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The synthesis and characterisation of a series of linear triphos $\{PhP(CH_2CH_2PPh_2)_2\}$ bridged iron/tungsten or molybdenum bimetallic complexes

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Abstract

The reaction of $[Fe_2(CO)_9]$ with 2 equiv. of $L_{a,b,c}$ $\{L_{a,b,c} = [MX_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}RC_2R')]$ $\{M = W, X = I;$ L_a, $R = R' = Me$; $L_b = R = R' = Ph$; $L_c = R = Me$, $R' = Ph\}$ in CH_2Cl_2 at room temperature gives the bimetallic linear triphos-bridged complexes $[Fe(CO)_4L_{a,b,c}]$ (**1**–**3**) in good yield. Equimolar quantities of [FeI(CO)$_2$Cp or Cp′] and $L_{a,b,c,d,e,f}$ (L_d, $M = Mo$, $X = I$, $R = R' = Me$; L_e, $M = Mo$, $X = I$, $R = R' = Ph$; L_f, $M = W$, $X = Br$, $R = R' = Ph$) react in CH_2Cl_2 at room temperature to afford the cationic phosphine-bridged complexes [Fe(CO)$_2$($L_{a,b,c,d,e,f}$)(Cp or Cp′)]I (for $L_{a,b,c}$, Cp or Cp′; for $L_{d,e,f}$, Cp only) **4**–**12** in good yield. Treatment of $[Fe(CO)_2L_aCp]I$ with 1 equiv. of $Na[BPh_4]$ in CH_2Cl_2 at room temperature yields the iodide exchanged product, $[Fe(CO)_2L_aCp][BPh_4]$ (**13**). Equimolar quantities of $[Fe(CO)_4L_a]$ and L $\{L = CNBu^t$ or $P(OMe)_3\}$ gives the iron-carbonyl substituted products $[Fe(CO)_3LL_a]$ (**14**–**15**) in good yield. Complexes **1**–**15** have been characterised by elemental analysis (C, H and N), IR and ^1H and ^{31}P NMR spectroscopy. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Iron complexes; Tungsten complexes; Alkyne complexes; Bimetallic complexes; Linear triphos-bridged complexes; Carbonyl complexes

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1. Introduction

Since the early reports of the synthesis of trimethylphosphine by Thenard and Hebd [1] in 1847 and triphenylphosphine by Michaelis and Soden [2] in 1885, phosphine donor ligands have played a very significant role in transition metal chemistry over many years [3–5], including homogeneous catalysis [6–10]. In recent years, the development of bi- and multimetallic complexes containing phosphine bridges has flourished [11–27]. Very recent examples of Fe/Cr, Mo and W dppm-bridged $\{dppm = Ph_2P(CH_2)PPh_2\}$ complexes $[CpFe(CO)(\mu\text{-}I)(\mu\text{-}dppm)M(CO)_4]$ (M = Cr, Mo, W) have been reported in 1998 [28]. Up until this paper, no examples of Fe, W or Mo bimetallic complexes containing bridging linear triphos $\{PhP(CH_2CH_2PPh_2)_2\}$ have been reported.

In 1996 [29], we described the synthesis and crystallographic characterisation (for $R = R' = Me$; $R = Me$, $R' = Ph$) of the organotungsten–phosphine ligands, $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}RC_2R')]$ ($R = R' = Me$, Ph; $R = Me$, $R' = Ph$). In this paper we describe the reactions of these organotungsten–phosphine ligands, $L_{a,b,c}\{[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}RC_2R')]$; L_a, $R = R' = Me$; L_b, $R = R' = Ph$; L_c, $R = Me$, $R' = Ph\}$ and the related complexes, $L_{d,e,f}\{[MX_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}RC_2R)]$; L_d, $M = Mo$, $X = I$, $R = Me$; L_e, $M = Mo$, $X = I$, $R = Ph$; L_f, $M = W$, $X = Br$, $R = Ph\}$, which have recently been described [30] with $[Fe_2(CO)_9]$, [FeI(CO)$_2$Cp or Cp′] to give a range of new bimetallic linear triphos-bridged complexes.

2. Experimental

All reactions described in this paper were carried out using standard vacuum/Schlenk line techniques under an atmosphere of dry nitrogen. The starting materials, [FeI(CO)$_2$Cp or Cp′] ($Cp = C_5H_5$; $Cp' = C_5H_4Me$) [31] and $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}RC_2R')]$

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(R = R′ = Me, Ph; R = Me, R′ = Ph) [29] and $[MX_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}RC_2R)]$ (M = Mo, X = I, R = Me or Ph; M = W, X = Br, R = Ph) [30] were prepared by published methods. All other chemicals used were purchased from commercial sources. All solvents used were dried and distilled before use.

Elemental analysis (C, H and N) results were recorded on a Carlo Erba Elemental Analyser MOD 1108, using helium as a carrier gas. The IR spectra were recorded as thin $CHCl_3$ films between NaCl plates on a Perkin–Elmer 1600 series FT IR spectrophotometer. ^1H, ^{31}P and the ^{11}B NMR spectra were recorded on a Bruker AC 250 NMR spectrometer; ^1H NMR spectra are referenced to $SiMe_4$, ^{31}P NMR spectra were referenced to 85% H_3PO_4 and the ^{11}B NMR spectrum to 50% boronic acid. Molecular weight measurements were made using Rast's method [32] using camphor as the solvent.

2.1. Preparation of $[Fe(CO)_4L_c]$ $\{L_c = [WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}MeC_2Ph)]\}$ *(**3**)*

To a solution of $[Fe_2(CO)_9]$ (0.05 g, 0.15 mmol) dissolved in CH_2Cl_2 (30 cm^3) in a Schlenk tube at room temperature (r.t.), $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}MeC_2Ph)]$ (0.32 g, 0.29 mmol) was added and the reaction mixture was stirred for 24 h. The resulting green solution was filtered through Celite and the solvent was removed in vacuo giving a green crystalline powder of $[Fe(CO)_4L_c]$ (**3**), which was recrystallised from CH_2Cl_2/Et_2O. The yield of pure product was 0.27 g, 77%.

Similar reactions of 2 equiv. of L_a or L_b with $[Fe_2(CO)_9]$ in CH_2Cl_2 gave the bimetallic complexes $[Fe(CO)_4(L_a$ or $L_b)]$ (**1**) and **2**. For physical and analytical data see Table 1.

2.2. Preparation of $[Fe(CO)_2L_aCp]I$ $\{L_a = [WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}MeC_2Me)]\}$ *(**4**)*

To a solution of $[FeI(CO)_2Cp]$ (0.14 g, 0.47 mmol) dissolved in CH_2Cl_2 (30 cm^3) in a Schlenk tube in a warm water bath (40°C) $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}MeC_2Me)]$ (0.5 g, 0.47 mmol) was added and the reaction mixture was stirred for 2 h. The resulting green solution was filtered through Celite and the solvent was removed in vacuo giving a green crystalline powder of $[Fe(CO)_2L_aCp]I$ $\{L_a = WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}MeC_2Me)]\}$ (**4**), which was recrystallised from CH_2Cl_2/Et_2O. The yield of pure product was 0.51 g, 81%.

Similar reactions of equimolar quantities of $[FeI(CO)_2(Cp$ or $Cp')]$ ($Cp = C_5H_5$; $Cp' = C_5H_4Me$), and L_a, L_b, L_c, L_d, L_e or L_f (see Section 1 for definition of L_a to L_f; for $L_{a,b,c}$, Cp or Cp′; $L_{d,e,f}$, Cp only) in CH_2Cl_2 gives the bimetallic complexes $[Fe(CO)_2(L_a,L_b,L_c,L_d,L_e$ or $L_f)$ (Cp or Cp′)]I (**5**–**12**). See Table 1 for physical and analytical data.

2.3. Preparation of $[Fe(CO)_2L_aCp][BPh_4]$ *(**13**)*

To a solution of $[Fe(CO)_3L_aCp]I$ (**4**) (0.4 g, 0.25 mmol) in CH_2Cl_2 (30 cm^3), $Na[BPh_4]$ (0.02 g, 0.29 mmol) was added and the solution was stirred for 17 h. The resultant green solution was filtered through Celite and the solvent was removed in vacuo to give the green crystalline powder, $[Fe(CO)_2L_aCp][BPh_4]$ (**13**), which was recrystallised from CH_2Cl_2/Et_2O. The yield of pure product was 0.28 g, 61%.

Table 1
Physical and analytical data [a] for the Fe/W or Mo bimetallic $\{PhP(CH_2CH_2PPh_2)_2\}$-bridged complexes **1**–**15**

Complex no.	Complex	Colour	Yield	Analysis (%) [a]	
				C	H
1	$[Fe(CO)_4L_a]\cdot CH_2Cl_2$	green	84	40.4 (40.4)	3.0 (3.0)
2	$[Fe(CO)_4L_b]$	green	81	47.3 (47.3)	3.6 (3.2)
3	$[Fe(CO)_4L_c]$	green	77	44.3 (44.8)	3.5 (3.2)
4	$[Fe(CO)_2L_aCp]I$	green	81	40.8 (40.7)	3.7 (3.3)
5	$[Fe(CO)_2L_bCp]I$	green	85	45.1 (45.4)	3.4 (3.3)
6	$[Fe(CO)_2L_cCp]I$	green	82	43.3 (43.1)	3.7 (3.3)
7	$[Fe(CO)_2L_dCp]I$	brown	85	44.3 (43.5)	3.7 (3.5)
8	$[Fe(CO)_2L_eCp]I\cdot 0.5CH_2Cl_2$	brown	87	47.3 (47.2)	3.6 (3.4)
9	$[Fe(CO)_2L_fCp]I\cdot CH_2Cl_2$	green	84	46.3 (46.5)	3.5 (3.4)
10	$[Fe(CO)_2L_aCp']I$	brown	86	43.3 (42.9)	3.7 (3.8)
11	$[Fe(CO)_2L_bCp']I$	green	83	47.0 (47.2)	4.1 (3.8)
12	$[Fe(CO)_2L_cCp']I$	green	81	45.1 (45.1)	3.4 (3.9)
13	$[Fe(CO)_2L_aCp][BPh_4]$	green	61	54.5 (54.2)	4.0 (4.2)
14	*trans*-$[Fe(CO)_3(CNBu^t)L_a]$	green	74	42.9 (42.2)	3.8 (3.3)
15	*trans*-$[Fe(CO)_3\{P(OMe)_3\}L_a]$	green	85	42.3 (41.0)	4.0 (3.7)

[a] Calculated values in parentheses.

Table 2
Infrared data[a] for the Fe/W or Mo bimetallic $\{PhP(CH_2CH_2PPh_2)_2\}$-bridged complexes **1**–**15**

Complex	$\nu(C\equiv O)$ (cm^{-1})	$\nu(C\equiv C)$ (cm^{-1})
1	2049(m), 1978(br), 1958(sh)	1589(w)
2	2049(m), 1969(br), 1929(sh)	1658(w)
3	2039(m), 1992(br), 1963(sh)	1589(w)
4	2040(s), 1981(s), 1962(s)	1588(w)
5	2039(s), 1994(s), 1957(s)	1587(w)
6	2039(s), 1994(s), 1956(s)	1587(w)
7	2041(s), 1995(s), 1954(sh)	1601(w)
8	2039(s), 1993(s), 1960(sh)	1573(w)
9	2041(s), 1986(s), 1965(s)	1601(w)
10	2035(s), 1978(sh), 1950(s)	1588(w)
11	2036(s), 1978(br), 1963(s)	1686(w)
12	2035(s), 1988(br), 1955(s)	1601(w)
13	2040(s), 1981(s), 1961(s)	1601(w)
14[b]	1956(s), 1886(m)	1590(w)
15	1961(br), 1883(m)	1589(w)

[a] Spectra obtained in $CHCl_3$ as thin films between NaCl plates; s, strong; m, medium; brs, broad strong; sh, shoulder.

[b] $\nu(C\equiv N) = 2132\ cm^{-1}$.

Table 3
^1H NMR data[a] for the Fe/W or Mo bimetallic $\{PhP(CH_2CH_2PPh_2)_2\}$-bridged complexes **1**–**15**

Complex	^1H NMR data [δ (ppm)]
1	7.8–7.4 (m, 25H, *Ph*); 5.3 (s, 2H, CH_2Cl_2); 3.1 (s, 6H, C_2Me); 2.6–2.4 (m, 8H, CH_2)
2	7.8–7.4 (m, 35H, *Ph*); 2.6–2.4 (m, 8H, CH_2)
3	7.9–7.6 (m, 30H, *Ph*); 3.0 (s, 3H, C_2Me); 2.6–2.4 (m, 8H, CH_2)
4	7.8–7.4 (m, 25H, *Ph*); 4.3 (m, 5H, *Cp*); 3.1 (s, 6H, C_2Me); 2.6–2.4 (m, 8H, CH_2)
5	7.8–7.4 (m, 35H, *Ph*); 4.3 (m, 5H, *Cp*); 2.6–2.4 (m, 8H, CH_2)
6	7.8–7.4 (m, 30H, *Ph*); 4.3 (m, 5H, *Cp*); 3.0 (s, 3H, C_2Me); 2.6–2.4 (m, 8H, CH_2)
7	7.8–7.6 (m, 25H, *Ph*); 4.3 (m, 5H, *Cp*); 3.1 (s, 6H, C_2Me); 2.6–2.4 (m, 8H, CH_2)
8	7.8–7.6 (m, 35H, *Ph*); 5.3 (s, 1H, CH_2Cl_2); 4.3 (s, 5H, *Cp*); 2.7–2.4 (m, 8H, CH_2)
9	7.8–7.4 (m, 35H, Ph); 5.3 (s, 2H, CH_2Cl_2); 4.3 (m, 5H, *Cp*); 3.0 (s, 6H, C_2Me); 2.6–2.4 (m, 8H, CH_2)
10	7.7–7.4 (m, 25H, *Ph*); 4.9, 4.8 (2s, H, *Cp′*); 3.1, 3.0, 2.95, 2.9 (4s, 6H, C_2Me); 2.6–2.4 (m, 8H, CH_2); 1.15 (s, 3H, Cp′–*Me*)
11	7.8–7.4 (m, 35H, *Ph*); 4.95, 4.85 (2s, 4H, *Cp′*); 2.6–2.4 (m, 8H, CH_2); 1.3 (s, 3H, Cp′–*Me*)
12	7.9–7.4 (m, 30H, *Ph*); 4.9, 4.8 (2s, 4H, *Cp′*); 3.1 (s, 3H, C_2Me); 2.7–2.5 (m, 8H, CH_2); 1.0 (s, 3H, Cp′–*Me*)
13	7.7–7.3 (m, 45H, *Ph*); 4.3 (m, 5H, *Cp*); 3.0 (s, 6H, C_2Me); 2.8–2.6 (m, 8H, CH_2)
14	7.9–7.6 (m, 25H, *Ph*); 3.1 (s, 6H, C_2Me); 2.8–2.6 (m, 8H, CH_2); 1.1 (s, 9H, Bu^t)
15	7.8–7.4 (m, 25H, *Ph*); 3.5 (d, 9H, OMe); 3.1 (s, 6H, C_2Me); 2.6–2.4 (m, 8H, CH_2)

[a] Spectra recorded in $CDCl_3$ (+25°C) and referenced to $SiMe_4$; d, doublet; m, multiplet; s, singlet.

2.4. Preparation of $[Fe(CO)_3(CNBu^t)L_a]$ (**14**)

To a solution of $[Fe(CO)_4L_a]$ (**1**) (0.4 g, 0.33 mmol) in CH_2Cl_2 (30 cm^3), $CNBu^t$ (0.03 g, 0.04 ml, 0.33 mmol) was added and the solution was stirred for 30 min. The resultant green solution was filtered through Celite and the solvent was removed in vacuo to give the green crystalline powder $[Fe(CO)_3(CNBu^t)L_a]$ (**14**), which was recrystallised from CH_2Cl_2/Et_2O. The yield of pure product was 0.31 g, 74%.

A similar reaction of $[Fe(CO)_4L_a]$ (**1**) with an equimolar amount of $P(OMe)_3$ in CH_2Cl_2 gives the product $[Fe(CO)_3\{P(OMe)_3\}L_a]$ (**15**). See Table 1 for physical and analytical data.

3. Results and discussion

The molybdenum and tungsten–phosphine starting materials used in this research, namely $[MX_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}RC_2R')]$ ($M = W$, $X = I$, $R = R' = Me$, Ph; $R = Me$, $R' = Ph$ [29]; $M = Mo$, $X = I$, $R = R' = Me$ or Ph; $M = W$, $X = Br$, $R = R' = Ph$ [30]) have been prepared by reacting the bis(alkyne) complexes, $[MX_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ with 1 equiv. of $PhP(CH_2CH_2PPh_2)_2$ in CH_2Cl_2 at r.t. $L_{a,b,c}$ $\{L_{a,b,c} = [WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2 - P,P'\}(\eta^2RC_2R')]$ (L_a, $R = R' = Me$; L_b, $R = R' = Ph$; L_c, $R = Me$, $R' = Ph$) (2 equiv.) with $[Fe_2(CO)_9]$ (1 equiv.) in CH_2Cl_2 at r.t. to afford the bimetallic Fe(0)/W(II) linear triphos-bridged complexes $[Fe(CO)_4L_{a,b,c}]$ (**1**–**3**) in good yield. Complexes **1**–**3** have been characterised by elemental analysis (C, H and N) (Table 1), IR (Table 2) and ^1H and ^{31}P NMR spectroscopy (Tables 3 and 4). Complex **1** was confirmed as a CH_2Cl_2 solvate by repeated elemental analyses and ^1H NMR spectroscopy. Molecular weight studies using Rast's method [32] (Table 5) for complexes **1**–**3** confirm the bimetallic nature of these complexes. FAB mass spectrometry was attempted with these and other complexes described in this paper without success, as no parent ion was observed. Complexes **1**–**3** are soluble in dichloromethane and acetone, less soluble in chloroform, sparingly soluble in methanol and diethyl ether and insoluble in hydrocarbon sol-vents. The IR spectra (Table 2) of **1**–**3** all show the expected bands for the bimetallic complexes. For example, the IR spectrum for **1** shows bands at 2049, 1978 and 1958 cm^{-1}. The bands at 2049 and 1978 cm^{-1} are in similar positions to the complexes $[Fe(CO)_4L]$ $\{L = P(o\text{-tolyl})_3$, $\nu(CO)$, (hexane) = 2043, 1975 and 1947 $cm^{-1}\}$ [33]. The broad band at 1958 cm^{-1} must be due to a combination of the carbonyl group bonded to the tungsten centre in the unit $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2 - P,P'\}(\eta^2 - MeC_2Me)]$, which has $\nu(CO)$ $(CHCl_3) = 1957\ cm^{-1}$, and one band due to $[Fe(CO)_4L_a]$. It would not be expected that

Table 4
$^{31}P\{^1H\}$ NMR data [a] for the Fe/W or Mo bimetallic $\{PhP(CH_2CH_2PPh_2)_2\}$-bridged complexes **1**–**15**

Complex	$^{31}P\ \{^1H\}$ NMR data [δ (ppm)]
1	31.1 (brm, 2P, Fe–*P*Ph$_2$); 22.5 (m, 1P, W–*P*Ph); 20.1 (m, 1P, W–*P*Ph); 3.7 (m, 1P, W–*P*Ph$_2$); −2.3 (m, 1P, J_{W-P} = 220 Hz, W–*P*Ph$_2$
2	30.1 (brm, P, Fe–*P*Ph$_2$); 25.0 (m, 1P, W–*P*Ph); 20.6 (m, 1P, W–*P*Ph); −4.3 (m, 2P, W–*P*Ph$_2$)
3	30.6 (brm, 1P, Fe–*P*Ph$_2$); 23.4 (m, 1P, Fe–*P*Ph); 21.7 (m, 1P, W–PPh); 19.8 (m, 1P, W–*P*Ph); 6.5 (m, 1P, J_{W-P} = 198 Hz, W–PPh$_2$); −0.4 (brm, 1P, W–*P*Ph$_2$)
4	30.3 (brm, 2P, Fe–*P*Ph$_2$); 22.4 (m, 1P, W–*P*Ph); 19.2 (m, 1P, W–*P*Ph); 3.7 (m, 1P, J_{W-P} = 215 Hz, W–*P*Ph$_2$); −2.2 (m, 1P, W–*P*Ph$_2$)
5	30.1 (brm, 2P, Fe–*P*Ph$_2$); 23.3 (m, 1P, W–*P*Ph); 19.6 (m, 1P, W–*P*Ph); 7.0 (m, 1P, W–PPh$_2$); −1.1 (m, 1P, J_{W-P} = 207 Hz, W–*P*Ph$_2$)
6	52.9 (m, 2P, Fe–*P*Ph$_2$); 4.9 (m, 1P, W–*P*Ph); 47.8 (m, 1P, W–*P*Ph); 44.7 (d, 1P, Fe–*P*Ph$_2$); 32.8 (m, 2P, W–*P*Ph$_2$)
7	34.3 (brm, 1P, Fe–*P*Ph$_2$); 31.2 (m, 1P, Fe–*P*Ph$_2$); 19.8 (m, 1P, W–*P*Ph); 14.5 (m, 1P, W–*P*Ph); 4.4 (m, 1P, W–*P*Ph$_2$); −2.5 (m, 1P, W–*P*Ph$_2$)
8	35.2 (m, 1P, Fe–*P*Ph$_2$); 29.8 (m, 1P, W–*P*Ph); 5.2 (m, 1P, W–*P*Ph$_2$)
9	38.9 (m, 2P, Fe–*P*Ph$_2$); 22.7 (m, 1P, W–*P*Ph); 19.5 (m, 1P, W–*P*Ph); 6.7 (m, 1P, W–*P*Ph$_2$); −3.2 (m, 1P, W–*P*Ph$_2$)
10	64.6 (d, 1P, J_{P-P} = 28 Hz, Fe–*P*Ph$_2$); 63.7 (d, 1P, J_{P-P} = 28 Hz, Fe–*P*Ph$_2$); 40.1 (s, 1P, J_{W-P} = 280 Hz, Fe–*P*Ph$_2$); 24.0 (d, 1P, J_{P-P} = 28 Hz, W–*P*Ph); 22.1 (m, 1P, W–*P*Ph); 19.7 (m, 1P, W–*P*Ph); 4.5 (m, 1P, W–*P*Ph$_2$); −2.0 (s, 1P, W–*P*Ph$_2$); −4.4 (s, 1P, W–*P*Ph$_2$)
11	63.8 (m, 2P, Fe–*P*Ph$_2$); 25.7 (brs, 1P, W–*P*Ph); 20.0 (d, 1P, J_{P-P} = 31 Hz, 1P, W–*P*Ph); 7.5 (m, 1P, W–*P*Ph$_2$, J_{W-P} = 197 Hz); −4.3 (m, 2P, W–*P*Ph$_2$)
12	63.6 (m, 2P, Fe–*P*Ph$_2$); 27.0 (s, 1P, W–*P*Ph); 25.8 (s, 1P, W–*P*Ph); 19.6 (m, 1P, W–*P*Ph); 7.5 (m, 1P, W–*P*Ph$_2$, J_{P-P} = 30 Hz); −4.2 (m, 1P, W–*P*Ph$_2$, J_{W-P} = 270 Hz)
13	30.5 (m, 2P, Fe–*P*Ph$_2$); 25.2 (m, 1P, W–*P*Ph); 20.0 (m, 1P, W–*P*Ph); −3.9 (m, 2P, W–*P*Ph$_2$, J_{W-P} = 280 Hz)
14	31.0 (m, 2P, Fe–*P*Ph$_2$); 22.9 (m, 1P, W–*P*Ph); 19.9 (m, 1P, W–*P*Ph); 4.2 (m, 1P, W–*P*Ph$_2$); −2.5 (m, 1P, W–*P*Ph$_2$)
15	75.1 {d, 1P, J_{P-P} = 231 Hz, *trans*-*P*(OMe)$_3$}; 32.6 (d, 1P, J_{P-P} = 231 Hz, Fe–*P*Ph$_2$-*trans*); 31 (m, 1P, Fe–*P*Ph$_2$-*trans*); 24.5 (m, 1P, W–*P*Ph); 13.3 (s, 1P, W–*P*Ph); 4.1 (m, 1P, W–*P*Ph$_2$); −2.6 (m, 1P, W–*P*Ph$_2$)

[a] Spectra obtained in $CDCl_3$ (+25°C) and referenced to 85% H_3PO_4.

the carbonyl group would shift very much when the uncoordinated phosphine in $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}MeC_2Me)]$ becomes attached to the iron centre in **1**. Since the molecular structures of $[Fe(CO)_4L]$ {L = P(*o*-tolyl)$_3$ [33] or PPh$_3$ [34]} have been crystallographically determined and have an almost identical trigonal bipyramidal geometry to the phosphine ligand in the axial position, in view of the similar IR properties of **1**–**3** to $[Fe(CO)_4L]$ [33,34] it is likely the structures of **1**–**3** are as shown in Fig. 1. The reasons for the two isomers comes from the tungsten part of the molecule. The ^{31}P NMR spectra of **1**–**3** did not show a resonance at approximately −13 ppm, which is due to the uncoordinated phosphorus atoms in $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}RC_2R')]$. For example, the ^{31}P NMR spectrum of **1** showed five resonances at δ = 31.1 (brm, 2P, Fe–*P*Ph$_2$); 22.5 (m, 1P, W–PPh); 20.1 (m, 1P, W–*P*Ph); 3.7 (m, 1P, W–*P*Ph$_2$); −2.3 (m, 1P, W–PPh$_2$) ppm. This agrees with the spectrum obtained for $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}MeC_2Me)]$, which had resonances at δ = 23.1 (d, 1P, J_{P-P} = 30 Hz, C_2H_4PPh); 19.5 (d, 1P, J_{P-P} = 30 Hz, C_2H_4PPh); 4.3 (s, 1P, C_2H_4PPh); −2.7 (s, 1P, C_2H_4PPh); −13.7 (m, 2P, $C_2H_4PPh_2$) ppm. The X-ray crystal structure of this complex [29] showed that there were two diastereoisomers in a unit cell, one with the $-CH_2CH_2PPh_2$ (uncoordinated) pointing up, and the other with $-CH_2CH_2PPh_2$ (uncoordinated) pointing down. Several unsuccessful attempts to grow suitable single crystals for X-ray analysis of **1**–**3** were made. However, it is very likely that the structure of the two isomers of **1** are as shown in Fig. 1.

Treatment of $[FeI(CO)_2Cp$ or $Cp']$ ($Cp = C_5H_5$; $Cp' = C_5H_4Me$) with an equimolar amount of $L_{a,b,c,d,e,f}$ $\{[MX_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}RC_2R)]$; L_d, M = Mo, X = I, R = Me; L_e, M = Mo, X = I, R = Ph;

Table 5
Molecular weight studies [a] using Rast's method [32] for the Fe/W or Mo bimetallic $\{PhP(CH_2CH_2PPh_2)_2\}$-bridged complexes **1**–**15**

Complex	Molecular weight [calc. (found)]
1	1349 (1306)
2	1358 (1346)
3	1291 (1285)
4	1365 (1358)
5	1496 (1482)
6	1433 (1421)
7	1293 (1272)
8	1401 (1396)
9	1394 (1386)
10	1435 (1428)
11	1567 (1551)
12	1499 (1491)
13	1611 (1605)
14	1198 (1194)
15	1320 (1318)

[a] Camphor was used as the solvent in these measurements.

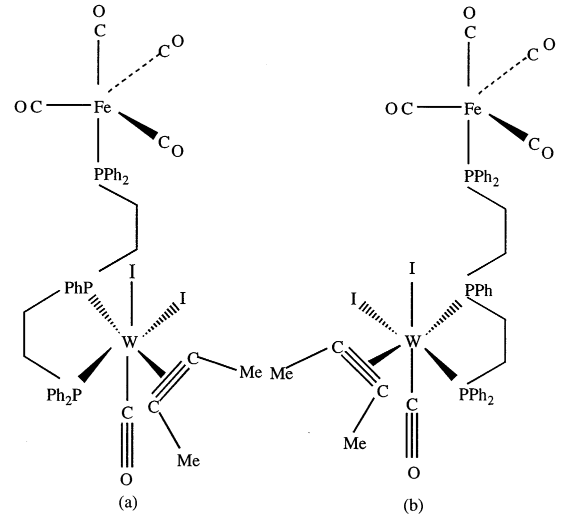

Fig. 1. Proposed structure of the two diastereoisomers of $[Fe(CO)_4L_a]$ (**1**).

L_f, M = W, X = Br, R = Ph} in warm (40°C) CH_2Cl_2 for 2 h gives excellent yields of the cationic bimetallic complexes $[Fe(CO)_2L_{a,b,c,d,e,f}(Cp$ or $Cp')]I$ (**4**–**12**) (for $L_{a,b,c}$, Cp or Cp′; for $L_{d,e,f}$, Cp only) presumably via displacement of the iodide attached to the iron by the uncoordinated phosphorus atom on the linear triphos ligand. The cationic nature of these complexes was established by an iodide exchange reaction. Equimolar quantities of $[Fe(CO)_2L_aCp]I$ (**1**) and $Na[BPh_4]$ react in CH_2Cl_2 at r.t. to give the tetraphenylborate complex $[Fe(CO)_2L_aCp][BPh_4]$ (**13**) in 61% yield. Complexes **4**–**13** have been characterised in the normal manner (see Tables 1–5). Molecular weight studies [32] (Table 5) again suggest the bimetallic nature of these complexes. Complexes **8** and **9** were confirmed as $0.5CH_2Cl_2$ and CH_2Cl_2 solvates, respectively, by repeated elemental analyses and ^1H NMR spectroscopy. Complexes **4**–**9** are more soluble in methanol, MeOH, CH_2Cl_2, $CHCl_3$ and acetone than complexes **1**–**3**, and are similarly insoluble in hydrocarbon solvents. Complex **8** was more soluble in the above solvents than complex **5**. Complexes **10**–**12** were more soluble than complexes **1**–**9**. Complex **13** was sparingly soluble in methanol and less soluble in $CHCl_3$ than complexes **4**–**12**, and was insoluble in CH_2Cl_2 and acetone. Complexes **1**–**13** were stable when stored in the solid state under nitrogen for 2 months, but considerably less stable in solution. The IR spectrum of **4** shows carbonyl resonances at 2040 and 1981 cm^{-1} due to *cis*-carbonyl groups attached to the iron centre, and the band at $\nu(CO) = 1962$ cm^{-1} due to the single carbonyl group on the tungsten centre. The two carbonyl bands due to the iron centre are similar to those found for the related simple phosphine complexes $[Fe(CO)_2(PR_3)Cp]I$. For example, $[Fe(CO)_2(PPh_3)Cp]I$ has carbonyl bands at $\nu(CO)$ $(CHCl_3) =$ 2045 and 1995 cm^{-1} [35]. Again, the band at 1962 cm^{-1} is very similar to that found in $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}MeC_2Me)]$ $\{\nu(CO) = 1957$ $cm^{-1}\}$. Both the ^1H (multiple Cp resonances) and ^{31}P NMR spectra again showed the presence of at least two isomers of most of complexes **4**–**13** due to the two diastereoisomers of the organotungsten phosphine ligand precursor, $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}\text{-}(\eta^2\text{-}MeC_2Me)]$. It is interesting to note that the $^{13}P\{^1H\}$ NMR spectrum for $[Fe(CO)_2L_eCp]I{\cdot}0.5CH_2Cl_2$ (**8**) has just three resonances (see Table 4), and a single resonance for the cyclopentadienyl group in its ^1H NMR spectrum (see Table 3), hence, only one isomer is present in solution for this complex. The J_{W-P} coupling was clearly observed in several complexes, hence, assignment of the spectra was done by comparison with the organometallic ligands $[MX_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}RC_2R)]$ [29,30]. Many attempts were made to grow single crystals of **4**–**13** for X-ray analysis without success. However, the proposed structure of two possible isomers of **4**–**13** is shown in Fig. 2. The ^{11}B NMR spectrum of **13** has a resonance at $\delta = -7$ ppm due to the BPh_4 counterion.

The reaction of equimolar quantities of $[Fe(CO)_4L_a]$ $\{L_a = [WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2$ - $P,P'\}(\eta^2\text{-}MeC_2Me)]\}$ and L {L = $CNBu^t$, or $P(OMe)_3$} in CH_2Cl_2 at r.t. affords the iron tricarbonyl complexes *trans*-$[Fe(CO)_3LL_a]$ (**14**, **15**) in good yield. Complexes **14** and **15** have been fully characterised in the normal manner (see Tables 1–5). Complexes **14** and **15** were more soluble than complexes **1**–**13** in polar solvents, such as $CHCl_3$ and CH_2Cl_2. As observed for other previously described complexes of the types, *trans*-$[Fe(CO)_2L_2]$ [36,37] and $[Fe(CO)_3LL']$ (L,L′ = phosphines and re-

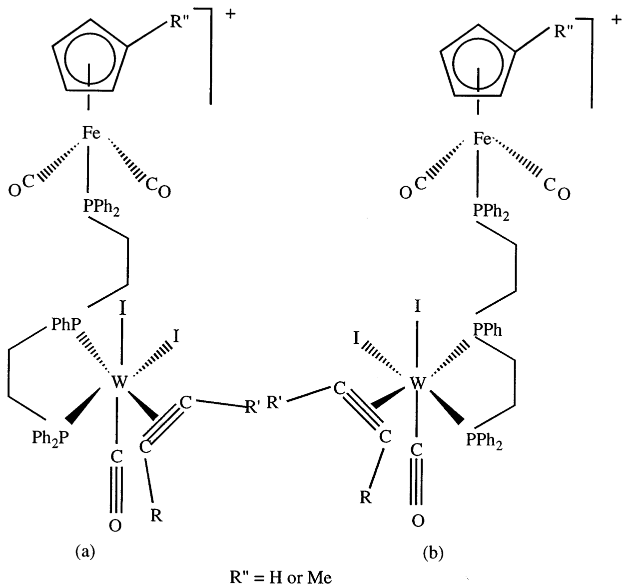

Fig. 2. Proposed structure of two of the diastereoisomers of $[Fe(CO)_2L_{a,b,c,d,e,f}(Cp$ or $Cp')]X$ (**4**–**13**).

lated ligands) have *trans*-geometry with the bulkier phosphine ligands in the axial positions 180° apart. It is very likely that the complexes *trans*-[Fe(CO)$_3$L,L$_a$] have the *trans*-geometry. This is confirmed by the IR spectra of **14** and **15**, which have two carbonyl stretching bands. The iron centre in *trans*-[Fe(CO)$_3$L,L$_a$] has an approximate D_{3h} symmetry if the L$_a$ is free to rotate about the phosphorus atoms attached to the metal. For example, the band at $\nu(CO) = 1886$ cm^{-1} for **14** is due to the Fe(CO)$_3$ unit, and the band at $\nu(CO) = 1956$ cm^{-1} due to the WI$_2$(CO) unit. It should be noted that the IR band for the bis(triphenylphosphine) complex *trans*-[Fe(CO)$_3$(PPh$_3$)$_2$] has a carbonyl band at ν(CO) (CH$_2$Cl$_2$) = 1885 cm^{-1} [37], which conforms with the expected value for complexes **14** and **15**. The *trans*-geometry would be expected on steric grounds. The ^{1}H and ^{31}P{^{1}H} NMR data for **14** and **15** (Tables 3 and 4), as expected, suggest that two isomers are present in solution. The proposed structure of the two possible isomers of **14** and **15** is shown in Fig. 3.

Several unsuccessful attempts were made to oxidise the iron centre with I$_2$ in [Fe(CO)$_4$L$_a$] to give the Fe(II)/W(II) complex, [FeI$_2$(CO)$_3$L$_a$]. The IR spectrum of the reaction products showed only a single band due to L$_a$. Similarly, the reaction of [Fe(CO)$_4$L$_a$] with 1 equiv. of Ag[BF$_4$] in acetonitrile is most likely to give the labile abstracted product, [Fe(CO)$_4${μ^2-[WI(CO)(NCMe){PhP(CH$_2$CH$_2$PPh$_2$)$_2$ - *P,P′,P″*}(η^2 - MeC$_2$Me)]}][BF$_4$], again although a reaction occurred no good elemental analyses and other characterisation of the product was obtained.

In conclusion, we have successfully prepared a range of new bimetallic Fe(0)/Mo(II) or W(II) linear triphos-bridged organometallic complexes, which have been characterised.

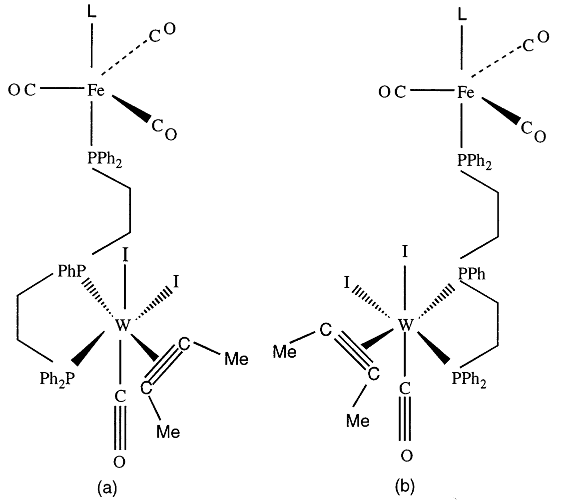

Fig. 3. Proposed structure of the two isomers of *trans*-[Fe(CO)$_3$LL$_a$] {L = CNBu^t (**14**), P(OMe)$_3$ (**15**)}.

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References

[1] P. Thenard, C.R. Hebd, Seances Acad. Ser. C 225 (1847) 892.
[2] A. Michaelis, H.V. Soden, Annalen 229 (1885) 295.
[3] L. Maier, in: L. Maier, G.M. Kosolapoff (Eds.), Organic Phosphorus Compounds, vol. 1, Wiley, New York, 1972, p. 1.
[4] C.A. McAuliffe, W. Levason, Phosphine, Arsine and Stibine Complexes of Transition Elements, Elsevier, Amsterdam, 1979.
[5] F.A. Cotton, B. Hong, Prog. Inorg. Chem. 40 (1992) 179 and refs. therein.
[6] L.H. Pignolet (Ed.), in: Homogeneous Catalysis with Metal Phosphine Complexes, vol. 1, Plenum, New York, 1972, p. 1.
[7] G. Natta, J. Polym. Sci. 16 (1955) 143.
[8] J.F. Young, J.A. Osborn, F.H. Jardine, G. Wilkinson, J. Chem. Soc., Chem. Commun. (1965) 131.
[9] D. Evans, J. Osborn, F.H. Jardine, G. Wilkinson, Nature (Canada) 208 (1965) 1203.
[10] W.S. Knowles, M.J. Sabacky, J. Chem. Soc., Chem. Commun. (1968) 1445.
[11] M.O. Albers, D.C. Liles, D.J. Robertson, E. Singleton, Organometallics 6 (1987) 2179.
[12] K. Pörschke, Y.-H. Tsay, C. Krüger, Inorg. Chem. 25 (1986) 2097.
[13] J.A. Davies, S. Dutremez, A.A. Pinkerton, M. Vilmer, Organometallics 10 (1991) 2956.
[14] L. Manojlović-Muir, K.W. Muir, A.A. Frew, S.S.M. Ling, M.A. Thomson, R.J. Puddephatt, Organometallics 3 (1984) 1637.
[15] Z. Yuan, N.H. Dryden, J.J. Vittal, R.J. Puddephatt, Can. J. Chem. 72 (1994) 1605.
[16] M.L.H. Green, N.M. Walker, J. Chem. Soc., Chem. Commun. (1989) 1865.
[17] T.T. Tadsdi, Y. Huang, D.W. Stephan, Inorg. Chem. 32 (1993) 347.
[18] B. Hessen, F. Van Bolhuis, J.H. Teuben, J.L. Petersen, J. Am. Chem. Soc. 110 (1988) 295.
[19] A.K. Kakker, N.J. Taylor, T.B. Marder, Organometallics 8 (1989) 1765.
[20] A. Del Zotto, A. Mezzetti, V. Novelli, P. Rigo, M. Lanfranchi, A. Tiripicchio, J. Chem. Soc., Dalton Trans. (1990) 1035.
[21] B.F. Hoskins, R.J. Shean, T.W. Turnery, Inorg. Chim. Acta 77 (1983) L69.
[22] F.S. Hassan, D.P. Markham, P.G. Pringle, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1985) 279.
[23] A.T. Hutton, P.G. Pringle, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1985) 1677.
[24] E.W. Stern, P.K. Maples, J. Catal. 27 (1972) 134.
[25] C.T. Hunt, A.L. Balsh, Inorg. Chem. 20 (1981) 2267.
[26] H. Schmidbaur, A. Wohlleben, F. Wagner, D. Orama, G. Huttner, Chem. Ber. 110 (1977) 1748.
[27] A.P. Gaughan, R.F. Ziolo, Z. Dori, Inorg. Chem. 10 (1972) 2776.
[28] M.-A. Hsu, W.-Y. Yeh, M.-Y. Chiang, J. Organomet. Chem. 552 (1998) 135.
[29] P.K. Baker, S.J. Coles, D.E. Evans, M.M. Meehan, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (1996) 3995.
[30] P.K. Baker, M.G.B. Drew, M.M. Meehan, J. Szewczyk, J. Organomet. Chem. 580 (1999) 265.
[31] T.S. Piper, G. Wilkinson, J. Inorg. Nucl. Chem. 3 (1956) 104.

[32] F.G. Mann, B.C. Saunders, Practical Organic Chemistry, Longmans Green, London, 1954, pp. 342–344.
[33] J.A.S. Howell, M.G. Palin, P. McArdle, D. Cunningham, Z. Goldschmidt, H.E. Gottlieb, D.H. Langerman, Inorg. Chem. 32 (1993) 3493.
[34] P.E. Riley, R.E. Davis, Inorg. Chem. 19 (1980) 159.
[35] N.J. Coville, E.A. Darling, A.W. Hearn, P. Johnston, J. Organomet. Chem. 328 (1987) 375.
[36] A.F. Clifford, A.K. Mukherjee, Inorg. Chem. 2 (1963) 151.
[37] P.K. Baker, N.G. Connelly, B.M.R. Jones, J.P. Maher, K. Somers, J. Chem. Soc., Dalton Trans. (1980) 579.