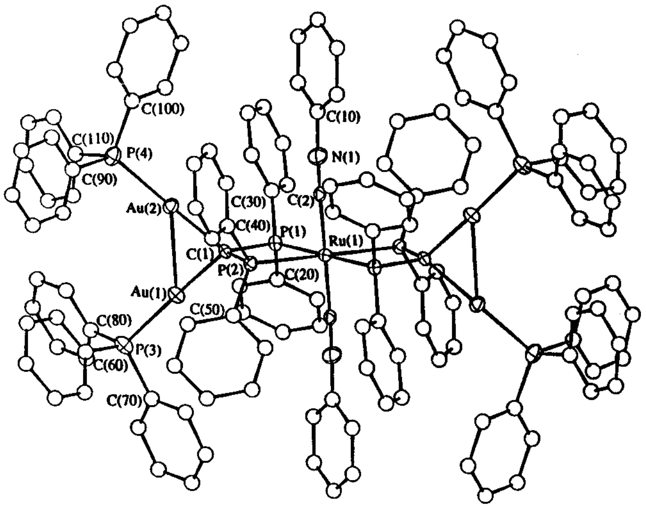

Figure 5. X-ray structure of the cation *trans*-[Ru(CNPh)$_2${(PPh$_2$)$_2$C(AuPPh$_3$)$_2$}$_2$]$^{2+}$ (**7e**).

For **6f**, four groups of signals were observed in the ^{31}P{^{1}H} NMR spectrum. As in complex **4f**, the phosphorus P$_A$ and P$_B$ of the diphosphines give two broad doublets. P$_C$ affords a well-defined triplet at δ 40.3, almost the same frequency as the corresponding phosphorus atoms in complexes **4f** (40.1) and **5f** (40.3), so we can consider this a characteristic chemical shift of the unit P$_2$CHAu*P*Ph$_3$. Finally, P$_D$ and P$_E$, which are not exactly chemically equivalent but very similar, appear as a slightly broad resonance at δ 36.1. This is also a characteristic chemical shift of the unit P$_2$C(Au*P*Ph$_3$)$_2$, as we will see below in the description of complex **7f**.

The pentametallic species *trans*-[Mn(CO)$_2${(PPh$_2$)$_2$C(AuPPh$_3$)$_2$}$_2$]$^+$ (**7f**) contains two types of phosphorus atoms, which appear in the ^{31}P{^{1}H} NMR spectrum as very slightly broad resonances at δ 70.5 (P$_A$) and 36.3 (P$_D$). Naturally neither methylene nor methyne hydrogen atoms were found in the proton spectrum. In the ^{13}C{^{1}H} NMR spectrum, a multiplet at δ 147.5 is assigned to the P$_2$CAu$_2$ carbon atom.

On the other hand, the pentametallic species *trans*-[Ru(CNR)$_2${(PPh$_2$)$_2$C(AuPPh$_3$)$_2$}$_2$]$^{2+}$ (**7d** and **7e**) were prepared following the same procedure as that for **7f**, starting from **1d** and **1e**, respectively. In this case, a stepwise controlled metalation of the dppm ligands was not possible and we failed to obtain the products of partial metalation of this ligand separately. Interestingly, the phosphorus spectra of **7d** and **7e** are resolved in two apparent quintets due to a deceptively simple A$_4$X$_4$ spin system with all nuclei being magnetically inequivalent. In the ^{13}C spectra, the resonance of the P$_2$CAu$_2$ carbon appears as a multiplet at δ 146.1 (**7d**) and 144.1 (**7e**).

In order to fully structurally characterize complexes **7**, an X-ray diffraction study was undertaken for **7e** (see Figure 5). The ruthenium atom lies on an inversion center, so the complex cation is centrosymmetric. The

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound 7e

Bond Lengths			
Ru(1)−P(1)	2.394(4)	C(1)−Au(2)	2.11(1)
Ru(1)−P(2)	2.390(4)	C(1)−Au(1)	2.10(1)
P(2)−C(1)	1.82(1)	Au(1)−Au(2)	2.8164(8)
P(1)−C(1)	1.78(1)	Au(1)−P(3)	2.259(4)
Ru(1)−C(2)	1.96(1)	Au(2)−P(4)	2.265(4)
P(1)−C(20)	1.86(1)	P(1)−C(30)	1.85(1)
P(2)−C(40)	1.91(1)	P(2)−C(50)	1.86(1)
P(3)−C(60)	1.85(2)	P(3)−C(70)	1.85(2)
P(3)−C(80)	1.86(2)	P(4)−C(90)	1.80(2)
P(4)−C(100)	1.77(2)	P(4)−C(110)	1.80(2)
N(1)−C(2)	1.18(2)	N(1)−C(10)	1.37(2)
Bond Angles			
P(1)−C(1)−P(2)	97.7(7)	C(1)−P(1)−Ru(1)	97.1(5)
P(1)−Ru(1)−P(2)	69.0(1)	C(1)−P(2)−Ru(1)	96.1(4)
Au(1)−C(1)−Au(2)	83.8(5)	P(1)−Ru(1)−C(2)	89.8(4)
Au(1)−Au(2)−C(1)	48.0(3)	P(2)−Ru(1)−C(2)	89.0(4)
Au(2)−Au(1)−C(1)	48.2(4)	P(1)−Ru(1)−C(2)′	90.2(4)
Au(2)−C(1)−P(2)	116.7(6)	P(2)−Ru(1)−C(2)′	91.0(4)
Au(1)−C(1)−P(1)	122.5(7)	P(1)−Ru(1)−P(2)′	111.0(1)
Au(2)−Au(1)−P(3)	133.3(1)	Au(1)−Au(2)−P(4)	133.8(1)
P(3)−Au(1)−C(1)	174.6(4)	P(4)−Au(2)−C(1)	175.8(4)
Au(1)−C(1)−P(1)	122.5(7)	Au(1)−C(1)−P(2)	115.7(7)
Ru(1)−P(1)−C(20)	119.3(5)	Ru(1)−P(2)−C(40)	118.7(6)
C(1)−P(1)−C(20)	109.6(7)	C(1)−P(2)−C(40)	112.2(7)
Ru(1)−P(1)−C(30)	120.3(6)	Ru(1)−P(2)−C(50)	118.8(6)
C(1)−P(1)−C(30)	110.2(7)	C(1)−P(2)−C(50)	110.4(8)
C(20)−P(1)−C(30)	100.3(7)	C(40)−P(2)−C(50)	100.9(9)
Au(1)−P(3)−C(60)	106.3(7)	Au(2)−P(4)−C(90)	112.1(6)
Au(1)−P(3)−C(80)	114.9(6)	Au(2)−P(4)−C(110)	114.8(7)
Au(1)−P(3)−C(70)	112.1(8)	Au(2)−P(4)−C(100)	111.9(8)
C(60)−P(3)−C(70)	108.2(9)	C(90)−P(4)−C(100)	108.4(9)
C(60)−P(3)−C(80)	109.0(10)	C(90)−P(4)−C(110)	104.0(9)
C(70)−P(3)−C(80)	106.2(10)	C(100)−P(4)−C(110)	105.0(11)
C(2)−N(1)−C(10)	176.9(19)		

coordination sphere around ruthenium has a distorted octahedral geometry because of the restricted bite angle P−Ru−P (69.0(1)°) of the metalated diphosphines. The two phosphorus atoms of the diphosphine and the two gold atoms form a very distorted tetrahedron around the central carbon atom (C(1)). There are short Au−Au contacts (2.8164(8) Å), as typically occurs with other linearly coordinated gold(I) complexes with close gold atoms due to the aurophilicity effect.[10] Note that the Au−Au distance is even shorter than the interatomic separation in metallic gold (2.884 Å) and a little longer than in the three-center two-electron system $[Fe(C_5H_5)\{C_5H_4(AuPPh_3)_2\}]^+$ (2.77 Å).[11] Other bond lengths and angles are listed in Table 4.

Experimental Section

General Considerations. All reactions were carried out under a nitrogen atmosphere with the use of Schlenk techniques. Solvents were dried and purified by standard techniques and distilled under nitrogen prior to use. All reactions were monitored by IR spectroscopy (Perkin-Elmer FT 1720-X and Paragon 1000 spectrophotometers). The C, H, and N analyses were performed on a Perkin-Elmer 240B elemental analyzer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured with Bruker AC-300 and AC-200 instruments. Chemical shifts are given in parts per million (ppm) relative to internal $SiMe_4$ (^{1}H, ^{13}C) or external 85% H_3PO_4 (^{31}P). The complexes **1a**,[3] **1b**−**e**,[4] **1f**,[5] and $[AuCl(PPh_3)]$[12] were prepared as described elsewhere.

***trans*-[RuCl(CO)(dppm)(dppm-H)] (2a).** To a solution of *trans*-$[RuCl(CO)(dppm)_2]Cl$ (**1a**) (100 mg, 0.103 mmol) in 15 mL of CH_2Cl_2 was added an excess of KOH (1.25 g). The mixture was stirred for 1 h at room temperature, after which time the IR spectrum of the yellow solution indicated the formation of the new compound. The mixture was filtered, and 20 mL of hexane was added to the filtrate to provide a yellow microcystalline solid. This was washed with hexane, collected, and dried under vacuum. Yield: 90 mg (96%). Anal. Calcd for $RuClOP_4C_{51}H_{43}$: C, 65.70; H, 4.65. Found: C, 65.10; H, 4.52.

***trans*-[RuCl(CN^{t}Bu)(dppm)(dppm-H)] (2b).** The procedure was the same as that used for the preparation of compound **2a**, except that in this case the deprotonating agent was NaMeO instead of KOH. Starting from *trans*-[RuCl(CN^{t}Bu)(dppm)$_2$](PF$_6$) (**1b**) (50 mg, 0.044 mmol) and NaMeO (30 mg, 0.56 mmol), after 10 min of reaction, 37 mg of **2b** was obtained (84% yield). Anal. Calcd for $RuClP_4C_{55}H_{52}N$: C, 66.90; H, 5.31; N, 1.42. Found: C, 66.76; H, 5.34; N, 1.34.

***trans*-[RuCl(CNPh)(dppm)(dppm-H)] (2c).** This was prepared similarly to **2a**, starting from *trans*-[RuCl(CNPh)(dppm)$_2$](PF$_6$)(**1c**) (50 mg, 0.043 mmol) and an excess of KOH (1 g). Yield: 33 mg, 78%. Anal. Calcd for $RuClP_4C_{57}H_{48}N$: C, 67.96; H, 4.80; N, 1.39. Found: C, 68.10; H, 4.45; N, 1.43.

***trans*-[Ru(CN^{t}Bu)$_2$(dppm)(dppm-H)]PF$_6$ (2d).** To a solution of *trans*-[Ru(CN^{t}Bu)$_2$(dppm)$_2$](PF$_6$)$_2$ (**1d**) (50 mg, 0.038 mmol) in 15 mL of CH_2Cl_2 was added NaMeO (30 mg, 0.56 mmol), and the resulting mixture was stirred for 10 min. The solution was filtered, and 20 mL of toluene was added to the filtrate to obtain a yellow crystalline solid, which was washed with toluene and dried under vacuum. Yield: 74 mg, 83%. Anal. Calcd for $RuF_6P_5C_{60}H_{61}N_2$: C, 61.07; H, 5.21; N, 2.37. Found: C, 60.92; H, 5.11; N, 2.28.

***trans*-[Ru(CNPh)$_2$(dppm)(dppm-H)]PF$_6$ (2e).** To a solution of *trans*-[Ru(CNPh)$_2$(dppm)$_2$](PF$_6$)$_2$ (**1e**) (50 mg, 0.037 mmol) in 10 mL of CH_2Cl_2 was added an excess of KOH (1.25 g). The mixture was then cooled to 0 °C and stirred for 40 min, after which time the IR spectrum of the solution showed only the presence of compound **2e**. The mixture was filtered, and the volume of the filtrate reduced to about 4 mL. A yellow solid was precipitated and washed with hexane. Yield: 38 mg, 86%. Anal. Calcd for $RuF_6P_5C_{64}H_{53}N_2$: C, 63.00; H, 4.38; N, 2.30. Found: C, 62.72; H, 4.11; N, 2.26.

***trans*-[Mn(CO)$_2$(dppm)(dppm-H)] (2f).** This compound was obtained as an orange solid following the same procedure as that used for **2a**, starting from *trans*-[Mn(CO)$_2$(dppm)$_2$](ClO$_4$) (**1f**) (0.15 g, 0.15 mmol) and an excess of KOH (1 g). Yield: 0.12 g, 90%. Anal. Calcd for $MnO_2P_4C_{52}H_{43}$: C, 71.07; H, 4.93. Found: C, 71.22; H, 4.84.

***trans*-[Ru(CN^{t}Bu)$_2$(dppm-H)$_2$] (3d).** To a solution of **1d** (100 mg, 0.075 mmol) in 10 mL of CH_2Cl_2 was added an excess of KOH (1.25 g), and the resulting mixture was stirred for 36 h. The solution was filtered and concentrated to about 3 mL, and from this a yellow precipitate was obtained by addition of ether. Yield: 70 mg, 93%. Anal. Calcd for $RuP_4C_{60}H_{60}N_2$: C, 69.55; H, 6.03; N, 2.70. Found: C, 68.97; H, 6,18; N, 2.46.

***trans*-[Ru(CNPh)$_2$(dppm-H)$_2$] (3e).** To a solution of **1e** (100 mg, 0.073 mmol) in 50 mL of CH_2Cl_2 was added an excess of KOH (1.25 g), and the resulting mixture was stirred for 2 h. The solution was filtered, and the filtrate was concentrated to about 5 mL causing the precipitation of a yellow solid. Yield: 63 mg, 80%. Anal. Calcd for $RuP_4C_{64}H_{52}N_2$: C, 71.57; H, 4.88; N, 2.61. Found: C, 70.93; H, 4.59; N, 2.75.

***trans*-[Mn(CO)$_2${(PPh$_2$)$_2$CH(AuPPh$_3$)}$_2$]ClO$_4$ (5f).** To a solution of **1f** (0.1 g, 0.10 mmol) in 20 mL of CH_2Cl_2 were added KOH (1 g, 17.8 mmol) and $[AuCl(PPh_3)]$ (0.1 g, 0.2 mmol). The mixture was stirred for 3 h, after which time the solution was filtered and evaporated to dryness to give an orange solid which was washed with ether and dried under vacuum. Yield: 0.17 g, 90%. Anal. Calcd for $MnAu_2O_6ClP_6C_{88}H_{72}$: C, 55.75; H, 3.83. Found: C, 55.33; H, 3.60.

***trans*-[Mn(CO)$_2${(PPh$_2$)$_2$CH(AuPPh$_3$)}{(PPh$_2$)$_2$C(AuPPh$_3$)$_2$}]ClO$_4$ (6f).** To a solution of **1f** (50 mg, 0.05 mmol) in 20 mL of CH_2Cl_2 were added KOH (1 g, 17.8 mmol) and [AuCl-

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(12) Braunstein, P.; Lehner, H.; Matt, D. *Inorg. Synth.* **1990**, *27*, 218.

(PPh$_3$)] (76 mg, 0.15 mmol), and the mixture stirred for 24 h, after which time the IR spectrum of the solution showed only the ν_{CO} band corresponding to **6f**. The solution was then filtered, and the solvent was evaporated to dryness to give an orange solid, which was washed with hexane and dried under vacuum. Yield: 0.1 g, 83%. Anal. Calcd for $MnAu_3ClO_6P_7C_{106}H_{86}$: C, 54.09; H, 3.68. Found: C, 54.31; H, 3.80.

***trans*-[Mn(CO)$_2${(PPh$_2$)$_2$C(AuPPh$_3$)$_2$}$_2$]ClO$_4$ (7f).** To a solution of **1f** (50 mg, 0.05 mmol) in 30 mL of CH_2Cl_2 were added KOH (2 g, 35.6 mmol) and [AuCl(PPh$_3$)] (0.1 g, 0.2 mmol), and the resulting mixture stirred for about 2 days. The completeness of the reaction was checked by IR spectroscopy. The solution was filtered and concentrated under vacuum to about 7 mL. Then 20 mL of toluene was added to provide an orange microcrystalline solid. Yield: 0.11 g, 77%. Anal. Calcd for $MnAu_4ClO_6P_8C_{124}H_{100}$: C, 52.96; H, 3.58. Found: C, 52.51; H, 3.58.

***trans*-[Ru(CN^{t}Bu)$_2${(PPh$_2$)$_2$C(AuPPh$_3$)$_2$}$_2$](PF$_6$)$_2$ (7d).** This compound was prepared similarly to **7f**, starting from **1d** (90 mg, 0.068 mmol), KOH (2 g, 35.6 mmol), and [AuCl(PPh$_3$)] (0.135 g, 0.27 mmol). Reaction time: 21 h. White crystals were obtained from CH_2Cl_2/Et_2O. Yield: 0.17 g, 78%. Anal. Calcd for $RuAu_4F_{12}P_{10}C_{132}H_{118}N_2$: C, 50.19; H, 3.76; N, 0.89. Found: C, 49.80; H, 3.73; N, 0.78.

***trans*-[Ru(CNPh)$_2${(PPh$_2$)$_2$C(AuPPh$_3$)$_2$}$_2$](PF$_6$)$_2$ (7e).** This compound was prepared similarly to **7f**, starting from **1e** (50 mg, 0.039 mmol), KOH (2g, 35.6 mmol), and [AuCl(PPh$_3$)] (80 mg, 0.16 mmol). Reaction time: 4 h. White crystals were obtained by recrystallization from CH_2Cl_2/hexane. Yield: 0.1 g, 81%. Anal. Calcd for $RuAu_4F_{12}P_{10}C_{136}H_{110}$: C, 51.06; H, 3.47; N, 0.88. Found: C, 50.82; H, 3.31; N, 0.83.

X-ray Crystallography. Crystals of **2a** and **7e** suitable for X-ray diffraction analysis were grown from dichloromethane solutions layered with hexane at 25 °C. The crystals were mounted in Lindemann capillaries, and the crystal of **7e** was covered with an inert oil, because it immediately lost solvent and became efflorescent. Unit cell dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 well-centered reflections. Crystallographic data and other information are summarized in Table 2. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections (Difabs) were applied.[13] Computations were performed by using CRYSTALS.[14] Atomic form factors were taken from ref 15. Real and imaginary parts of anomalous dispersions were taken into account. The structures were solved by Patterson methods, and all non-hydrogen atoms were anisotropically refined. The drawings of the complexes showed in Figures 3 and 5 were made using CAMERON.[16]

Acknowledgment. We gratefully acknowledge the Ministerio de Educación y Ciencia for financial assistance (Project No. PB91-0678) and for a research grant (M.E.G.M.).

Supporting Information Available: Text giving details of the crystal data, tables of crystal data, atomic coordinates and *U* values, anisotropic thermal parameters, and interatomic distances and angles, and ORTEP diagrams for **2a** and **7e** (22 pages). Ordering information is given on any current masthead page.

OM9701433

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