Transition-metal derivatives of the functionalized cyclopentadienyl ligand. XVIII. Syntheses and structures of a series of tetranuclear cyclic complexes $[\{(CO)_3M(\mu,\eta^5\text{-}C_5H_4PPh_2)\}_2M'M'']$ (M = Cr, Mo or W, M′ = M″ = Ag; M = Cr or Mo, M′ = M″ = Au; M = Mo, M′ = Ag, M″ = Au). Isotopomerism and NMR evidence of a double epimerization process

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Reaction of the lithium salts of the anionic complexes $[(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3]^-$ [M = Cr (**1**), Mo (**2**) or W (**3**)] with $AgBF_4$ or $AuClPPh_3$ easily affords the compounds $[(CO)_3M(\mu,\eta^5\text{-}C_5H_4PPh_2)M']_2$ [M = Cr, M′ = Ag (**4**); M = Mo, M′ = Ag (**5**); M = W, M′ = Ag (**6**); M = Cr, M′ = Au (**7**); M = Mo, M′ = Au (**8**)], which have been fully characterized by elemental analysis, DCI mass spectrometry, IR, ^1H and $^{31}P\{^1H\}$ NMR. X-Ray diffraction studies of the four complexes **4**–**6** and **8** revealed an eight-membered tetrametallacyclic structure built from two [M′—P—(Cp)—M] sequences [(Cp) being the centroid of the cyclopentadienyl ring] assembled ‘head-to-tail’ by M—M′ metal—metal bonds [$d_{Cr-Ag} = 2.6579(8)$, $d_{Mo-Ag} = 2.7467(4)$, $d_{W-Ag} = 2.7593(5)$, $d_{Mo-Au} = 2.7146(5)$ Å], while the observed M···M distances (around 6 Å) exclude any metal–metal interaction. Interestingly, the Ag···Ag distances in **4** [3.0884(8) Å] and in **5** [3.1780(8) Å], and the Au···Au distance in **8** [3.3755(3) Å], are approximately in the range of metallophilic attractions. These centro-symmetrical molecules **4**–**8**, being composed of two enantiomeric $[(CO)_3M(\mu,\eta^5\text{-}C_5H_4PPh_2)M']$ fragments, can be considered as *meso* diastereoisomers. Moreover, the complexes **4**, **5** and **6**, which include two silver atoms, are formed of the three isotopomers ^{107}Ag–^{107}Ag, ^{107}Ag–^{109}Ag and ^{109}Ag–^{109}Ag, and the variation with temperature of the ^{31}P resonance of **5** suggests that a double epimerization process is operating in these compounds.

Formation of **7** and **8** from the reaction of **1** and **2** with $AuClPPh_3$ was also briefly studied. Finally, synthesis of the mixed silver–gold metal complex $[\{(CO)_3Mo(\mu,\eta^5\text{-}C_5H_4PPh_2)\}_2AgAu]$ (**9**) can be achieved in two ways, either by mixing solutions of **5** and **8** or by adding one equivalent of $AuClPPh_3$ to a solution of **5**.

Synthèses et structures d’une série de composés tétramétalliques $[\{(CO)_3M(\mu,\eta^5\text{-}C_5H_4PPh_2)\}_2M'M'']$ (M = Cr, Mo ou W, M′ = M″ = Ag; M = Cr ou Mo, M′ = M″ = Au; M = Mo, M′ = Ag, M″ = Au). Isotopomérie et mise en évidence par RMN d’un processus de double épimérisation.

La réaction des anions $[(CO)_3M(\eta^5\text{-}C_5H_4PPh_2)]^-$ [M = Cr (**1**), Mo (**2**), ou W (**3**)] à l’état de sels de lithium, avec $AgBF_4$ ou avec $AuClPPh_3$ conduit aisément aux composés $[(CO)_3M(\mu,\eta^5\text{-}C_5H_4PPh_2)M']_2$ [M = Cr, M′ = Ag (**4**); M = Mo, M′ = Ag (**5**); M = W, M′ = Ag (**6**); M = Cr, M′ = Au (**7**); M = Mo, M′ = Au (**8**)]. Ceux-ci ont été entièrement caractérisés par analyse élémentaire, spectrométrie de masse, IR, RMN ^1H et $^{31}P\{^1H\}$. L’analyse par diffraction des rayons X des quatre composés **4**–**6** et **8** met en évidence une structure en couronne, résultant de l’association ‘tête à queue’ de deux séquences [M′—P—(Cp)—M] [(Cp) étant le centroïde du cycle cyclopentadienyle] grâce à deux liaisons M—M′ [$d_{Cr-Ag} = 2.6579(8)$; $d_{Mo-Ag} = 2.7467(4)$; $d_{W-Ag} = 2.7593(5)$; $d_{Mo-Au} = 2.7146(5)$ Å]. Dans ces composés, les distances M···M de l’ordre de 6 Å ne permettent aucune interaction metal–metal, tandis que les distances Ag···Ag observées dans **4** [3.0884(8) Å] et dans **5** [3.1780(8) Å], ainsi que la distance Au···Au dans **8** [3.3755(3) Å], font penser à de possibles interactions ‘metallophiles’. Etant formés de deux fragments énantiomères $[(CO)_3M(\mu,\eta^5\text{-}C_5H_4PPh_2)M']$, les complexes tétramétallacyclo-octaniques **4** à **8** peuvent être considérés comme des diastéréoisomères *meso.* Les dérivés de l’argent **4**, **5** et **6** sont par ailleurs constitués de trois isotopomères, respectivement ^{107}Ag–^{107}Ag, ^{107}Ag–^{109}Ag et ^{109}Ag–^{109}Ag, et l’évolution des figures de résonance du phosphore ^{31}P de **5** en fonction de la température peut être interprétée dans l’hypothèse d’un processus de double épimérisation.

La formation de **7** et **8** par réaction de **1** et **2** avec $AuClPPh_3$ a été brièvement étudiée ainsi que celle du complexe mixte argent–or $[\{(CO)_3Mo(\mu,\eta^5\text{-}C_5H_4PPh_2)\}_2AgAu]$ (**9**). Le complexe **9** s’obtient soit en mélangeant des solutions de **5** et de **8**, soit en ajoutant un équivalent de $AuClPPh_3$ à une solution de **5**.

Following our investigations on the transition-metal derivatives of functionalized cyclopentadienyl ligands,[1] we have recently reported the synthesis of the group 6 homobinuclear derivatives $[(\mu,\eta^5\text{-}C_5H_4PPh_2)M(CO)_2]_2$ using the mononuclear anionic complexes $[(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3]^-$ [M = Cr (**1**), Mo (**2**) or W (**3**)] as the starting materials. Implying basically oxidative processes, four synthetic approaches

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were investigated.[1d] Interestingly, the attempt to use silver tetrafluoroborate as the oxidant led to the novel bimetallic M—Ag cyclic complexes $[(CO)_3M(\mu,\eta^5\text{-}C_5H_4PPh_2)Ag]_2$ [M = Cr (**4**), Mo (**5**) or W (**6**)].

The synthesis and structure of the molybdenum complex **5** have already been described in an earlier short communication[1a] Our new results now concern the whole series of analogous title complexes, which exemplify a new type of 'ring-shaped' polymetallic compounds. Other types of ring-shaped compounds are already known, for instance those including diphosphines[2a] or thiolato[2b] groups as bridging ligands.

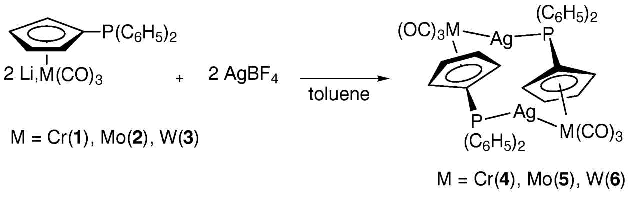
Preparation of the Tetranuclear Cyclic Complexes

The preparations of the three compounds **4**–**6** recall the procedures used for the syntheses of the analogous cyclopentadienyl parent compounds.[3a,b] In each case, powdered silver tetrafluoroborate (1 equiv.) was added at room temperature to a solution in toluene of the lithium salt of one of the anions **1**, **2** or **3** in a Schlenk tube protected from light by aluminium foil (Scheme 1). The suspension was stirred for about 4 h until a grey precipitate of lithium tetrafluoroborate, as well as a silver mirror on the tube, were formed. The precipitate was easily removed by filtration and concentration of the filtrate afforded the complexes **4**, **5** or **6** as yellow powders in moderate yields.

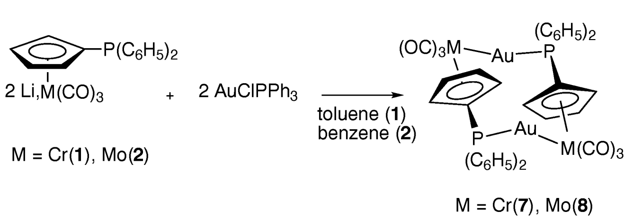
Formation of the silver mirror was attributed to a redox side-reaction whose efficiency, evaluated from the mass of metallic silver covering the inner side of the tube, nevertheless does not exceed 7%. This explanation is supported by a cyclic voltammetry study of the electrochemical oxidation of anions **1** and **2**. The peak potentials of **1** at $E_p = -1.03$ V and of **2** at $E_p = -0.89$ V justify their oxidation by the Ag/Ag^+ system (redox potential at 0.89 V).[4]

For the main pathway, one can envisage processes involving addition of the silver cation to both the phosphorus atom of one $[(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3]^-$ anion and the molybdenum centre of another anion. These processes are possibly favoured by the ionic charges of the reactants.

Following an already known procedure,[3c,d] the gold complexes $[(CO)_3M(\mu,\eta^5\text{-}C_5H_4PPh_2)Au]_2$ [M = Cr (**7**, Mo (**8**)] were prepared by adding one equivalent of $AuClPPh_3$ at room temperature to a solution in toluene of the lithium salt of one of the anions, **1** or **2** (Scheme 2). In both cases, after a short period of stirring a white precipitate of LiCl formed. It was removed by filtration and concentration of the filtrate afforded the complexes **7** or **8** as yellow powders in good yields.



Scheme 1



Schemr 2

In the present series of complexes, the substitution of silver by gold can be easily observed. This is exemplified by **7** or **8**, which are easily obtained by reacting **4** or **5**, respectively, with two equivalents of $AuClPPh_3$ and taking advantage of the precipitation of AgCl.

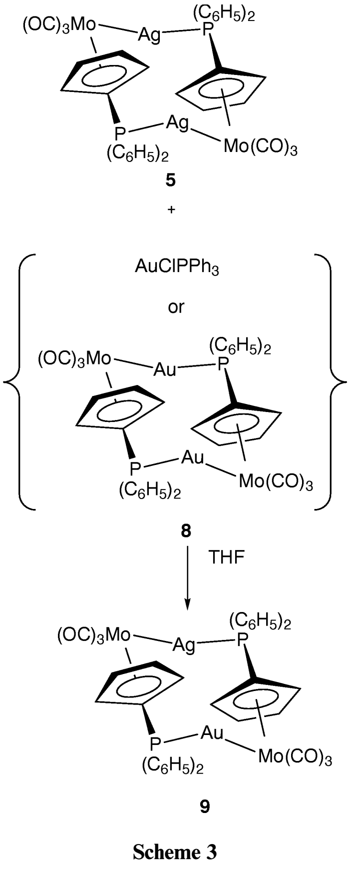
The mixed silver–gold complex $[\{(CO)_3Mo(\mu,\eta^5\text{-}C_5H_4PPh_2)\}_2AgAu]$ (**9**) was easily obtained by mixing at room temperature THF solutions of **5** and **8** in stoichiometric proportions (Scheme 3). The afforded solution contained approximately the 1 : 2 : 1 statistical mixture of the three compounds **5**, **9** and **8**, respectively, but by concentrating this solution only **9**, possibly the last soluble complex, crystallized to afford a yellow powder in high yield.

Finally, **9** was also obtained in high yield by adding $AuClPPh_3$ to a solution of **5** in a stoichiometric ratio, a protocol that probably combines the substitution of Ag by Au in **5** leading to **8**, and the above reaction of **5** with **8**.

The compounds **4**–**9** have been fully authenticated by elemental analysis and characterized by IR (Table 1) and $^{31}P\{^1H\}$ (Table 2) NMR spectroscopies. DCI mass spectrometric measurements with ammonia were especially meaningful as they directly demonstrated, through the isotopic pattern of the parent peak, the presence of four metal atoms.

As shown in Table 1, these complexes exhibit three very strong C—O stretching bands as expected for the 'four-legged piano stool' structure of each $-[Cp(CO)_3M-]$ fragment. Nevertheless, shoulders are often distinguishable at the low frequency side; they were assigned to the expected ^{13}C—O stretching mode. In other words, the assignment of the four bands to four distinct C—O modes, which would suppose some coupling between the two $(CO)_3$ groups, was not retained.

Surprisingly, in contrast with its asymmetric structure, the infrared spectrum of **9** appeared to be quite simple. In fact, as shown in Fig. 1, this spectrum results from the fortuitous exact superposition of the spectra of **5** and **8**. This observation confirms therefore the absence of vibrational interactions between the two $(CO)_3$ groups.



Scheme 3

Table 1 Comparison of the CO stretching vibrations (cm^{-1}) in the $[(CO)_3M\{\mu\text{-}C_5H_4P(C_6H_5)_2\}M']_2$ complexes

4	(*a*)	1933vs	1853s	1824vs	1841s
	(*b*)	1933vs	1855s	1829vs	1816s
	(*d*)	1929vs	1849s		1809vs
5	(*a*)	1941vs	1857s	1832vs	1821s
	(*c*)	1942vs	1860s	1838vs	1829s
	(*d*)	1937vs	1851s		1814vs
6	(*a*)	1935vs	1850s	1824vs	1817s
	(*c*)	1937vs	1853s	1831vs	1822s
	(*d*)	1930vs		1826s	1808vs
7	(*b*)	1940vs	1868s	1844vs	
	(*c*)	1939vs	1867s	1843vs	
8	(*a*)	1949vs	1867s	1850vs	
	(*c*)	1949vs	1870s	1856vs	1833m
	(*d*)	1948vs		1836vs	
9	(*c*)	1942vs	1849vs	1823m	

(*a*) in CH_2Cl_2, (*b*) in $C_6H_5CH_3$, (*c*) in THF, (*d*) in KBr.

Table 2 $^{31}P\{^1H\}$ NMR spectra of the $[\{(CO)_3M(\mu,\eta^5\text{-}C_5H_4PPh_2)\}_2M']$ complexes in CD_2Cl_2 at 161.99 MHz

	At 293 K δ	Low temperature δ	$J_{P\text{–}Ag}$/Hz
4	9.81(d)^a	9.48^b	493^d, 426^e
5	9.03(d)	8.73^b	486^d, 423^e
6	13.60(d)	13.30^c	494^d, 427^e
7	44.94(s)		—
8	45.97(s)		—
9	6.01(d), 48.86(s)	with	497^d, 439^e

[a] Unresolved structure. [b] 253 K and [c] 183 K (temperature has been chosen to give the best resolution). [d] $J_{P\text{–}^{109}Ag}$ in the $^{109}Ag\text{–}^{109}Ag$ isotopomer. [e] $J_{P\text{–}^{107}Ag}$ in the $^{107}Ag\text{–}^{107}Ag$ isotopomer.

The ^1H NMR spectra are easily interpreted, nevertheless some shift variations of the peaks assigned to the C_5H_4 protons, are noteworthy (See Experimental).

The $^{31}P\{^1H\}$ NMR data call for comments on three points: (*i*) for the six compounds **4**–**9**, a noticeable shift was observed between the peaks of the phosphorus atoms coordinated to a silver atom and those coordinated to a gold atom. Such a shift has been shown to be related to the increase of the spin-orbit coupling;[5] (*ii*) for compound **9**, consisting of two different $[M'{-}PPh_2{-}Cp{-}Mo(CO)_3]$ fragments, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ 48.86 assigned to the phosphorus atom bonded to the gold centre, and two doublets at δ 6.01, assigned to the one bonded to the silver centre; (*iii*) in complexes **4**–**6** and **9** the coupling constants, respectively $J_{P\text{–}^{107}Ag}$ around 420–440 Hz and $J_{P\text{–}^{109}Ag}$ around 490 Hz, are in agreement with the literature[6] (*vide infra*).

Structural Characterization of Complexes 4–6 and 8

The solid state structure of the tetranuclear complex **5** being known,[1a] those of the **4**, **6** and **8** analogs were now determined by single crystal X-ray diffraction studies. Yellow crystals suitable for these studies were obtained by slow diffusion of diethyl ether in saturated toluene (**4**), acetonitrile (**6**) or dichloromethane (**8**) solutions.

Relevant crystallographic data are provided in Table 3. Atomic scattering factors (f', f'') were taken from a standard source.[8] The initial structural solutions were obtained either by direct methods or by Patterson analysis (SHELXS 86[9]). Atoms not located from the initial structure solution were found by successive difference Fourier maps and least-squares refinement processes (SHELXS 76[10]). All non-hydrogen atoms were refined anisotropically, except those of the phenyl rings in **4** and **6**. Full-matrix least-squares refinements were used in

Table 3 Crystallographic data^a for complexes **4**, **6** and **8**

	4	**6**	**8**
Formula	$C_{47}H_{36}Ag_2Cr_2O_6P_2$	$C_{42}H_{31}Ag_2NO_6P_2W_2$	$C_{41}H_{30}Au_2Cl_2O_6Mo_2P_2$
FW	1076.48	1290.1	1337.35
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	11.652(1)	8.385(1)	8.2579(6)
b/Å	12.260(1)	21.942(2)	15.7382(8)
c/Å	18.077(2)	11.970(1)	16.1382(7)
β/deg	106.93(2)	108.33(2)	98.096(5)
U/Å^3	2470.5(8)	2090.5(9)	2076.5(2)
$F(000)$	1076	1220	1260
Z	2	2	2
D_{calc}/g cm^{-3}	1.450	2.051	2.139
μ(MoKα)/mm^{-1}	1.30	6.30	7.86
T_{min}–T_{max}^{b}	0.941–0.999	0.453–0.692	0.860–0.998
2θ range/deg	3–48	3–60	3–48
Scan mode	$\omega - 2\theta$	$\omega - 1.3\theta$	$\omega - 2\theta$
No. of data collected	4057	6430	3499
No. of unique data	3857	6069	3259
R_{ave} (on I)	0.022	0.023	0.016
No. of observed data $[F_o^2 > 3\sigma(F_o^2)]$	2636	2263	2492
No. of variable parameters	172	163	257
Isotropic empirical extinction parameter			0.24×10^{-7}
S	1.307	1.027	1.080
w	Unit weights	$[\sigma^2(F_o) + 0.001\ F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.00014\ F_o^2]^{-1}$
$(\Delta/\sigma)_{max}$	0.008	0.199	0.111
R^c	0.027	0.036	0.020
R_w^{d}	0.030	0.044	0.022
(Δ/ρ) max, min/e Å^{-3}	0.25, −0.29	0.90, −0.88	0.54, −0.51

[a] All data collected at $T = 293$ K on an Enraf-Nonius CAD4 diffractometer with graphite monochromatized MoKα radiation ($\lambda = 0.71073$ Å). [b] From empirical absorption corrections[7a] for **4** and **8** and from Gaussian absorption corrections[7b] for **6**. [c] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [d] $R_w = [\Sigma(w|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

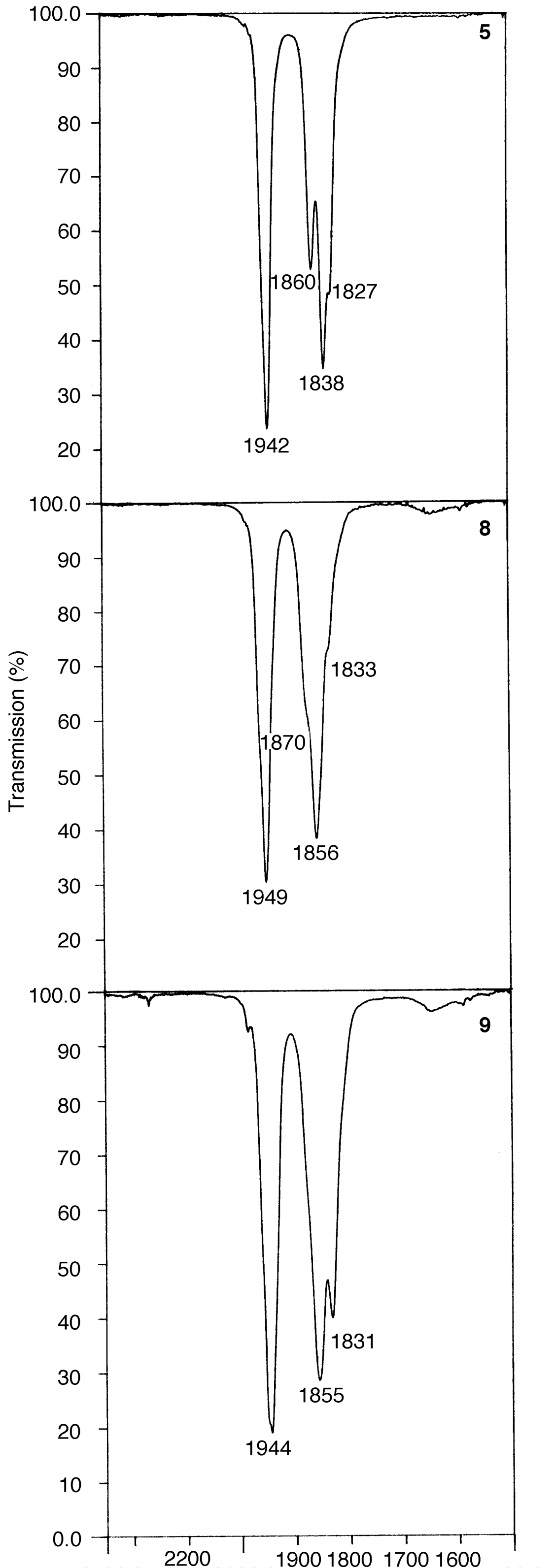


Fig. 1 IR spectra of the [{(CO)$_3$M(μ,η^5-C$_5$H$_4$PPh$_2$)}$_2$M′M″] complexes [M = Mo, M′ = M″ = Ag (**5**); M = Mo, M′ = M″ = Au (**8**); M = Mo, M′ = Ag, M″ = Au (**9**)]

Table 4 Selected bond lengths (Å) and angles (deg) with e.s.d.s in parentheses for **4**

Ag---Ag′	3.0884(8)	Cr---Cr′	6.728(2)
Ag—Cr	2.6579(8)	Ag---C(1)	2.506(6)
Ag—P	2.380(1)	Ag---C(3)	2.501(6)
Cr—Cp	1.849(5)	Cr—C(4)	2.212(5)
Cr—C(1)	1.825(6)	Cr—C(5)	2.203(5)
Cr—C(2)	1.835(6)	Cr—C(6)	2.225(5)
Cr—C(3)	1.849(6)	Cr—C(7)	2.195(4)
P—C(4′)	1.790(6)	Cr—C(8)	2.211(5)
P—C(9)	1.803(3)	C(1)—O(1)	1.151(7)
P—C(15)	1.777(3)	C(2)—O(2)	1.142(8)
C(4)—C(5)	1.406(7)	C(3)—O(3)	1.155(8)
C(6)—C(7)	1.428(8)	C(5)—C(6)	1.432(8)
C(8)—C(4)	1.417(7)	C(7)—C(8)	1.429(8)
Ag—Cr—Cp	113.1(2)	Cp—Cr—C(2)	120.1(2)
Cp—Cr—C(1)	128.3(3)	Cp—Cr—C(3)	121.5(2)
Ag—Cr—C(1)	64.9(2)	C(1)—Cr—C(2)	83.4(3)
Ag—Cr—C(2)	126.8(2)	C(1)—Cr—C(3)	104.4(2)
Ag—Cr—C(3)	64.5(2)	C(2)—Cr—C(3)	85.6(3)
Ag—P—C(4′)	115.5(2)	C(2)—Cr—C(4)	136.7(2)
Ag—P—C(9)	112.9(1)	C(4′)—P—C(9)	107.8(2)
Ag—P—C(15)	111.8(1)	C(4′)—P—C(15)	104.3(2)
Cr—C(1)—O(1)	174.8(6)	C(9)—P—C(15)	103.5(2)
Cr—C(2)—O(2)	179.0(6)	Cr—Ag—P	168.97(4)
Cr—C(3)—O(3)	172.5(5)		

Symmetry operations: ′ = 1 − *x*, 1 − *y*, 1 − *z*; ″ = 2 − *x*, 1 − *y*, 2 − *z*. Cp is the centroid of the cyclopentadienyl ring C(4)—C(5)—C(6)—C(7)—C(8). Phenyl rings were refined as isotropic rigid groups with *d*(C—C) = 1.395 Å.

Table 5 Selected bond lengths (Å) and angles (deg) with e.s.d.s in parentheses for **6**

Ag---Ag′	3.610(1)	W---W′	6.3169(5)
Ag—W	2.7593(5)	Ag---C(1)	2.563(6)
Ag—P	2.384(2)	Ag---C(3)	2.611(6)
W—Cp	2.009(6)	W—C(4)	2.335(6)
W—C(1)	1.959(6)	W—C(5)	2.363(6)
W—C(2)	1.937(7)	W—C(6)	2.359(5)
W—C(3)	1.949(7)	W—C(7)	2.330(5)
P—C(4′)	1.822(7)	W—C(8)	2.334(6)
P—C(9)	1.809(5)	C(1)—O(1)	1.200(8)
P—C(15)	1.816(4)	C(2)—O(2)	1.176(8)
C(4)—C(5)	1.412(8)	C(3)—O(3)	1.153(9)
C(6)—C(7)	1.385(9)	C(5)—C(6)	1.442(9)
C(8)—C(4)	1.412(8)	C(7)—C(8)	1.433(9)
Ag—W—Cp	113.1(2)	Cp—W—C(2)	121.3(2)
Cp—W—C(1)	130.6(3)	Cp—W—C(3)	122.2(2)
Ag—W—C(1)	63.1(2)	C(1)—W—C(2)	83.3(2)
Ag—W—C(2)	125.5(2)	C(1)—W—C(3)	101.2(3)
Ag—W—C(3)	64.7(2)	C(2)—W—C(3)	83.2(3)
Ag—P—C(4′)	110.4(2)	C(2)—W—C(4)	127.2(2)
Ag—P—C(9)	111.4(2)	C(4′)—P—C(9)	102.1(2)
Ag—P—C(15)	119.2(1)	C(4′)—P—C(15)	105.2(2)
W—C(1)—O(1)	174.1(5)	C(9)—P—C(15)	107.1(2)
W—C(2)—O(2)	177.7(6)	W—Ag—P	167.56(4)
W—C(3)—O(3)	172.5(5)		

Symmetry operations: ′ = 1 − *x*, 1 − *y*, 1 − *z*; ″ = 2 − *x*, 1 − *y*, 2 − *z*. Cp is the centroid of the cyclopentadienyl ring C(4)—C(5)—C(6)—C(7)—C(8). Phenyl rings were refined as isotropic rigid groups with *d*(C—C) = 1.395 Å.

all cases. Hydrogen atoms located by difference Fourier maps were introduced in idealized positions. Final *R* values are provided in Table 3, Selected bond lengths and angles are summarized in Tables 4, 5 and 6. The molecular plots of the three studied compounds are presented in Fig. 2. These structures are similar to those of **5**.[1a]

All four compounds exhibit a ‘head-to-tail’ disposition of the μ-η^5,η^1-C$_5$H$_4$PPh$_2$ bridging ligands, as in the parent dinuclear [(μ,η^5-C$_5$H$_4$PPh$_2$)M(CO)$_2$]$_2$ compound.[1d] The coordination of the cyclopentadienyl group of these ligands to the

Table 6 Selected bond lengths (Å) and angles (deg) with e.s.d.s in parentheses for **8**

Au---Au′	3.3755(3)	Mo---Mo′	6.934(1)
Au—P	2.274(1)	Au—Mo	2.7146(5)
Mo—Cp	2.028(5)	Mo—C(4)	2.329(5)
Mo—C(1)	1.965(5)	Mo—C(5)	2.347(5)
Mo—C(2)	1.969(6)	Mo—C(6)	2.380(5)
Mo—C(3)	1.970(6)	Mo—C(7)	2.368(6)
P—C(4′)	1.797(5)	Mo—C(8)	2.357(5)
P—C(9)	1.815(5)	C(1)—O(1)	1.163(7)
P—C(15)	1.812(5)	C(2)—O(2)	1.151(7)
C(4)—C(5)	1.436(7)	C(3)—O(3)	1.16
C(6)—C(7)	1.400(8)	0(8)C(5)—C(6)	1.398(8)
C(8)—C(4)	1.416(7)	C(7)—C(8)	1.401(8)
Au—Mo—Cp	111.7(2)	Cp—Mo—C(2)	124.8(2)
Cp—Mo—C(1)	132.8(2)	Cp—Mo—C(3)	121.4(2)
Au—Mo—C(1)	65.3(2)	C(1)—Mo—C(2)	79.3(2)
Au—Mo—C(2)	126.9(2)	C(1)—Mo—C(3)	98.7(2)
Au—Mo—C(3)	68.0(2)	C(2)—Mo—C(3)	80.5(2)
Au—P—C(4′)	118.9(2)	C(2)—Mo—C(4)	139.2(2)
Au—P—C(9)	112.4(2)	C(4′)—P—C(9)	104.7(2)
Au—P—C(15)	110.5(2)	C(4′)—P—C(15)	104.4(2)
Mo—C(1)—O(1)	173.0(5)	C(9)—P—C(15)	104.7(2)
Mo—Au—P	169.83(4)	Mo—C(2)—O(2)	177.9(6)

Symmetry operations: ′ = 1 − x, 1 − y, 1 − z; ″ = 2 − x, 1 − y, 2 − z. Cp is the centroid of the cyclopentadienyl ring C(4)—C(5)—C(6)—C(7)—C(8). Phenyl rings were refined as isotropic rigid groups with *d*(C—C) = 1.395 Å.

group 6 transition metal atom M still plays the central role, while the phosphine function ensures their bonding to the late transition metal atom M′. The conformation around the group 6 metal atoms M in the four complexes is not different from that observed in the numerous complexes built on the 'four-legged piano stool' [η^5-$C_5R_5M(CO)_3$] fragment.[11] Nevertheless, the most salient features are the bonding of the coinage metal M′ with the group 6 metal centre M and the resulting catenation —[Cp—Mo—Ag—P—]$_2$, which shapes the compounds in the form of a 'ring-shaped' tetranuclear complex. As compared in Table 7, the M—M distances are too long to suggest any metal–metal interaction. The M—M′ distances vary as expected, that is, in the series of the silver complexes, it increases from chromium to tungsten, following the increase of the covalent radii along the series of transition metals M, while it decreases in **8** with respect to **5**, as a consequence of the smaller constant radius of gold compared to silver. Values of nonbridged M—M′ bond lengths (M = Cr, Mo, W; M′ = Ag, Au) are rather scarce[12c] but the present values compare well with the most related ones reported in the literature.[12]

The values of the angles M—Ag—P (M = Cr, Mo and W) and Mo—Au—P lead to a description of the complexes **4**, **6** and **8**, as well as **5**, as examples of near linear, twofold coordinated coinage metal–transition metal compounds. As shown in Table 7, the Ag---Ag distances in **4** and **5** are shorter than the expected Van der Waals contact (3.54 Å in Bondi's work[13]) while the Au---Au distance in **8** approximates this Van der Waals contact (3.32 Å[13]). Therefore, with the exception of the Ag---Ag distance in **6**, such a short contact could well be related to the existence of some metallophilic attraction[14] Nevertheless, the slight approach of the M′ atoms appearing in the ORTEP diagrams and the deviation from linearity of the M—M′—P angles observed in the four compounds **4**–**6**, **8** more probably result from a combination of angular constraints around the cyclic structure.

Table 7 Comparison of the metal–metal distances (Å) in the [$(CO)_3M(\mu,\eta^5$-$C_5H_4PPh_2)M']_2$ complexes (including data on **5**[1a])

4	Ag---Ag: 3.0884(8)	Cr---Cr: 6.728(2)	Cr—Ag: 2.6579(8)
5	Ag---Ag: 3.1780(8)	Mo---Mo: 6.7438(7)	Mo—Ag: 2.7467(4)
6	Ag---Ag: 3.610(1)	W---W: 6.3169(5)	W—Ag: 2.7593(5)
8	Au---Au: 3.3755(3)	Mo---Mo: 6.934(1)	Mo—Au: 2.7146(5)

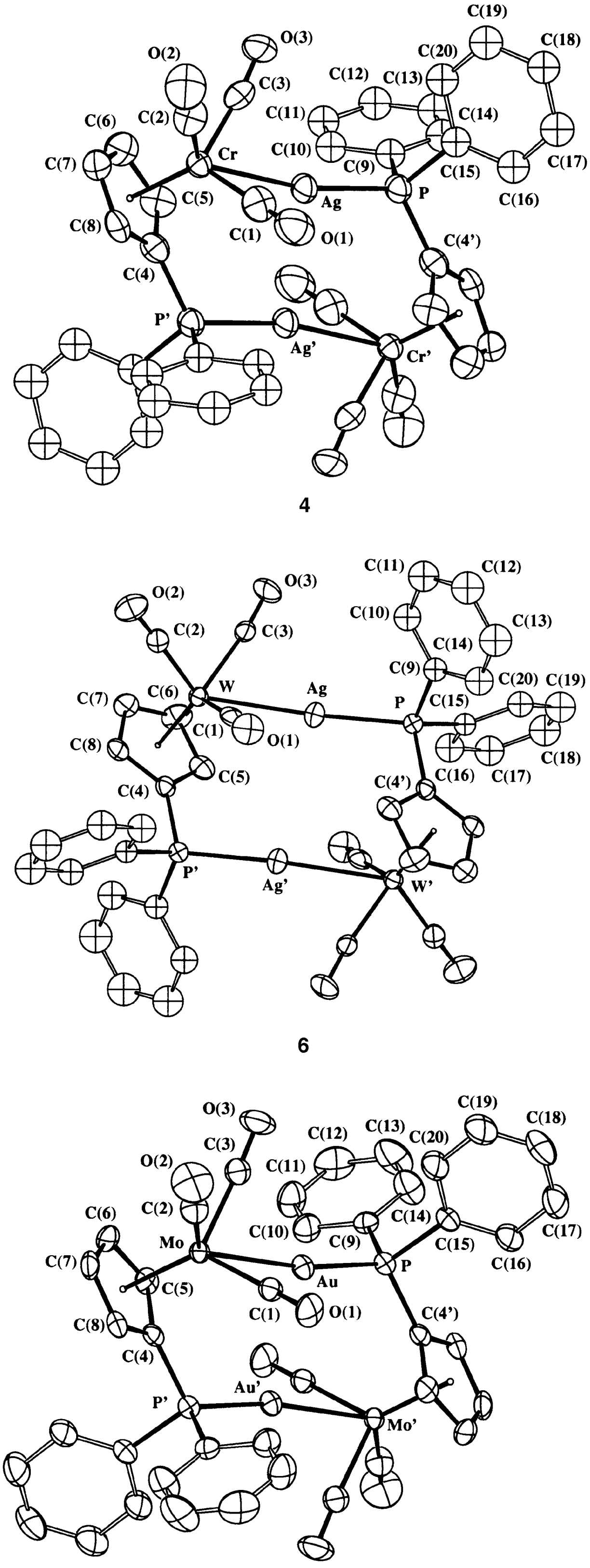


Fig. 2 ORTEP plots of the [$(CO)_3M(\mu,\eta^5$-$C_5H_4PPh_2)M']_2$ complexes [M = Cr, M′ = Ag (**4**); M = W, M′ = Ag (**6**); M = Mo, M′ = Au (**8**)]

Variable Temperature NMR Study of the Three ^{107}Ag–^{107}Ag, ^{107}Ag–^{109}Ag and ^{109}Ag–^{109}Ag Isotopomers of [(CO)$_3$Mo(μ,η^5-C$_5$H$_4$PPh$_2$Ag]$_2$ (5)

Phosphorus–silver couplings have long been observed. They range from *ca.* 20 Hz to values higher than 900 Hz and in organometallic compounds more often from 400 to 600 Hz[15a] In addition, the study of the bi- or trimetallic hexa-nuclear cluster compounds [MM′Ru$_4$(μ$_3$-H)$_2${μ-Ph$_2$P(CH$_2$)$_n$PPh$_2$}(CO)$_{12}$] (M = Cu, M′ = Ag or Au; M = Ag, M′ = Au; *n* = 1–6) has exemplified the possibility to use the ^{31}P{^{1}H} NMR spectra to obtain information on the dynamic behaviour of these clusters[15b–f]

The ^{31}P{^{1}H} NMR spectra [Fig. 3(*a*)] of the tetranuclear crown complex [(CO)$_3$Mo(μ,η^5-C$_5$H$_4$PPh$_2$)Ag]$_2$ (**5**) shows some remarkable features. As already noted, this complex exists as three isotopomers containing respectively the three isotopic couples ^{107}Ag–^{107}Ag, ^{107}Ag–^{109}Ag and ^{109}Ag–^{109}Ag. For evident statistical reasons, the isotopic ratio close to 1 of the two spin $\frac{1}{2}$ isotopes ^{107}Ag and ^{109}Ag (natural abundance 48.2% and 51.8%, respectively) leads to a distribution of the isotopomers close to 1 : 2 : 1. The ^{31}P{^{1}H} NMR subspectra due to each isotopomer could be *a priori* described as an AA′XX′ spin system (A = A′ = Ag; X = X′ = P).[16] Actually, the ^{31}P{^{1}H} NMR spectra of **5** at room temperature appears to be the superposition, with an intensity ratio of 1 : 2 : 1, of three 'simple' doublets at the same chemical shift δ 6.3 in C$_6$D$_6$. These doublets can be tentatively interpreted in the first-order approximation, in agreement with the very small values expected for $J_{\mathrm{Ag-Ag}}$ and for long distance $J_{\mathrm{P-Ag}}$ coupling constants, both occurring through four bonds. Considering their intensity, the two sharp doublets (1 : 1) were assigned to the ^{107}Ag—^{107}Ag and ^{109}Ag—^{109}Ag isotopomers, giving the two phosphorus–silver coupling constants $J_{\mathrm{P-^{107}Ag}} = 414$ Hz and $J_{\mathrm{P-^{109}Ag}} = 477$ Hz. These values are in agreement with those measured in the above cited silver–ruthenium hexanuclear cluster compounds[15d] and their ratio ($J_{\mathrm{P-^{107}Ag}}/J_{\mathrm{P-^{109}Ag}} = 0.868$) is, as expected, close to the gyromagnetic ratio ($\gamma^{107}\mathrm{Ag}/\gamma^{109}\mathrm{Ag} = 0.869$) of these isotopes. The third doublet, of intensity 2 and presenting an intermediate value for its coupling constant, was assigned to the ^{109}Ag–^{107}Ag isotopomer. It is surprisingly broad at room temperature.

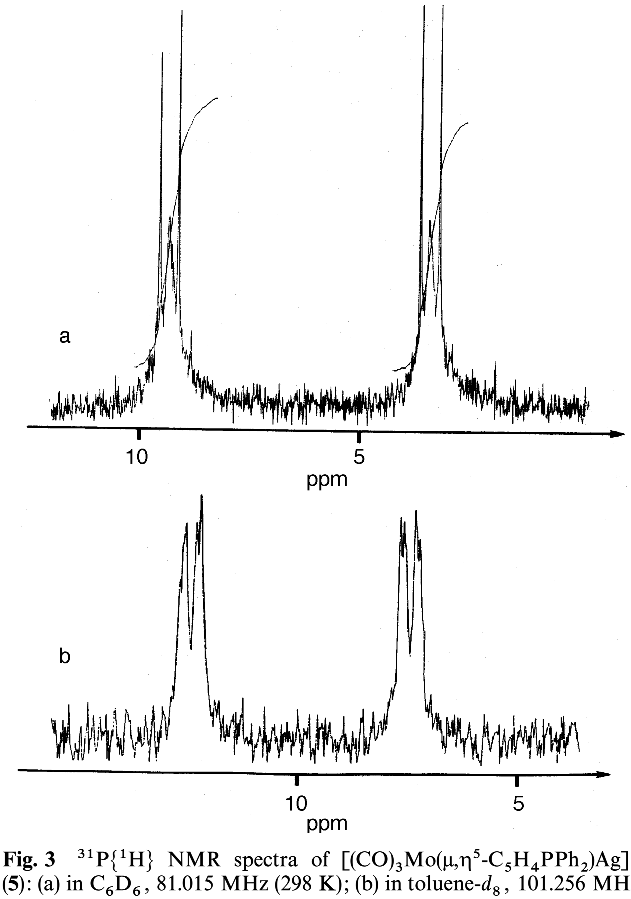


Fig. 3 ^{31}P{^{1}H} NMR spectra of [(CO)$_3$Mo(μ,η^5-C$_5$H$_4$PPh$_2$)Ag]$_2$ (**5**): (a) in C$_6$D$_6$, 81.015 MHz (298 K); (b) in toluene-*d*$_8$, 101.256 MHz (183 K)

To understand the reason for the broadness of the third doublet assigned to the ^{109}Ag–^{107}Ag isotopomer (for which in the first-order approximation, two doublets are expected), variable-temperature ^{31}P{^{1}H} NMR experiments in toluene-*d*$_8$ have been performed. When the temperature is progressively lowered, each component of this doublet disappears and then is replaced by two peaks [Fig. 3(b)]. Indeed, at low temperature, the spectra of **5** consist of four doublets.

The two new doublets are tentatively assigned each to one of the phosphorus atoms respectively bonded to the ^{107}Ag and the ^{109}Ag isotopes. In this hypothesis, the observed change of the spectrum with temperature suggests that the framework of **5** is stereochemically labile in solution. As the phosphorus–silver coupling still persists during the exchange this dynamic behaviour should involve a site exchange that preserves the phosphorus–silver bond.

As shown in Fig. 4, the —[AgPPh$_2$(η^5-C$_5$H$_4$)Mo—] fragments present an axial chirality. Therefore, the tetranuclear molecule consists, in the solid state, of two asymmetric units that are related by an inversion operation. Therefore, this conformation of the eight-membered molecule corresponds to one of the three possible diastereoisomers, namely the 'Δ-Λ' *meso* diastereoisomer containing two centres of opposite chirality. Evidently, the 'Δ-Λ' and 'Λ-Δ' molecules are the 'one and only' *meso* diastereoisomer, but as isotopically substituted compounds they consist of two different isotopomers, [Δ-^{107}Ag—PPh$_2$(η^5-C$_5$H$_4$)Mo][Λ-^{109}Ag—PPh$_2$(η^5-C$_5$H$_4$)Mo] and [Λ-^{107}Ag—PPh$_2$(η^5-C$_5$H$_4$)Mo][Δ-^{109}Ag—PPh$_2$(η^5-C$_5$H$_4$)Mo]. In solution, the postulated site exchange could be therefore described as a double epimerization process leading from the 'Δ-Λ' to the 'Λ-Δ' *meso* diastereoisomer. During these epimerizations, the successive inversions of the two —[AgPPh$_2$(η^5-C$_5$H$_4$)Mo— fragments can involve, *a priori*, either an intramolecular process without any bond breaking or a disruptive process involving the breaking of one or two Mo—P bonds.

The first hypothesis supposes that one or both of [Δ-^{107}Ag—PPh$_2$(η^5-C$_5$H$_4$)Mo][Δ-^{109}Ag—PPh$_2$(η^5-C$_5$H$_4$)Mo] and [Λ-^{107}Ag—PPh$_2$(η^5-C$_5$H$_4$)Mo][Λ-^{109}Ag—PPh$_2$(η^5-C$_5$H$_4$)Mo] diastereoisomers, containing the two asymmetric [—Ag—PPh$_2$(η^5-C$_5$H$_4$)Mo—] fragments with the same chirality, exist at least as intermediates or as transition states. This is very improbable for such a small ring. The second hypothesis, which is finally preferred, could involve quite complicated pathways and needs further investigation.

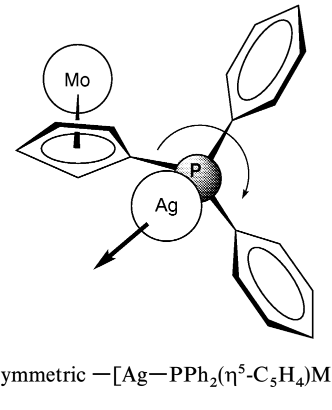


Fig. 4 The asymmetric —[Ag—PPh$_2$(η^5-C$_5$H$_4$)Mo—] fragment

A question finally remains concerning the small differences observed between the values of the phosphorus–silver coupling constants $J_{P-^{107}Ag}$ in the isotopomers $^{107}Ag–^{107}Ag$ and $^{107}Ag–^{109}Ag$ and of the coupling constants $J_{P-^{109}Ag}$ in the isotopomers $^{109}Ag–^{109}Ag$ and $^{109}Ag–^{107}Ag$. Therefore, we abandon the hypothesis of first-order subspectra and attribute these differences to a non-negligible direct Ag—Ag coupling produced in these compounds by the observed shortening of the Ag---Ag distances.[17]

Experimental

Reagents and general techniques

All manipulations involving air-sensitive organometallic compounds were carried out by standard Schlenk techniques or in an inert atmosphere glovebox. Toluene, diethyl ether, THF and pentane were distilled under nitrogen from dark purple solutions of sodium benzophenone ketyl immediately prior to use. CH_2Cl_2 and acetonitrile were distilled from CaH_2, then P_2O_5.

The complexes Li[(η^5-$C_5H_4PPh_2$)M(CO)$_3$] [M = Cr (**1**), Mo (**2**), W (**3**)] were obtained by a method described in a recent paper[1a] AuClPPh$_3$ was prepared as described in the literature.[18]

^1H NMR spectra were obtained on a Bruker AC200 spectrometer. $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker AC80 (81.015 MHz) or AC200 (32.40 MHz) spectrometer. Infrared spectra were measured on a Perkin–Elmer 225 (FT) spectrometer. Mass spectral data (DCI/NH$_3$) were recorded on a NERMAG R10-10 spectrometer at the University of Toulouse. Elemental analyses were performed by the Service de Microanalyse of the Laboratoire de Chimie de Coordination of the CNRS, in Toulouse.

CCDC reference 440/056.

Synthesis

[(CO)$_3$Cr(μ,η^5-C$_5$H$_4$PPh$_2$)Ag]$_2$, 4. One equivalent of AgBF$_4$ (399 mg, 2.05 mmol) was added, at room temperature and in the dark, to an orange solution of Li[(η^5-C$_5$H$_4$PPh$_2$)Cr(CO)$_3$] (**1**), (804 mg, 2.05 mmol) in 50 mL of toluene and was stirred for 4 h. A silver mirror was observed on the wall of the Schlenk tube. Then, the orange solution was filtered and the solvent was concentrated to allow precipitation of **4** as a yellow powder. Yield: 69%. Yellow crystals of **4** suitable for an X-ray diffraction study were isolated by slow diffusion of diethyl ether in a saturated toluene solution. ^1H NMR (200 MHz, acetone-d_6): δ 7.89–7.80 (m 8H, *ortho*), 7.72–7.58 (m, 8H, *meta*), 7.40–7.21 (m, 4H, *para*), 5.37 (br s, 4H, C_4H_4), 5.20 (br s, 4H, C_5H_4); ^1H NMR (400.14 MHz, CD_2Cl_2): δ 7.68–7.63 (m, 8H, *ortho*), 7.54–7.51 (m, 4H, *para*), 7.45–7.42 (m, 8H, *meta*), 5.01 (s, 4H, C_5H_4), 4.99 (s, 4H, C_5H_4); $^{31}P\{^1H\}$ NMR (81.015 MHz, acetone-d_6): δ 12.3 (d, $^1J_{P-Ag}$ = 454 Hz); IR (CH_2Cl_2, ν_{CO}): 1933vs, 1853s, 1824vs, 1814sh cm^{-1}. The elemental analysis was performed on crystals of [(CO)$_3$Cr(μ,η^5-C$_5$H$_4$PPh$_2$)Ag]$_2$·C$_6$H$_5$CH$_3$. Anal. calcd. for $C_{47}H_{36}O_6P_2Ag_2$: C, 52.34; H, 3.36. Found: C, 52.59; H, 3.51.

[(CO)$_3$Mo(μ,η^5-C$_5$H$_4$PPh$_2$)Ag]$_2$, 5[1a]. The same procedure was followed with AgBF$_4$ (76 mg, 0.39 mmol) and Li[(η^5-C$_5$H$_4$PPh$_2$)Mo(CO)$_3$] (**2**), (170 mg, 0.39 mmol) in 20 mL of toluene. A yellow powder (250 mg) of **5** was isolated in moderate yield: 60%. ^1H NMR (200 MHz, C_6D_6): δ 7.69 (m, 8H, *ortho*), 7.15 (m, 12H, *meta* and *para*), 5.36 (br m, 4H, C_5H_4), 4.96 (br m, 4H, C_5H_4); ^1H NMR (200 MHz, acetone-d_6): δ 7.87–7.79 (m, 8H, *ortho*), 7.66–7.50 (m, 12H, *meta* and *para*), 5.88 (m, 4H), 5.75 (m, 4H); $^{31}P\{^1H\}$ NMR (81.015 MHz, C_6D_6), IR (CH_2Cl_2, ν_{CO}), MS (DCI/NH$_3$) and elemental analysis data have been already reported.[1a]

[(CO)$_3$W(μ,η^5-C$_5$H$_4$PPh$_2$)Ag]$_2$, 6. The same procedure was used with AgBF$_4$ (54 mg, 0.28 mmol) and Li[(η^5-C$_5$H$_4$PPh$_2$)W(CO)$_3$] (**3**), (145 mg, 0.28 mmol) in 30 mL of THF. After filtration and concentration, a yellow powder was isolated. Yield: 53%. Yellow crystals of **6** suitable for an X-ray diffraction study were isolated by slow diffusion of diethyl ether in a saturated dichloromethane solution. ^1H NMR (200 MHz, acetone-d_6): δ 7.80 (m, 8H, *ortho*), 7.64 (m, 12H, *meta* and *para*), 5.92 (br m, 4H, C_5H_4), 5.79 (br m, 4H, C_5H_4); ^1H NMR (400.14 MHz, CD_2Cl_2): δ 7.70–7.62 (m, 8H, *ortho*), 7.58–7.51 (m, 4H, *para*), 7.47–7.41 (m, 8H, *meta*), 5.58 (s, 4H, C_5H_4), 5.54 (s, 4H, C_5H_4); $^{31}P\{^1H\}$ NMR (32.40 MHz, C_6D_6): δ 10.1 (d, $^1J_{P-^{109}Ag}$ = 482 Hz and $^1J_{P-^{107}Ag}$ = 382 Hz); IR (CH_2Cl_2, ν_{CO}): 1935vs, 1850s, 1824vs, 1817sh cm^{-1}. Anal. calcd. for $C_{40}H_{28}O_6P_2W_2Ag_2 \cdot CH_3CN$: C, 39.07; H, 2.42. Found: C, 38.76; H, 2.93.

[(CO)$_3$Cr(μ,η^5-C$_5$H$_4$PPh$_2$)Au]$_2$, 7. One equivalent of AuClPPh$_3$ (0.72 mmol) was added, at room temperature, to an orange solution of Li[(η^5-C$_5$H$_4$PPh$_2$)Cr(CO)$_3$] (**1**), (0.72 mmol) in 25 mL of toluene. After 10 min of stirring, a precipitate was observed. After filtration and concentration, a yellow powder was isolated. Yield: 70%. ^1H NMR (200 MHz, acetone-d_6): δ 7.92 (m, 8H, *ortho*), 7.63 (m, 12H, *meta* and *para*), 5.86 (t, 4H), 5.83 (t, 4H); ^1H NMR (400.14 MHz, CD_2Cl_2): δ 7.74 (br s, 8H, *ortho*), 7.45 (br s, 12H, *meta* and *para*), 5.11 (s, 4H, C_5H_4), 5.02 (s, 4H, C_5H_4); $^{31}P\{^1H\}$ NMR (161.99 MHz, CD_2Cl_2): δ 44.94 (s); IR ($C_6H_5CH_3$, ν_{CO}): 1940vs, 1868s, 1844vs cm^{-1}; MS (DCI/NH$_3$): *m/z* 1164 [MH]$^+$ showing two simulated isotopic patterns at M + 1 and M + 18. Anal. calcd. for $C_{40}H_{28}O_6P_2Mo_2Au_2$: C, 41.26; H, 2.42. Found: C, 41.90; H, 2.57.

[(CO)$_3$Mo(μ,η^5-C$_5$H$_4$PPh$_2$)Au]$_2$, 8. One equivalent of AuClPPh$_3$ (0.53 mmol) was added, at room temperature, to an orange solution of Li[(η^5-C$_5$H$_4$PPh$_2$)Mo(CO)$_3$] (**2**), (0.53 mmol) in 15 mL of toluene. After 10 min of stirring, a precipitate was observed. After filtration and evaporation, yellow crystals of **8** (250 mg) suitable for an X-ray diffraction study were isolated by slow diffusion of diethyl ether in a saturated dichloromethane solution. Yield: 75%. ^1H NMR (200 MHz, acetone-d_6): δ 7.98–7.87 (m, 8H, *ortho*), 7.71–7.57 (m, 12H, *meta* and *para*), 5.86 (t, 4H), 5.83 (t, 4H); ^1H NMR (400.14 MHz, CD_2Cl_2): δ 7.77–7.72 (m, 8H, *ortho*), 7.53–7.49 (m, 4H, *para*), 7.45–7.42 (m, 8H, *meta*), 5.57 (s, 8H, C_5H_4); $^{31}P\{^1H\}$ NMR (81.015 MHz, acetone-d_6): δ 48.5 (s); IR (CH_2Cl_2, ν_{CO}): 1949vs, 1850vs cm^{-1} with two shoulders at higher frequencies; MS (DCI/NH$_3$): *m/z* 1252 [MH]$^+$ showing two simulated isotopic patterns at M + 1 and M + 18. Anal. calcd. for $C_{40}H_{28}O_6P_2Mo_2Au_2$: C, 38.36; H, 2.25. Found: C, 38.20; H, 2.60.

[(CO)$_3$Mo(μ,η^5-C$_5$H$_4$PPh$_2$)$_2$AgAu], 9. This compound has been obtained at room temperature by two different stoichiometric reactions: (*a*) one equivalent of [(CO)$_3$Mo(μ,η^5-C$_5$H$_4$PPh$_2$)Au]$_2$ (**8**) (47 mg, 3.72×10^{-5} mol) was added to a yellow solution of [(CO)$_3$Mo(μ,η^5-C$_5$H$_4$PPh$_2$)Ag]$_2$ (**5**) (40 mg, 3.72×10^{-5} mol) in 20 mL of THF; (*b*) one equivalent of AuClPPh$_3$ (18 mg, 3.72×10^{-5} mol) was added to a yellow solution of [(CO)$_3$Mo(μ,η^5-C$_5$H$_4$PPh$_2$)Ag]$_2$ (**5**), (40 mg, 3.72×10^{-5} mol) in 20 mL of THF. The resulting solutions were stirred for 3 h and then concentrated. In each of the two experiments, a yellow powder of **9** was precipitated, separated by filtration and washed with pentane, Yields: (*a*) 99%, (*b*) 90%. ^1H NMR (200 MHz, acetone-d_6): δ 7.79 (m, 8H, *ortho*), 7.15 (m, 12H, *meta* and *para*), 5.38 (s, 4H), 4.95 (m, 4H); ^1H NMR (400.14 MHz, CD_2Cl_2): δ 7.77–7.70 (m, 8H, *ortho*), 7.53–7.41 (m, 4H, *para*), 7.25–7.17 (m, 8H, *meta*), 5.57–5.54 (br s, 4H, C_5H_4), 4.73 (s, 4H, C_5H_4); $^{31}P\{^1H\}$ NMR (81.015 MHz, C_6D_6): δ 46.6 (s), 1.2 (d with unresolved structure); IR (CH_2Cl_2, ν_{CO}): 1946vs, 1850vs, 1830m cm^{-1}. Anal. calcd. for

$C_{40}H_{28}O_6P_2Mo_2AgAu$: C, 41.30; H, 2.43. Found: C, 41.84; H, 2.76.

References

1 (*a*) B. Brumas, D. de Caro, F. Dahan, M. de Montauzon and R. Poilblanc, *Organometallics*, 1993, 1503; (*b*) I. Lee, F. Dahan and R. Poilblanc, *J. Organomet. Chem.*, 1997, **532**, 159; (*c*) A. I. Philippopoulos, N. Hadjiliadis, C. E. Hart, B. Donnadieu, P. C. McGowan and R. Poilblanc, *Inorg. Chem.*, 1997, **36**, 1842; (*d*) B. Brumas-Soula, F. Dahan and R. Poilblanc, *New J. Chem.*, 1998, **22**, 15.

2 (*a*) R. Uson, A. Laguna, M. Laguna and M. C. Gimens, *J. Chem. Soc.*, *Dalton Trans.*, 1989, 1883; (*b*) J. Devillers, A. Maisonnat and R. Poilblanc, *J. Cluster Sci.*, 1997, **8**, 1.

3 (*a*) C. E. Coffey, J. Lewis and R. S. Nyholm, *J. Chem. Soc.* (*A*), 1964, 1741; (*b*) R. J. Haines, R. S. Nyholm and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 1968, 46; (*c*) P. Hackett and A. R. Manning, *J. Chem. Soc.*, *Chem. Commun*, 1973, 71; (*d*) P. Hackett and A. R. Manning, *J. Chem. Soc.*, *Dalton Trans.*, 1975, 1606.

4 D. de Montauzon, B. Brumas-Soula and R. Poilblanc, unpublished results.

5 (*a*) A. A. Cheremisin and P. V. Shastnev, *J. Magn. Reson.*, 1980, **40**, 459; (*b*) R. K. Harris and B. E. Mann (Ed.), *NMR and Periodic Table*, Academic Press, London, 1978; (*c*) P. Granger and R. K. Harris (Ed.), *Multinuclear Magnetic Resonance in Liquids and Solids*, Reidel, Dordrecht, 1990.

6 (*a*) A. Blagg, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 769; (*b*) S. J. Loeb and G. K. H. Shimizu, *Inorg. Chem.*, 1993, **32**, 1001; (*c*) H. Deng and S. G. Shore, *Organometallics*, 1991, **10**, 3486.

7 (*a*) A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr.*, *Sect. A*, 1968, **24**, 351; (*b*) P. Coppens, L. Leiserowitz and D. Rabinovitch, *Acta Crystallogr.*, 1965, **18**, 1035.

8 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, The Kynoch Press, Birmingham, England, 1974, vol. IV.

9 G. M. Sheldrick, *SHELXS 86. Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, 1986.

10 G. M. Sheldrick, *SHELXS 76. Program for Structure Determination*, University of Cambridge, Cambridge, England, 1976.

11 M. J. Morris, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, 1995, vol. 5, p. 393.

12 (*a*) P. Braunstein, U. Schubert and M. Burgard, *Inorg. Chem.*, 1984, **23**, 4057. (*b*) A. L. Balch, B. C. Noll, M. M. Olmsteadt and D. V. Toronto, *Inorg. Chem.*, 1992, **31**, 5226. (*c*) M. J. Chetenti, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, 1995, vol. 10, p. 23.

13 A Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

14 (*a*) S. R. Pathaneni and G. R. Desiraju *J. Chem. Soc.*, *Dalton Trans.*, 1993, 319; (*b*) A. Grohmann and H. Schmidbaur, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, 1995, vol. 3, p. 1; (*c*) H. Schmidbaur, *Chem. Soc. Rev.*, 1995, 391. (*d*) P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597; (*e*) P. Pyykkö, N. Runeberg and F. Mendizabal, *Chem. Eur. J.*, 1997, **3**, 1451; (*f*) P. Pyykkö and F. Mendizabal, *Chem. Eur. J.*, 1997, **3**, 1458.

15 (*a*) P. S. Pregosin, in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, ed. J. G. Verkade and L. D. Quin, VCH, Weinheim, 1987, pp. 465–557; (*b*) S. S. D. Brown, I. J. Colquhoun, W. McFarlane, M. Murray, I. D. Salter and V. Sik, *J. Chem. Soc.*, *Chem. Commun.*, 1986, 53; (*c*) M. J. Freeman, A. G. Orpen and I. D. Slater, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 379; (*d*) S. S. D. Brown, I. D. Salter, V. Sik, I. J. Colquhoun, W. McFarlane, P. A. Bates, M. B. M. Hursthouse and M. Murray, *J. Chem. Soc.*, *Dalton Trans.*, 1988, 2177; (*e*) S. S. D. Brown, I. D. Salter, D. J. Smith, N. J. Clayden and C. M. Dobson, *J. Organomet. Chem.*, 1991, **408**, 439; (*f*) S. S. D. Brown, I. D. Salter and T. Adiata, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 559 and references cited therein.

16 Such a spin system is typically exemplified by the clusters $[Ag_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ ($n = 1$–6), which show second-order spectra in agreement with significant values of the $^1J_{Ag-Ag}$ and $^2J_{P-Ag}$ coupling constants (respectively in the range of 33–48 and 5–13 Hz), mainly due to the presence of a Ag—Ag bond.[15b]

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18 M. I. Bruce, B. K. Nicholson, O. Bin Shawkataly, J. R. Shapley and T. Henly, *Inorganic Synthesis*, ed. H. D. Koesz, Wiley, New York, 1989, vol. 26, p. 325.

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