Journal of Organometallic Chemistry, 426 (1992) 247–259
Elsevier Sequoia S.A., Lausanne
JOM 22332

Synthesis and evaluation of the catalytic properties of homo- and hetero-bimetallic complexes containing bridging diphenylphosphido ligands

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(Received July 30, 1991)

Abstract

The bimetallic complex $[(CO)_3Ru(\mu\text{-}PPh_2)_2Ru(CO)_3]$ (**1**) has been prepared in 42% yield by the reaction of $[Ru_3(CO)_{12}]$ with tetraphenyldiphosphine in refluxing THF. Other new heterobimetallic complexes containing bridging diphenylphosphido ligands, *e.g.*, $[(CO)_3Ru(\mu\text{-}PPh_2)_2Fe(CO)_3]$ (**2**), $[(CO)_3Ru(\mu\text{-}PPh_2)_2M(CO)_4]$ (**4**: M = Cr; **5**: M = Mo; **6**: M = W) and $[(PPh_3)M'(\mu\text{-}PPh_2)_2M(CO)_4]$ (**7**: M′ = Pd, M = Cr; **8**: M′ = Pd, M = Mo; **10**: M′ = Pt, M = Mo) have been synthesized by the "bridge-assisted" synthetic method. The X-ray structure of $[(PPh_3)Pd(\mu\text{-}PPh_2)_2Mo(CO)_4]$ (**8**) is reported. These complexes, along with $[(CO)_3Fe(\mu\text{-}PPh_2)_2Fe(CO)_3]$, $[(PPh_3)Pd(\mu\text{-}PPh_2)_2W(CO)_4]$, and $[(PPh_3)Pt(\mu\text{-}PPh_2)_2W(CO)_4]$ have been screened as catalyst precursors for (i) the hydroformylation of styrene (120°C, 20 bar, $CO/H_2 = 1$), and (ii) the hydrogenation of cyclohexanone (140°C, 40 bar H_2). The most efficient precursor for the first catalytic reaction was found to be the RuFe complex **2**: a synergistic effect between iron and ruthenium has been observed, the turn-over frequency (TOF) increasing from 0.4 h^{-1} for the RuRu complex **1** and 0.9 h^{-1} for the FeFe complex **3**, to 4.0 h^{-1} for the FeRu compound **2**. The three complexes were recovered at the end of the catalytic reaction. In the catalytic hydrogenation of cyclohexanone, the most active was found to be the RuMo complex **5** but it was not recovered at the end of the reaction.

Introduction

Interest in the use of polynuclear transition-metal complexes in homogeneous catalysis is due in part to their potential to induce unique activity as a result of cooperative interaction between the adjacent metal centres. However, proof of such a cooperative effect is always a challenge as it is difficult to attribute the

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observed activity, if any, to the polymetallic complex itself or to monometallic complexes generated under catalytic reaction conditions [1].

Many efforts have been devoted to increase the stability of the polymetallic framework under the catalytic reaction conditions, with more or less success, using capping ligands such as carbyne [2] or phosphinidene [3], or bridging ligands such as phosphido groups [4]. The latter have the advantage of allowing large metal–metal bond variations, from bonding to non-bonding metal–metal distances [5] but have the disadvantage of being sometimes reactive towards the reactants of the catalytic mixture [4a,6]. For instance, we have recently observed that addition of molecular hydrogen to the cluster $[Ru_3(\mu_3\text{-}\eta^2\text{-PPhpy})(CO)_8(\mu\text{-PPh}_2)]$ [7] promotes the conversion of the bridging diphenyl phosphido group into a terminal PPh_2H ligand, to give $[(\mu\text{-H})Ru_3(\mu_3\text{-}\eta^2\text{-PPhpy})(CO)_8(PPh_2H)]$. Although this reaction shows that stabilization of polynuclear complexes by bridging phosphido groups cannot be taken for granted as soon as the complexes are under a dihydrogen atmosphere, it also shows that bridging phosphido groups may serve as hydrogen reservoir through transient PR_2H intermediates and may help to activate molecular hydrogen heterolytically.

This observation led us to investigate the catalytic activity of some homo- and hetero-binuclear complexes in which the two metal centres are bridged by *two* diphenylphosphido groups. This type of complex has been retained because the synthetic strategy, called "bridge-assisted", is now very well established [8] and can allow several combinations of metal centres. The binuclear complexes we selected for this study are of the types $[(CO)_3M(\mu\text{-PPh}_2)_2M'(CO)_n]$ ($M = M' = Fe$ ($n = 3$); $M = M' = Ru$ ($n = 3$); $M = Ru$, $M' = Cr$, Mo, W ($n = 4$)) and $[PPh_3M(\mu\text{-PPh}_2)_2M'(CO)_4]$ ($M = Pd$, $M' = Cr$, Mo, W; $M = Pt$, $M' = Mo$, W). The catalytic test reactions we used are the hydrogenation of cyclohexanone and the hydroformylation of styrene. This last reaction, requiring a mixture of hydrogen and carbon monoxide, represents severe conditions for testing the stability of these bimetallic systems.

Experimental

All synthetic manipulations were carried out under a dinitrogen atmosphere, using standard Schlenk tube techniques. Tetrahydrofuran used both for the synthesis and the catalytic runs was distilled under argon from sodium benzophenone ketyl just before use. Other solvents were purified following standard procedures, and stored under argon. The following reagent grade chemicals, tetraphenyldiphosphine (Aldrich), n-butyllithium (Aldrich) were used without further purification. Styrene (Aldrich) and cyclohexanone (Aldrich) were distilled trap-to-trap and stored under argon. The complexes $Fe(CO)_3(PPh_2H)_2$ [9], $[\{Ru(CO)_3Cl_2\}_2]$ [10], $[(CO)_3Fe(\mu\text{-PPh}_2)_2Fe(CO)_3]$ [11], $PdCl_2(PPh_3)_2$ [12], $PtCl_2(PPh_3)_2$ [13], $[(PPh_3)Pd(\mu\text{-PPh}_2)_2W(CO)_4]$ [14], and $[(PPh_3)Pt(\mu\text{-PPh}_2)_2W(CO)_4]$ [14], were prepared by published procedures. The complexes $[M(CO)_4(PPh_2H)_2]$ ($M = Cr$, Mo or W) were prepared by the procedure described for the corresponding PPh_3 complexes [15] using 2-ethoxyethanol ($M = Cr$) or diglyme ($M = Mo$ or W) as solvents.

Infrared spectra were recorded in solution using a Perkin–Elmer 225 spectrophotometer with 0.1 mm cells equipped with CaF_2 windows. ^1H and ^{31}P NMR spectra were obtained either with a Bruker WH90 or with a Bruker WM250 spectrometer. ^1H NMR spectra are referenced to tetramethylsilane. ^{31}P NMR spectra are referenced to external 85% H_3PO_4 in D_2O. Microanalyses of C, H, and P elements were carried out by the "Service Central de Microanalyse du CNRS" or by the "Service de Microanalyse du Laboratoire de Chimie de Coordination". Chromatographic separation of the complexes was performed on silica gel columns [Kieselgel 60 (Merck), 70–230 mesh ASTM].

GC analyses of the organic products of the catalytic tests were performed on an Intersmat IGC 120FL flame-ionization detector gas chromatograph, fitted with a 3 m × 1/8 in column (10% Carbowax 20M on Chromosorb W 80/100 mesh) using N_2 as carrier gas. Hexadecane and trimethylbenzene were used as internal standards for the catalytic hydrogenation of cyclohexanone, and for the catalytic hydroformylation of styrene, respectively.

Synthesis of [(CO)$_3$Ru(μ-PPh$_2$)$_2$Ru(CO)$_3$] (1)

A solution of $[Ru_3(CO)_{12}]$ (200 mg, 0.31 mmol) and of tetraphenyldiphosphine (200 mg, 0.54 mmol) in toluene (40 mL) was heated under reflux for 3 h. The initially orange solution turned brown. After cooling, the solution was evaporated to dryness and the residue was chromatographed on silica gel. Elution with a dichloromethane/hexane (1/3) solvent mixture gave two bands. The first one, almost colourless, contained the expected complex **1** while the second one, which was orange, contained several unidentified complexes. The eluate from the first band was evaporated to dryness and the residue was recrystallized from CH_2Cl_2/MeOH to give **1** as pale yellow crystals (160 mg). Spectroscopic and analytical data for compound **1** are given in Table 1.

1 (yield 46%). Found: C, 48.12; H, 2.81. $C_{30}H_{20}O_6P_2Ru_2$ calc.: C, 48.66; H, 2.72%.

Synthesis of [(CO)$_3$Ru(μ-PPh$_2$)$_2$M(CO)$_n$] (2: M = Fe, n = 3; 4: M = Cr, n = 4; 5: M = Mo, n = 4; 6: M = W, n = 4)

A typical experiment for the synthesis of $[(CO)_3Ru(\mu\text{-}PPh_2)_2Fe(CO)_3]$ (**3**) is described below. $Li_2[Fe(CO)_3(PPh_2)_2]$ was generated *in situ* by dropwise addition of n-butyllithium (0.75 mL of a 1.6 *M* solution in hexane, 1.2 mmol) to a stirred

Table 1

Spectroscopic data for compounds $[(CO)_3Ru(\mu\text{-}PPh_2)_2M(CO)_n]$ (**1**, **2** and **4–6**)

	M	*n*	IR [a] (cm^{-1})	^{31}P NMR [b] (ppm) $\delta(\mu\text{-}PPh_2)$	*J*(PW) (Hz)
1 [c]	Ru	3	2068s, 2064m, 2037s, 2008s, 2004m, 1982s, 1974m	109.6	
2	Fe	3	2064s, 2039w, 2021s, 2006m, 1981s, 1968m	125.3	
4	Cr	4	2075w, 2020s, 2010s, 1968m, 1950s, 1935m	226.1	
5	Mo	4	2078w, 2035s, 2012s, 1961s, 1941m	204.0	
6	W	4	2078w, 2033s, 2013s, 1970m, 1953s, 1933m	177.9	163

[a] Methylcyclohexane solutions. [b] $CDCl_3$ solutions. [c] See also Refs. 22a, 23, 24.

solution of [Fe(CO)$_3$(PPh$_2$H)$_2$] (300 mg, 0.59 mmol) in freshly distilled THF (30 mL). After 15 min, the solution was added dropwise *via* a cannula to a stirred solution of [{Ru(CO)$_3$Cl$_2$}$_2$] (150 mg, 0.29 mmol) in THF (15 mL). Stirring was continued for 30 min. The resulting brown solution was evaporated to dryness and the residue was chromatographed on silica gel. Elution with a dichloromethane/heptane (1/8) mixture gave a yellow band. After evaporation of the eluate containing this band, the residue was recrystallized from CH$_2$Cl$_2$/MeOH to give **2** as yellow platelets (170 mg).

The complexes [(CO)$_3$Ru(μ-PPh$_2$)$_2$Cr(CO)$_4$] (**4**), [(CO)$_3$Ru(μ-PPh$_2$)$_2$Mo(CO)$_4$] (**5**) and [(CO)$_3$Ru(μ-PPh$_2$)$_2$W(CO)$_4$] (**6**) were prepared following a similar procedure, using [{Ru(CO)$_3$Cl$_2$}$_2$] and [M(CO)$_n$(PPh$_2$H)$_2$] [M = Cr, Mo, or W (n = 4)] as starting materials. Spectroscopic data for compounds **1**, **2**, **4**, **5** and **6** are gathered in Table 1.

2 · 0.5CH$_2$Cl$_2$ (yield 42%). Anal. Found: C, 49.07; H, 2.60; P, 8.38. C$_{31.5}$H$_{21}$ClFeO$_6$P$_2$Ru calc.: C, 49.65; H, 2.87; P, 8.40%.

4 (yield 28%). Anal. Found: C, 51.67; H, 2.71; P, 8.38. C$_{31}$H$_{20}$CrO$_7$P$_2$Ru calc.: C, 51.75; H, 2.80; P, 8.61%.

5 (yield 44%). Anal. Found: C, 48.74; H, 2.47; P, 7.80. C$_{31}$H$_{20}$MoO$_7$P$_2$Ru calc.: C, 48.77; H, 2.64; P, 8.11%.

6 (yield 53%). Anal. Found: C, 43.44; H, 2.28; P, 6.99. C$_{31}$H$_{20}$O$_7$P$_2$RuW calc.: C, 43.73; H, 2.37; P, 7.28%.

*Synthesis of [(PPh$_3$)M(μ-PPh$_2$)$_2$M'(CO)$_4$] (**7**: M = Pd, M' = Cr; **8**: M = Pd, M' = Mo; **10**: M = Pt, M' = Mo)*

A typical procedure used for the synthesis of [(PPh$_3$)Pd(μ-PPh$_2$)$_2$Cr(CO)$_4$] (**7**) is described below. Li$_2$[Cr(CO)$_4$(PPh$_2$)$_2$] was generated *in situ* by dropwise addition of n-butyllithium (0.8 mL of a 1.6 *M* solution in hexane, 1.3 mmol) to a stirred solution of [Cr(CO)$_4$(PPh$_2$H)$_2$] (300 mg, 0.56 mmol) in freshly distilled THF (20 mL). After 15 min, the solution was then added *via* a cannula to a slurry of

Table 2

Spectroscopic data for compounds [(PPh$_3$)M'(μ-PPh$_2$)$_2$M(CO)$_4$] (**7**–**11**)

	M' M	IR [a] (cm^{-1})	^{31}P NMR [b] (ppm)		J(PP) (Hz)	J(PPt) (Hz)		J(PW) (Hz) μ-PPh$_2$
			δ(PPh$_3$)	δ(μ-PPh$_2$)		PPh$_3$	μ-PPh$_2$	
7	Pd Cr	2018m, 1945m, 1934s	37.9	217.0	24			
8 [c]	Pd Mo	2034m, 1958m, 1938s	43.7	201.4	25			
	minor isomer		44.3	223.3	22			
9 [d]	Pd W	2031m, 1950m, 1931s	35.6	167.3	17			170
10 [c,e]	Pt Mo	2033m, 1956m, 1939s	55.7	208.7	59	5220	2749	
	minor isomer		58.4	232.5	62	5206	2976	
11 [c]	Pt W	2030m, 1949m, 1932s	53.6	180.0	48	5185	2669	152

[a] Methylcyclohexane solutions. [b] CDCl$_3$ solutions. [c] Two isomers are observed in the ^{31}P NMR spectrum. [d] See also Ref. 14. [e] See also Ref. 27.

$[Pd(PPh_3)_2Cl_2]$ (392 mg, 0.56 mmol) in THF (20 mL). Stirring was maintained overnight. The resultant red–orange solution was evaporated to dryness and the residue was chromatographed on silica gel. Elution with a mixture of dichloromethane/heptane (1/8) gave two bands. The first band contained traces of $[Cr(CO)_4(PPh_2H)_2]$ among other complexes, which were not characterized. The second red band contained $[(PPh_3)Pd(\mu\text{-}PPh_2)_2Cr(CO)_4]$ (**7**). The eluate from the second band was evaporated to dryness and the residue was recrystallized from CH_2Cl_2/MeOH to give **7** as red crystals (110 mg).

A similar procedure was used to prepare $[(PPh_3)Pd(\mu\text{-}PPh_2)_2Mo(CO)_4]$ (**8**) and $[(PPh_3)Pt(\mu\text{-}PPh_2)_2Mo(CO)_4]$ (**10**) using $[M(PPh_3)_2Cl_2]$ (M = Pd or Pt) and $[Mo(CO)_4(PPh_2H)_2]$ as starting materials. Spectroscopic data for compounds **7**, **8** and **10** along with those for $[(PPh_3)Pd(\mu\text{-}PPh_2)_2W(CO)_4]$ (**9**) and $[(PPh_3)Pt(\mu\text{-}PPh_2)_2W(CO)_4]$ (**11**) are in Table 2.

7 (yield 22%). Anal. Found: C, 61.44; H, 3.89. $C_{46}H_{35}CrO_4P_3Pd$ calc.: C, 61.18; H, 3.91%.

8 (yield 26%). Anal. Found: C, 58.29; H, 3.72. $C_{46}H_{35}MoO_4P_3Pd$ calc.: C, 58.34; H, 3.73%.

10 (yield 15%). Anal. Found: C, 53.45; H, 3.28. $C_{46}H_{35}MoO_4P_3Pt$ calc.: C, 53.34; H, 3.41%.

Table 3

Experimental data for X-ray study of compound $[(PPh_3)Pd(\mu\text{-}PPh_2)_2Mo(CO)_4]$ (**8**)

Formula	$C_{46}H_{35}O_4P_3MoPd$
F_W(amu)	947.05
a (Å)	11.679(1)
b (Å)	18.779(1)
c (Å)	19.865(2)
β (°)	96.09(1)
V (Å^3)	4332(5)
Z	4
$\rho_{calc.}$ (g cm^{-3})	1.452
Space group	$P2_1/c$
T (°C)	22
Radiation	monochromated graphite, Mo-K_α, λ(Mo-K_{α_1}) = 0.7093 Å
Linear absorption coefficient (cm^{-1})	8.40
Transmission factors [a]	0.930–0.999
Receiving aperture (mm)	3.5×3.5
Take off angle (deg)	4.5
Scan speed, (deg min^{-1})	2
Scan mode	$\omega-2\theta$
Scan range (deg)	0.8 below K_{α_1} to 0.8 above K_{α_2}
2θ limit (deg)	3–50
Unique data used in final refinement, $F_o^2 > 3\sigma(F_o^2)$	6083
Final no. of variables	244
R (on F_o, $F_o^2 > 3\sigma(F_o^2)$) [b]	0.053
R_w (on F_o, $F_o^2 > 3\sigma(F_o^2)$) [c]	0.056
Error in observation of unit weight (e^2)	3.0

[a] Ψ-scan method. [b] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/(\Sigma w|F_o|^2)]^{1/2}$, unit weights.

Table 4

Fractional atomic coordinates, with e.s.d.s in parentheses, for compound **8**

Atom	*x*	*y*	*z*
Pd	0.78060(4)	0.24810(3)	0.40037(3)
Mo	0.85519(5)	0.10978(3)	0.41671(3)
P(1)	0.7185(2)	0.3625(1)	0.39146(9)
P(2)	0.9612(2)	0.2162(1)	0.3804(1)
P(3)	0.6655(2)	0.1625(1)	0.4370(1)
C(1)	0.8028(6)	0.0879(4)	0.3192(4)
O(1)	0.7751(6)	0.0716(4)	0.2650(3)
C(2)	0.9126(9)	0.1292(4)	0.5159(5)
O(2)	0.9458(8)	0.1363(4)	0.5707(4)
C(3)	0.7788(8)	0.0190(5)	0.4413(4)
O(3)	0.7354(7)	−0.0327(4)	0.4540(4)
C(4)	1.0017(7)	0.0564(4)	0.4060(4)
O(4)	1.0834(5)	0.0253(4)	0.3997(4)
C(12)	0.5970(5)	0.4205(4)	0.4942(3)
C(13)	0.5882(5)	0.4434(4)	0.5603(3)
C(14)	0.6850(5)	0.4425(4)	0.6079(3)
C(15)	0.7905(5)	0.4187(4)	0.5895(3)
C(16)	0.7992(5)	0.3958(4)	0.5235(3)
C(11)	0.7024(5)	0.3967(4)	0.4758(3)
C(22)	0.5535(4)	0.4358(2)	0.3023(3)
C(23)	0.4434(4)	0.4450(2)	0.2687(3)
C(24)	0.3565(4)	0.3962(2)	0.2782(3)
C(25)	0.3797(4)	0.3382(2)	0.3214(3)
C(26)	0.4898(4)	0.3290(2)	0.3550(3)
C(21)	0.5766(4)	0.3778(2)	0.3455(3)
C(32)	0.8587(5)	0.4086(3)	0.2964(3)
C(33)	0.9263(5)	0.4577(3)	0.2657(3)
C(34)	0.9428(5)	0.5259(3)	0.2928(3)
C(35)	0.8915(5)	0.5451(3)	0.3505(3)
C(36)	0.8238(5)	0.4960(3)	0.3811(3)
C(31)	0.8074(5)	0.4278(3)	0.3540(3)
C(42)	0.9130(3)	0.2270(3)	0.2415(3)
C(43)	0.9399(3)	0.2339(3)	0.1750(3)
C(44)	1.0547(3)	0.2350(3)	0.1616(3)
C(45)	1.1426(3)	0.2291(3)	0.2145(3)
C(46)	1.1157(3)	0.2222(3)	0.2810(3)
C(41)	1.0009(3)	0.2211(3)	0.2945(3)
C(52)	1.1645(5)	0.2069(2)	0.4710(3)
C(53)	1.2588(5)	0.2364(2)	0.5103(3)
C(54)	1.2760(5)	0.3099(2)	0.5106(3)
C(55)	1.1990(5)	0.3539(2)	0.4716(3)
C(56)	1.1048(5)	0.3245(2)	0.4322(3)
C(51)	1.0875(5)	0.2510(2)	0.4320(3)
C(62)	0.4452(6)	0.0994(4)	0.4126(2)
C(63)	0.3485(6)	0.0782(4)	0.3701(2)
C(64)	0.3431(6)	0.0907(4)	0.3006(2)
C(65)	0.4344(6)	0.1245(4)	0.2737(2)
C(66)	0.5311(6)	0.1457(4)	0.3162(2)
C(61)	0.5365(6)	0.1332(4)	0.3857(2)
C(71)	0.6270(7)	0.1661(4)	0.5234(4)
C(72)	0.6040(8)	0.2296(5)	0.5507(4)
C(73)	0.5792(9)	0.2356(6)	0.6173(5)
C(74)	0.578(1)	0.1794(6)	0.6569(5)
C(75)	0.598(1)	0.1153(7)	0.6314(5)
C(76)	0.625(1)	0.1096(6)	0.5647(5)

Crystallographic studies

Crystals of **8** suitable for X-ray diffraction analysis were obtained through recrystallization from a $CH_2Cl_2/MeOH$ solution at room temperature. Data were collected on an Enraf–Nonius CAD4 diffractometer. Cell constants were obtained by the least-squares refinement of the setting angles of 25 reflections in the range $24° < 2\theta(\text{Mo-}K_{\alpha_1}) < 28°$. The space group was determined by careful examination of systematic extinctions in the listing of the measured reflections. Data reductions were carried out using the SDP crystallographic computing package [16]. Table 3 presents further crystallographic information.

The structure was solved and refined using a combination of the SDP crystallographic computing package [16] and the SHELX-76 package [17]. The position of the Pd, Mo, and P atoms was determined by direct methods. All remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron-density syntheses. Atomic scattering factors were taken from the usual tabulations [18]. Anomalous dispersion terms for Mo, Pd, and P atoms were included in F_c [19]. Empirical absorption correction was applied [20]. The final refinements were conducted using the SHELX-76 program. Ruthenium, phosphorus, oxygen, and carbon atoms (of carbonyl ligands) were allowed to vibrate anisotropically. The carbon atoms of one of the phenyl rings attached to P(3) (C(71) $\cdots$ C(76)) were also allowed to vibrate anisotropically but all the remaining phenyl rings were refined as isotropic rigid groups in order to reduce the number of variable parameters (D_{6h} symmetry, C–C = 1.395 Å). Hydrogen atoms were entered in idealized positions (C–H = 0.97 Å) and held fixed during refinements. Scattering factors for the hydrogen atoms were taken from Stewart *et al.* [21].

Final atomic coordinates for non-hydrogen atoms are given in Table 4. Tables S1, S2, and S3 are available from the authors: Table S1 lists the anisotropic thermal parameters ($Å^2 \times 100$); Table S2 lists the anisotropic thermal parameters ($Å^2 \times 100$); structure amplitudes ($10|F_o|$ *vs.* $10|F_c|$) are in Table S3.

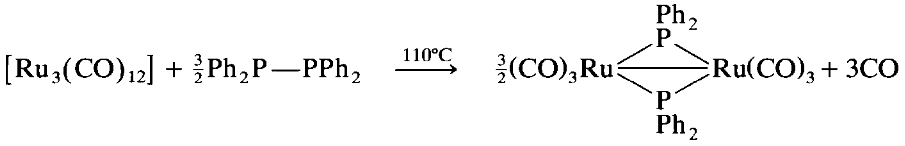
Catalytic runs

All catalytic runs were performed in a 100 mL home-made stainless-steel autoclave equipped with gas and liquid inlets, a heating device, and magnetic stirring. The reactions were carried out in a Teflon vessel fitted to the internal wall of the autoclave, thus preventing undesirable effects due to the metal of the reactor. The starting complex was weighed directly into the Teflon vessel. The autoclave was closed and degassed through three vacuum–argon cycles. A solution of the substrate (cyclohexanone or styrene, 20 mmol) in THF (20 mL) was introduced under argon, and gases (H_2 or H_2/CO) were admitted up to the desired pressure. At the end of each catalytic run, the autoclave was cooled in a cold water bath and slowly vented. A sample of the homogeneous reaction mixture was then analysed by gas chromatography.

Results and discussion

Synthesis and characterization of the bimetallic complexes

The compound $[(CO)_3Ru(\mu\text{-}PPh_2)_2Ru(CO)_3]$ (**1**) has been mentioned several times in the literature as a by-product in the pyrolysis [22] or photolysis [23] of



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Scheme 1.

phosphine-substituted $[Ru_3(CO)_{12}]$ derivatives, or in the dehalogenation of $[RuCl_2(PPh_2Cl)(p\text{-cymene})]$ [24]. To our knowledge, no reaction giving **1** in a reasonable yield has been published so far. The method of preparation we have used is similar to the one previously described for the preparation of $[Ru_2(CO)_6(\mu\text{-}PMe_2)_2]$ [25], *i.e.* by reaction of tetraphenyldiphosphine with $[Ru_3(CO)_{12}]$ (Scheme 1).

Compound **1** produced in this manner was spectroscopically identical (for IR and ^{31}P NMR, see Table 1) with that reported in the literature [22a,23,24]. It was isolated in 46% yield.

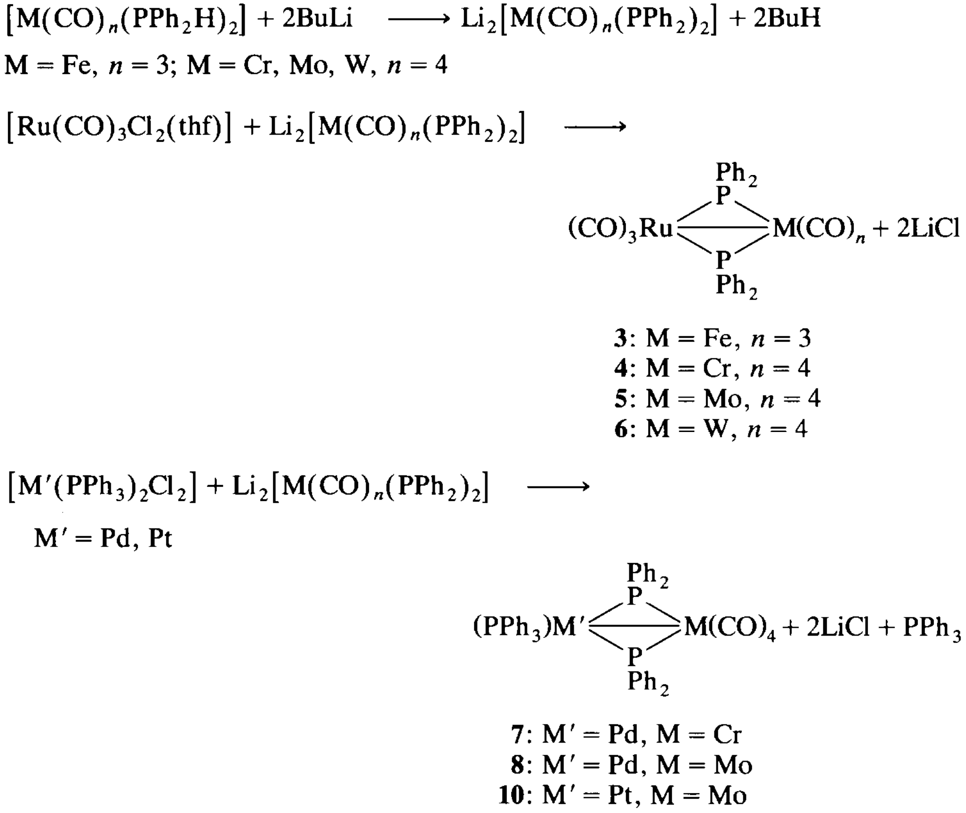
All the other new heterobimetallic complexes, *i.e.* $[(CO)_3Ru(\mu\text{-}PPh_2)_2Fe(CO)_3]$ (**2**), $[(CO)_3Ru(\mu\text{-}PPh_2)_2Cr(CO)_4]$ (**4**), $[(CO)_3Ru(\mu\text{-}PPh_2)_2Mo(CO)_4]$ (**5**), $[(CO)_3Ru(\mu\text{-}PPh_2)_2W(CO)_4]$ (**6**), $[(PPh_3)Pd(\mu\text{-}PPh_2)_2Cr(CO)_4]$ (**7**), $[(PPh_3)Pd(\mu\text{-}PPh_2)_2Mo(CO)_4]$ (**8**), and $[(PPh_3)Pt(\mu\text{-}PPh_2)_2Mo(CO)_4]$ (**10**) were synthesized by the "bridge-assisted" synthetic method [8] (Scheme 2).

Spectroscopic data for all the new complexes, and those for $[(PPh_3)Pd(\mu\text{-}PPh_2)_2W(CO)_4]$ (**9**) and $[(PPh_3)Pt(\mu\text{-}PPh_2)_2W(CO)_4]$ (**11**), which have already been reported by Geoffroy *et al.* [14], are given in Tables 1 and 2.

The complexes **2**–**6** have chemical analysis consistent with the proposed formulae. The IR spectra of compounds **4**–**6** are very similar and show that the compounds have the same symmetry and distribution of carbonyl ligands. The ^{31}P NMR spectra show a single resonance (except for the RuW complex (**6**) in which two additional satellites due to $J(P\text{–}^{183}W)$ are also observed). The chemical shift for each compound is in the range expected for $\mu\text{-}PPh_2$ in binuclear compounds with a metal–metal bond [26]. These observations are consistent with one of the structures shown below, in which the $Ru(\mu\text{-}PPh_2)_2M$ unit is either planar or bent.

For the synthesis of the PdCr (**7**), PdMo (**8**), and PtMo (**10**) complexes, we followed the procedure given by Geoffroy *et al.* for the preparation of $[(PPh_3)Pd(\mu\text{-}PPh_2)_2W(CO)_4]$ (**9**) and $[(PPh_3)Pt(\mu\text{-}PPh_2)_2W(CO)_4]$ (**11**) [14]. For $M = Cr$, $M' = Pt$, the yields of the reaction were too low to even consider the study of the catalytic activity of the resulting dinuclear CrPt complex.

Spectroscopic data for the PdCr complex (**7**) are very similar to those of the PdW (**9**) and the PtW (**11**) complexes, and are consistent with the proposed formula. Although the PdMo (**8**) and the PtMo (**10**) complexes display the same IR spectra as other compounds in the series, their ^{31}P NMR spectra show two sets of phosphorus resonances, suggesting the presence of two isomers in solution, in an approximate ratio of 5/95 for **8**, and 15/85 for **10**. While this work was in progress, Powell *et al.* [27] reported that **10** can also be prepared by refluxing toluene solutions of $[(CO)_4Mo(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)(PPh_2H)]$ for 2 h, and they observed only one compound. Since our reaction conditions were different, we



$$[M(CO)_n(PPh_2H)_2] + 2BuLi \longrightarrow Li_2[M(CO)_n(PPh_2)_2] + 2BuH$$

$M = Fe, n = 3; M = Cr, Mo, W, n = 4$

$$[Ru(CO)_3Cl_2(thf)] + Li_2[M(CO)_n(PPh_2)_2] \longrightarrow (CO)_3Ru(\mu\text{-}PPh_2)_2M(CO)_n + 2LiCl$$

3: M = Fe, $n = 3$
4: M = Cr, $n = 4$
5: M = Mo, $n = 4$
6: M = W, $n = 4$

$$[M'(PPh_3)_2Cl_2] + Li_2[M(CO)_n(PPh_2)_2] \longrightarrow (PPh_3)M'(\mu\text{-}PPh_2)_2M(CO)_4 + 2LiCl + PPh_3$$

M′ = Pd, Pt

7: M′ = Pd, M = Cr
8: M′ = Pd, M = Mo
10: M′ = Pt, M = Mo

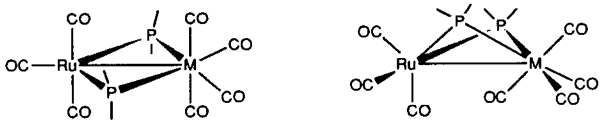
Scheme 2.

tried to heat samples of **8** and **10** we had prepared in refluxing toluene but no change was observed in the ^{31}P NMR spectra, the supposed isomers still being present after heating for 2 h.

Considering the $MM'(PPh_2)_2$ core, compounds such as **8** or **10**, could have, *a priori*, either a butterfly-type structure or a planar structure. Although only one type of crystal was apparent in the solid state, we undertook an X-ray diffraction analysis of **8** with the hope that the structure would differ from that already reported for the related complexes $[(PPh_3)Pt(\mu\text{-}PPh_2)_2W(CO)_4]$ (**11**) [14], $[(PEt_3)Pt(\mu\text{-}PPh_2)_2Mo(CO)_4]$ [27], and $[(PPh_3)Pd(\mu\text{-}PCy_2)_2Mo(CO)_4]$ [28], in which the $MM'(PPh_2)_2$ core is planar.

X-Ray structure of $[(PPh_3)Pd(\mu\text{-}PPh_2)_2Mo(CO)_4]$ (8)

An ORTEP drawing of **8** is shown in Fig. 1 along with the labelling scheme. Bond distances and angles of interest are in Table 5. The $MoPd(\mu\text{-}PPh_2)_2$ core of the



Scheme 3.

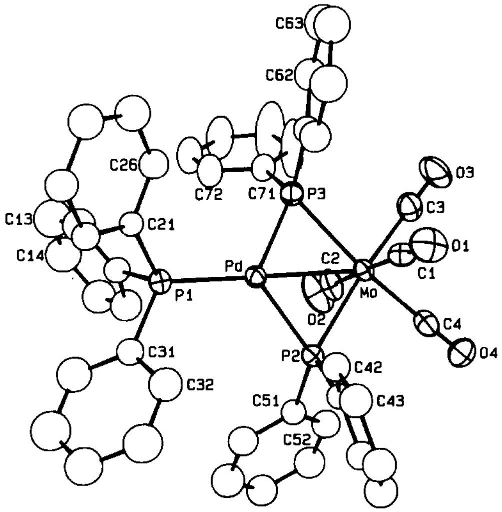


Fig. 1. A perspective view of the complex $[(PPh_3)Pd(\mu\text{-}PPh_2)_2Mo(CO)_4]$ (**8**). The ellipsoids are shown at the 30% probability level.

molecule is essentially planar with a dihedral angle of 178.3(1)° between {Pd–P(2)–Mo} and {Pd–P(3)–Mo} planes. Neglecting the Pd–Mo bond, the molybdenum centre has an octahedral coordination geometry while the palladium centre has a trigonal-planar arrangement of the three phosphorus atoms. The Pd–Mo bond length [2.748(1) Å] is within the range of Pd–Mo bonding distances [26].

In summary, **8** has essentially the same features as $[(PPh_3)Pt(\mu\text{-}PPh_2)_2W(CO)_4]$ (**11**) [14], $[(PEt_3)Pt(\mu\text{-}PPh_2)_2Mo(CO)_4]$ [27], and $[(PPh_3)Pd(\mu\text{-}PCy_2)_2Mo(CO)_4]$

Table 5

Bond distances (Å) and bond angles (deg) of interest for compound $[(PPh_3)Pd(\mu\text{-}PPh_2)_2Mo(CO)_4]$ (**8**), with e.s.d.s in parentheses

Pd–Mo	2.748(1)	Mo–C(2)	2.045(9)
Pd–P(1)	2.269(2)	Mo–C(3)	2.009(9)
Pd–P(2)	2.268(2)	Mo–C(4)	2.014(9)
Pd–P(3)	2.265(2)	C(1)–O(1)	1.13(1)
Mo–P(2)	2.496(2)	C(2)–O(2)	1.13(1)
Mo–P(3)	2.498(2)	C(3)–O(3)	1.14(1)
Mo–C(1)	2.010(8)	C(4)–O(4)	1.14(1)
Mo–Pd–P(1)	177.68(5)	Pd–Mo–C(4)	136.1(2)
Mo–Pd–P(2)	58.77(5)	C(1)–Mo–C(2)	178.0(3)
Mo–Pd–P(3)	58.84(5)	C(1)–Mo–C(3)	87.9(3)
P(1)–Pd–P(2)	122.17(7)	C(1)–Mo–C(4)	88.4(3)
P(1)–Pd–P(3)	120.12(7)	C(2)–Mo–C(3)	91.5(3)
P(2)–Pd–P(3)	117.59(7)	C(2)–Mo–C(4)	89.7(4)
Pd–Mo–P(2)	50.96(5)	C(3)–Mo–C(4)	90.4(3)
Pd–Mo–P(3)	50.88(5)	C(3)–Mo–C(4)	90.4(3)
Pd–Mo–C(1)	91.1(2)	Pd–P(2)–Mo	70.27(6)
Pd–Mo–C(2)	90.7(2)	Pd–P(3)–Mo	70.28(6)
Pd–Mo–C(3)	133.4(3)		

Table 6

Catalytic hydroformylation of styrene

Run[a]	Catalyst precursor	Ratio catalyst/substrate	Yield (%)	Selectivity[b] (%)	TON[c]	TOF[d] (h^{-1})
1	**1** (RuRu)	307	3	60	8.3	0.4
2	**2** (RuFe)	217	42	58	92	4.0
3	**3** (FeFe)	240	9	44	22	0.9
4	$Fe(CO)_3(PPh_2H)_2$	235	10	84	23	1.0
5	**4** (RuCr)	251	2	69	4	0.2
6	**5** (RuMo)	256	2	69	4.8	0.2
7	**6** (RuW)	250	10	69	27	1.2
8	$W(CO)_4(PPh_2H)_2$	222	1	–	2	0.1
9	**7** (PdCr)	260	1	–	2	0.1
10	**8** (PdMo)	265	2	81	4.8	0.2
11	**9** (PdW)	216	15	67	31	1.3
12	**10** (PtMo)	222	1	–	9	0.4
13	**11** (PtW)	198	0	–	–	–

[a] Reactions conditions: 120°C, 20 bar ($CO/H_2 = 1$), 23 h, styrene 10 mmol, 8 mL THF. [b] [branched aldehyde]/([branched aldehyde]+[linear aldehyde]). [c] TON (turnover number) is defined as mol of product per mol of complex. [d] TOF (turnover frequency) is defined as mol of product per mol of complex per hour.

[28]. The reason why we observe two isomers in solution has not yet been elucidated.

Hydroformylation of styrene

The olefin styrene was used to avoid concurrent isomerization of the alkene. The hydroformylation reaction was performed at 120°C under 20 atm of a $CO + H_2$ (1/1) mixture and the reaction was stopped after 23 h. The results are in Table 6. Except for the complex **2** (run 2), the conversion to aldehydes is generally low and in no case was ethylbenzene detected. The most significant result is the comparison of complexes **1**, **2** and **3** (runs 1, 2 and 3), which shows that the heterobimetallic FeRu (**2**) complex is much more active than both the RuRu (**1**) and the FeFe (**3**) complexes, showing a synergistic effect between the two metals. At the end of these catalytic tests, IR analysis showed the presence only of the starting materials **1**, **2** or **3**. The RuM and PdM complexes are more active when M = W than when M = Cr or Mo (runs 5–7 and 9–11), but in no case was the starting material recovered at the end of the reaction, instead $[M(CO)_6]$ compounds are detected. The Pt–M complexes were also destroyed, and they showed only negligible activity (runs 11 and 12). Finally, in every case, the selectivity of the reaction for the formation of the branched aldehyde is poor, rhodium-based systems giving a selectivity better than 80% [29,30]. Moreover, the most active system (run 2), gives the poorest selectivity. This led us to check the activity and selectivity with another olefin, the 1-hexene. Under the same reaction conditions used for styrene, the activity of **2** was poor (1% yield) with a 60% selectivity to linear aldehyde.

To summarize, even though the bimetallic systems studied are poor catalysts for the hydroformylation of styrene, we have shown a synergistic effect between iron and ruthenium, the yield increasing from 3% for the RuRu complex (**1**) and 9% for

Table 7

Hydrogenation of cyclohexanone

Run [a]	Catalyst precursor	Ratio catalyst/substrate	Yield (%)	TON [c]	TOF [d] (h^{-1})
1	**1** (RuRu)	502	41	205	9
2 [b]	**1** (RuRu)	508	14	70	3
3	**2** (RuFe)	525	10	53	1.9
4 [b]	**2** (RuFe)	501	5	25	0.9
5	**3** (FeFe)	500	1	–	–
6 [b]	**3** (FeFe)	500	0	–	–
7	**4** (RuCr)	535	21	112	4.9
8	**5** (RuMo)	545	56	305	13.3
9	**6** (RuW)	480	6	29	1.3
10	**7** (PdCr)	523	0	–	–
11	**8** (PdMo)	523	0	–	–
12	**9** (PdW)	550	0	–	–
13	**10** (PtMo)	580	1	–	–
14	**11** (PtW)	509	0	–	–

[a] Reactions conditions: 140°C, 40 bar H_2, 23 h; cyclohexanone 20 mmol; 20 mL of THF. [b] Same as [a] but at 120°C. [c] As for Table 6. [d] As for Table 6.

the FeFe complex (**3**), to 42% for the FeRu compound (**2**). Furthermore, the occurrence of a synergistic effect seems to be supported by the fact that the three complexes are recovered unchanged at the end of the catalytic runs.

Hydrogenation of cyclohexanone

The reactions were performed under 40 atm of H_2 (room temperature) and at 120 or 140°C depending on the catalyst precursors. The results are in Table 7. The yields of the reaction are rather poor, the best results being observed for the RuRu (**1**) and the RuMo complexes (**5**) at 140°C (runs 1 and 8). In contrast to the hydroformylation reaction, **2** has a lower activity than **1** and increasing the temperature from 120 to 140°C has a more dramatic effect on the yield with **1** than with **2**. At the end of the reaction the IR spectra were unchanged in both cases, but the solution of **1** had turned from pale yellow to pink. Nevertheless, there was no change in the ^{31}P NMR spectrum of **1** and no hydride resonance was observed in the ^{1}H NMR spectrum of the pink solution.

Considering the MRu bimetallic systems, M being a metal of Group 6, the highest activity is observed for M = Mo (run 8) and the lowest activity for M = W (run 9). However, at the end of the reaction the bimetallic complexes were destroyed. The origin of this difference is not clear.

Acknowledgement

We thank the Conseil Régional de Midi-Pyrénées for financial support.

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