

## Carbonyl complexes of molybdenum and tungsten with anionic chelating donors

### VII \*. Tricarbonylphosphine complexes of molybdenum(0) and tungsten(0) with chelating uninegative (X,Y)-donor ligands (X, Y = S, N, O)

A.E. Sánchez-Peláez and M.F. Perpiñán \*

*Facultad de Ciencias Químicas, Departamento de Química Inorgánica I, Universidad Complutense, 28040 Madrid (Spain)*

(Received July 30th, 1990)

#### Abstract

The reactions of zerovalent tricarbonyl complexes  $M(\text{CO})_3\text{L}_3$  ( $M = \text{Mo}$ ,  $\text{L}_3 = \text{C}_7\text{H}_8$ ,  $3\text{CH}_3\text{CN}$ ,  $3\text{py}$ ;  $M = \text{W}$ ,  $\text{L} = \text{py}$ ) with a series of uninegative chelating (X,Y)-donor ligands (X, Y = xanthates, 2-picolinate, 2-quinaldinate and pyridine-2-thiolate) and trisubstituted phosphines,  $\text{PR}_3$  ( $\text{R} = \text{Ph}$ ,  $2\text{-CH}_2\text{CH}_2\text{CN}$ ) lead to new anionic tricarbonyl complexes *fac*- $[\text{Cat}][\text{M}(\text{X},\text{Y})(\text{CO})_3(\text{PR}_3)]$  ( $\text{Cat}^+ = \text{PPh}_4^+$ ,  $\text{Et}_3\text{NH}^+$ ,  $\text{Et}_4\text{N}^+$ ,  $[\text{Ni}(\text{phen})_3]^{2+}$ ). No products were isolated from reaction of  $\text{M}(\text{CO})_4(\text{PPh}_3)_2$  or  $\text{M}(\text{CO})_3(\text{PPh}_3)_3$  with the (X,Y)-donor ligands. Treatment of the previously reported complexes,  $[\text{Cat}][\text{M}(\text{X},\text{Y})(\text{CO})_4]$ , with  $\text{PPh}_3$  did not give phosphine derivatives. The new compounds have been characterized by IR and  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$ -NMR spectroscopy.

#### Introduction

Several examples of anionic carbonyl complexes of  $\text{Mo}^0$  and  $\text{W}^0$  containing uninegative potentially mono- or bidentate ligands have been reported [1–7]. We have previously investigated the reactions of  $\text{M}(\text{CO})_6$ ,  $\text{M}(\text{CO})_5(\text{Rpy})$  and  $\text{M}(\text{CO})_4\text{L}_2$  ( $M = \text{Mo}$ ,  $\text{W}$ ;  $\text{R} = \text{H}$ ,  $\text{Me}$ ;  $\text{L}_2 = 2 \text{Rpy}$ ,  $\text{bpy}$ ) with uninegative (X,Y)-donor ligands (X, Y = N, S, O, P) [8–10] to give complexes of the type  $[\text{M}(\text{X},\text{Y})(\text{CO})_n]^-$  ( $M = \text{W}$ ,  $n = 5, 4$ ;  $M = \text{Mo}$ ,  $n = 4$ ), in where the (X,Y)-ligand acts as a mono- or bidentate group. We have also studied the reactions of these compounds with Lewis acids as allyl bromide, methyl iodide and  $\text{HgX}_2$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ).

Until now carbonyl complexes with this type of the ligands also containing neutral *N*- or *P*- donor ligands have been practically unknown. The formation of

\* For Part VI see ref. 10.

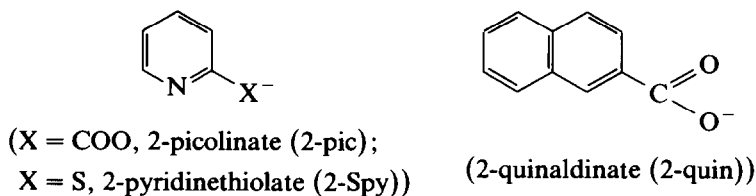


Fig. 1.

the anions  $[M(\beta\text{-diket})(\text{CO})_3\text{L}]^-$  ( $\text{L} =$  phosphine, pyridine or phosphite) in the reaction of  $[M(\beta\text{-diket})(\text{CO})_4]^-$  with the neutral ligand was reported by Doyle [3a]. We also investigated the reactions of  $\text{Mo}(\text{CO})_3(\text{bpy})(\text{py})$  with alkaline xanthates which gave the tetracarbonyl complexes,  $[\text{Mo}(\text{Rxant})(\text{CO})_4]^-$  [8].

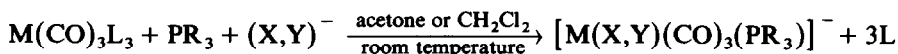
We considered it of interest to try to make new carbonyl derivatives containing the anionic (X,Y)-donors (xanthates:  $\text{ROCS}_2^-$  ( $\text{R} = \text{C}_2\text{H}_5, \text{C}_6\text{H}_{11}$ ),  $\text{R}_2\text{NCS}_2^-$  ( $\text{R} = \text{C}_2\text{H}_5$ ),  $\text{C}_3\text{H}_4\text{NS}$  (2-Spy), 2-picolinate (2-pic), 2-quinaldinate (2-quin)) (see Fig. 1) and phosphine ligands. Three possible routes were studied: i) substitution reactions of CO and/or L by (X,Y)-ligands in the carbonyl complexes:  $\text{Mo}(\text{CO})_4\text{L}_2$  ( $\text{L}_2 = \text{dppe}, 2 \text{ PPh}_3$ ) and  $\text{Mo}(\text{CO})_3(\text{bpy})(\text{PPh}_3)$ ; ii) reactions of the  $[\text{M}(\text{X,Y})(\text{CO})_4]^-$  complexes with phosphine ligands; and iii) reactions of the carbonyl complexes of  $\text{Mo}^0$  and  $\text{W}^0$  containing labile ligands ( $\text{Mo}(\text{CO})_3\text{L}_3$  ( $\text{L}_3 = \text{C}_7\text{H}_8, \text{L} = \text{CH}_3\text{CN}, \text{py}$ );  $\text{W}(\text{CO})_3(\text{Rpy})_3$  ( $\text{R} = \text{H}, \text{Me}$ )) with  $\text{PR}_3$  ( $\text{R} = \text{Ph}, \text{CH}_2\text{CH}_2\text{CN}$ ) and (X,Y)-ligands.

## Results and discussion

The molybdenum(0) carbonyl complexes containing *P*- or *P,P*-donor ligands,  $\text{Mo}(\text{CO})_4\text{dppe}$  and  $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$ , did not react with the anionic (X,Y)-donors under the conditions used, the starting complexes generally being recovered. From the reaction of  $\text{Mo}(\text{CO})_3(\text{bpy})(\text{PPh}_3)$  with alkaline xanthates the previously reported complex,  $\text{Mo}(\text{CO})_2(\text{bpy})(\text{PPh}_3)_2$  [11] was isolated as main product.

The poor CO-labilizing ability of the (X,Y) ligands used is evident from the fact that the  $[\text{M}(\text{X,Y})(\text{CO})_4]^-$  derivatives do not undergo CO ligand exchange with  $\text{PPh}_3$  in acetone solution.

However, the  $\text{M}(\text{CO})_3\text{L}_3$  complexes ( $\text{M} = \text{Mo}, \text{L}_3 = \text{C}_7\text{H}_8, \text{L} = \text{CH}_3\text{CN}, \text{py}$ ;  $\text{M} = \text{W}, \text{L} = \text{Rpy}$ ) were found to react with the salts of the (X,Y)-ligands (or the free ligand in a basic medium) and phosphine at room temperature with replacement of the cycloheptatriene or the neutral N-donor ligand by one uninegative (X,Y)-ligand and one trisubstituted phosphine, to give anionic zerovalent 6-coordinated complexes of the type  $[\text{M}(\text{X,Y})(\text{CO})_3(\text{PR}_3)]^-$ , according to follows equation:



( $\text{R} = \text{Ph}, \text{M} = \text{Mo}, \text{W}, (\text{X,Y}) = \text{S}_2\text{COR}'$ , 2-pic, 2-quin, 2-Spy;  $\text{R} = \text{CH}_2\text{CH}_2\text{CN}, \text{M} = \text{Mo}, \text{W}, (\text{X,Y}) = \text{S}_2\text{COC}_2\text{H}_5, \text{M} = \text{W}, (\text{X,Y}) = 2\text{-pic}$ )

The anionic complexes were isolated as their  $\text{PPh}_4^+$ ,  $\text{Et}_3\text{NH}^+$ ,  $[\text{Ni}(\text{phen})_3]^{2+}$  or  $\text{Et}_4\text{N}^+$  salts.

These new complexes can only be isolated when a solution of the starting carbonyl complex in acetone or  $\text{CH}_2\text{Cl}_2$  is added to a solution or suspension in the

Table 1  
Analytical and infrared data for the new complexes

Compound	Analysis (Found (calc.) (%))				Infrared data (cm <sup>-1</sup> )						
	C	H	N		$\nu(\text{C}\equiv\text{O})$	$\nu(\text{C}-\text{OR})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}-\text{S})$	$\nu_{\text{as}}(\text{OCO})$	$\nu_{\text{sym}}(\text{OCO})$	$\nu(\text{CN})_{\text{CEP}}^a$
[Et <sub>3</sub> N][Mo(S <sub>2</sub> COC <sub>2</sub> H <sub>5</sub> )(CO) <sub>3</sub> (PPh <sub>3</sub> )]	52.9 (53.0)	6.0 (6.1)	2.1 (2.1)		1893, 1780, 1759	1189, 1178	1156	1038			
[PPh <sub>3</sub> ][Mo(S <sub>2</sub> COC <sub>2</sub> H <sub>5</sub> )(CO) <sub>3</sub> (PPh <sub>3</sub> )]	62.9 (63.85)	4.4 (4.5)			1900, 1775, 1763	1190, 1182					2240
[PPh <sub>3</sub> ][Mo(S <sub>2</sub> COC <sub>2</sub> H <sub>5</sub> )(CO) <sub>3</sub> (P(CH <sub>2</sub> CH <sub>2</sub> CN) <sub>3</sub> )]	56.2 (56.3)	4.3 (4.3)	5.0 (5.0)		1901, 1790, 1757	1188		1038			
[PPh <sub>3</sub> ][Mo(S <sub>2</sub> COC <sub>2</sub> H <sub>11</sub> )(CO) <sub>3</sub> (PPh <sub>3</sub> )]	65.0 (65.25)	4.7 (4.8)			1898, 1784, 1755	1200-1178	1145	1047			
[Et <sub>3</sub> NH][Mo(2-pic)(CO) <sub>3</sub> (PPh <sub>3</sub> )]	58.7 (59.4)	5.1 (5.3)	4.1 (4.2)		1902, 1790, 1762				1612, 1584		
[Et <sub>3</sub> NH][Mo(2-quin)(CO) <sub>3</sub> (PPh <sub>3</sub> )]	60.9 (61.8)	5.3 (5.5)	3.7 (3.9)		1898, 1788, 1756				1607		
[PPh <sub>3</sub> ][W(S <sub>2</sub> COC <sub>2</sub> H <sub>5</sub> )(CO) <sub>3</sub> (PPh <sub>3</sub> )]	58.0 (58.2)	4.0 (4.1)			1898, 1782, 1756	1190	1152	1045			
[PPh <sub>3</sub> ][W(S <sub>2</sub> COC <sub>2</sub> H <sub>5</sub> )(CO) <sub>3</sub> (P(CH <sub>2</sub> CH <sub>2</sub> CN) <sub>3</sub> )]	50.6 (50.8)	4.0 (4.1)	4.5 (4.55)		1886, 1783, 1749	1212, 1205		1036			2240
[PPh <sub>3</sub> ][W(2-pic)(CO) <sub>3</sub> (PPh <sub>3</sub> )]	61.0 (61.8)	3.9 (3.95)	1.4 (1.4)		1886, 1772, 1747				1638, 1625	1340	
[Ni(phen) <sub>3</sub> ][W(2-pic)(CO) <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	56.6 (56.8)	3.2 (3.3)	5.85 (5.9)		1886, 1769, 1748				1621		
[PPh <sub>3</sub> ][W(2-pic)(CO) <sub>3</sub> (P(CH <sub>2</sub> CH <sub>2</sub> CN) <sub>3</sub> )]	53.2 (53.4)	3.9 (3.9)	6.0 (6.1)		1890, 1778, 1742				1626	1348	2238
[Et <sub>3</sub> NH][W(2-pic)(CO) <sub>3</sub> (P(CH <sub>2</sub> CH <sub>2</sub> CN) <sub>3</sub> )]	42.0 (42.05)	4.6 (4.7)	10.0 (10.2)		1883, 1770, 1748				1620	1338	2230
[Ni(phen) <sub>3</sub> ][W(2-quin)(CO) <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	58.6 (58.6)	3.5 (3.9)	5.5 (5.6)		1885, 1768, 1747				1622		
[Et <sub>3</sub> NH][W(2-Spy)(CO) <sub>3</sub> (PPh <sub>3</sub> )]	51.7 (51.8)	4.7 (4.7)	3.7 (3.8)		1883, 1771, 1747						
[Et <sub>3</sub> N][W(2-Spy)(CO) <sub>3</sub> (PPh <sub>3</sub> )]	53.0 (53.0)	4.95 (5.0)	3.6 (3.6)		1880, 1760, 1740						

<sup>a</sup> CEP = P(CH<sub>2</sub>CH<sub>2</sub>CN)<sub>3</sub>.

Table 2.  $^1\text{H}$  NMR spectral data for the  $[\text{Cat}][\text{M}(\text{X},\text{Y})(\text{CO})_3(\text{PR}_3)]$  complexes

Compound <sup>a</sup>	$\delta$	$J$	Assignment	
$[\text{Et}_4\text{N}][\text{Mo}(\text{S}_2\text{COC}_2\text{H}_5)(\text{CO})_3(\text{PPh}_3)]$	DMSO- $d_6$	0.93–1.60 (m)	$\text{CH}_3-$	$(\text{Et}_4\text{N}^+ + (\text{X},\text{Y})\text{-ligand})$
		2.87–3.67 (m)	$-\text{CH}_2-$	$(\text{Et}_4\text{N}^+)$
		3.98 (q)	$-\text{CH}_2-$	$((\text{X},\text{Y})\text{-ligand})$
		7.00–8.33 (m)	$\text{H}_{\text{arom.}}$	$(\text{PPh}_3)$
$[\text{PPh}_4][\text{Mo}(\text{S}_2\text{COC}_2\text{H}_5)(\text{CO})_3(\text{PPh}_3)]$	acetone- $d_6$	1.06 (t)	7.20 $\text{CH}_3-$	$((\text{X},\text{Y})\text{-ligand})$
		3.94 (q)	$-\text{CH}_2-$	$((\text{X},\text{Y})\text{-ligand})$
		7.20–8.10 (m)	$\text{H}_{\text{arom.}}$	$(\text{PPh}_4^+)$
$[\text{PPh}_4][\text{Mo}(\text{S}_2\text{COC}_2\text{H}_5)(\text{CO})_3(\text{CEP})]$	acetone- $d_6$	1.31 (t)	7.15 $\text{CH}_3-$	$((\text{X},\text{Y})\text{-ligand})$
		4.42 (q)	$-\text{CH}_2-$	$((\text{X},\text{Y})\text{-ligand})$
		2.20 (m)	$\text{CH}_2-\text{CN}$	(CEP)
		2.80 (m)	$\text{CH}_2-\text{P}$	(CEP)
		7.80–8.06 (m)	$\text{H}_{\text{arom.}}$	$(\text{PPh}_4^+)$
$[\text{PPh}_4][\text{Mo}(\text{S}_2\text{COC}_6\text{H}_{11})(\text{CO})_3(\text{PPh}_3)]$	DMSO- $d_6$	0.80–1.90 (m)	$(\text{CH}_2)$	$((\text{X},\text{Y})\text{-ligand})$
		4.50–4.93 (m)	$>\text{CH}-\text{O}$	$((\text{X},\text{Y})\text{-ligand})$
		7.00–8.33 (m)	$\text{H}_{\text{arom.}}$	$(\text{PPh}_4^+ + \text{PPh}_3)$
	acetone- $d_6$	1.00–2.50 (m)		
		5.10–5.30 (m)		
	7.00–8.30 (m)			
$[\text{Et}_3\text{NH}][\text{Mo}(2\text{-pic})(\text{CO})_3(\text{PPh}_3)]$		1.10 (t)	$\text{CH}_3-$	$(\text{Et}_3\text{NH}^+)$
		2.80 (q)	$-\text{CH}_2-$	$(\text{Et}_3\text{NH}^+)$
		7.00–8.40 (m)	$\text{H}_{\text{arom.}}$	$(\text{PPh}_3 + 2\text{-pic})$
$[\text{Et}_3\text{NH}][\text{Mo}(2\text{-quin})(\text{CO})_3(\text{PPh}_3)]$		1.26 (t)	$\text{CH}_3-$	$(\text{Et}_3\text{NH}^+)$
		3.15 (q)	$-\text{CH}_2-$	$(\text{Et}_3\text{NH}^+)$
		6.70–8.10 (m)	$\text{H}_{\text{arom.}}$	$(\text{PPh}_3 + 2\text{-quin})$
		8.20 (m)	$\text{H}_{\text{arom.}}$	(2-quin)
		8.60 (m)	$\text{H}_{\text{arom.}}$	(2-quin)
		9.20 (m)	$\text{H}_{\text{arom.}}$	(2-quin)
	10.1–10.7 (a)	NH	$(\text{Et}_3\text{NH}^+)$	
$[\text{PPh}_4][\text{W}(\text{S}_2\text{COC}_2\text{H}_5)(\text{CO})_3(\text{PPh}_3)]$	$\text{CDCl}_3$	1.37 (t)	7.15 $\text{CH}_3-$	$((\text{X},\text{Y})\text{-ligand})$
		4.45 (q)	$-\text{CH}_2-$	$((\text{X},\text{Y})\text{-ligand})$
		7.20–7.58 (m)	$\text{H}_{\text{arom.}}$	$(\text{PPh}_3)$
		7.58–7.96 (m)	$\text{H}_{\text{arom.}}$	$(\text{PPh}_4^+)$
$[\text{PPh}_4][\text{W}(\text{S}_2\text{COC}_2\text{H}_5)(\text{CO})_3(\text{CEP})]$	acetone- $d_6$	1.33 (t)	$\text{CH}_3-$	$((\text{X},\text{Y})\text{-ligand})$
		4.43 (q)	$-\text{CH}_2-$	$((\text{X},\text{Y})\text{-ligand})$
		2.30 (m)	$\text{CH}_2-\text{CN}$	(CEP)
		2.85 (m)	$\text{CH}_2-\text{P}$	(CEP)
		7.00–8.10 (m)	$\text{H}_{\text{arom.}}$	$(\text{PPh}_4^+)$
$[\text{PPh}_4][\text{W}(2\text{-pic})(\text{CO})_3(\text{PPh}_3)]$		7.20–8.94 (m)	$\text{H}_{\text{arom.}}$	$(\text{PPh}_4^+, \text{PPh}_3, 2\text{-pic})$
		7.40–7.56 (m)	$\text{H}_{\text{arom.}}$	(2-pic)
		8.06–8.11 (m)	$\text{H}_{\text{arom.}}$	(2-pic)
		8.86–8.94 (m)	$\text{H}_{\text{arom.}}$	(2-pic)
$[\text{Et}_4\text{N}][\text{W}(2\text{-Spy})(\text{CO})_3(\text{PPh}_3)]$	$\text{CDCl}_3$	1.32 (t)	7.00 $\text{CH}_3-$	$(\text{Et}_4\text{N}^+)$
		3.34 (q)	$-\text{CH}_2-$	$(\text{Et}_4\text{N}^+)$
		6.14 (m)	$\text{H}^3$	(2-Spy)
		6.27 (m)	$\text{H}^5$	(2-Spy)
		6.75–6.90 (m)	H	(2-Spy)
		7.10–7.60 (m)	$\text{H}_{\text{arom.}}$	$(\text{PPh}_3)$
		7.62–7.72 (m)	H	(2-Spy)

<sup>a</sup> CEP =  $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ .

Table 3

 $^{13}\text{C}$  NMR spectral data ( $\delta$  (ppm),  $J$  (Hz)) for some of the  $[\text{Cat}][\text{M}(\text{X}, \text{Y})(\text{CO})_3(\text{PPh}_3)]$  complexes <sup>a</sup>

Compound	$\text{PPh}_3^+$		$\text{PPh}_3$		(X,Y)-ligand		CO	
	$\delta$	$J$	$\delta$	$J$	$\delta$	$J$	$\delta$	$J$
$[\text{PPh}_3]_4[\text{Mo}(\text{S}_2\text{COC}_2\text{H}_5)(\text{CO})_3(\text{PPh}_3)]$	118.9 (d)	89.8 (P-C <sub>a</sub> )	127.3 (d)	7.7 (P-C <sub>c</sub> )	13.6 (s) CH <sub>3</sub> -		219.6 (d)	43.5 (CO- <i>trans</i> -P)
	130.3 (d)	12.2 (P-C <sub>b</sub> )	128.4 (d)	0 (P-C <sub>d</sub> )	65.7 (s) -CH <sub>2</sub> -		225.9 (d)	9.2 (CO- <i>cis</i> -P)
	134.4 (d)	10.7 (P-C <sub>c</sub> )	133.5 (d)	12.2 (P-C <sub>b</sub> )	226.3 (s) OCS <sub>2</sub>			
	135.2 (d)	3.0 (P-C <sub>d</sub> )	135.9 (d)	24.4 (P-C <sub>a</sub> )				
$[\text{PPh}_3]_4[\text{Mo}(\text{S}_2\text{COC}_2\text{H}_5)(\text{CO})_3(\text{CEP})]$	118.9 (d)	89.6 (P-C <sub>a</sub> )	13.4 (d)	7.3 (C-C)	14.4 (s) CH <sub>3</sub> -		217.9 (d)	46.5 (CO- <i>trans</i> -P)
	131.4 (d)	13.0 (P-C <sub>b</sub> )	23.6 (d)	10.6 (C-P)	67.2 (s) -CH <sub>2</sub> -		226.2 (d)	9.1 (CO- <i>cis</i> -P)
	135.7 (d)	10.3 (P-C <sub>c</sub> )	120.7 (d)	14.9 (CN)	227.5 (s) OCS <sub>2</sub>			
	136.4 (d)	3.1 (P-C <sub>d</sub> )						
$[\text{PPh}_3]_4[\text{W}(\text{S}_2\text{COC}_2\text{H}_5)(\text{CO})_3(\text{PPh}_3)]$	118.9 (d)	88.8 (P-C <sub>a</sub> )	128.0 (d)	8.4 (P-C <sub>c</sub> )	14.0 (s) CH <sub>3</sub> -		214.6 (d)	43.1 (CO- <i>trans</i> -P)
	131.3 (d)	16.1 (P-C <sub>b</sub> )	129.1 (s)	0 (P-C <sub>d</sub> )	65.5 (s) -CH <sub>2</sub> -		218.5 (d)	6.1 (CO- <i>cis</i> -P)
	135.6 (d)	10.3 (P-C <sub>c</sub> )	135.2 (d)	11.5 (P-C <sub>b</sub> )	227.3 (s) OCS <sub>2</sub>			
	136.3 (d)	2.6 (P-C <sub>d</sub> )	138.0 (d)	29.8 (P-C <sub>a</sub> )				
$[\text{PPh}_3]_4[\text{W}(\text{S}_2\text{COC}_2\text{H}_5)(\text{CO})_3(\text{CEP})]$	118.9 (d)	89.6 (P-C <sub>a</sub> )	13.6 (d)	5.7 (C-C)	14.2 (s) CH <sub>3</sub> -		217.0 (d)	5.7 (CO- <i>cis</i> -P)
	131.3 (d)	12.9 (P-C <sub>b</sub> )	23.8 (d)	15.3 (C-P)	66.7 (s) -CH <sub>2</sub> -		219.5 (d)	27.8 (CO- <i>trans</i> -P)
	135.6 (d)	10.3 (P-C <sub>c</sub> )	120.7 (d)	14.8 (CN)	227.7 (s) OCS <sub>2</sub>			
	136.3 (d)	3.0 (P-C <sub>d</sub> )						

<sup>a</sup> Phosphine  $\delta(J)$ : CEP = 14.2 (20.6) C-CN, 22.3 (15.6) C-P, 120.5 (11.6) C≡N, PPh<sub>3</sub> = 137.2a (12), 133.6b (20), 128.4c (7), 128.5d (0).

Table 4

<sup>31</sup>P NMR spectral data ( $\delta$  (ppm),  $J$  (Hz)) for some of the [Cat][M(X,Y)(CO)<sub>3</sub>(PR<sub>3</sub>)] complexes

Compound	acetone- <i>d</i> <sub>6</sub>		Assign.	CDCl <sub>3</sub>	
	$\delta$	$J$		$\delta$	$J$
[PPh <sub>4</sub> ][Mo(S <sub>2</sub> COC <sub>6</sub> H <sub>11</sub> )(CO) <sub>3</sub> (PPh <sub>3</sub> )]	24.4(s)		PPh <sub>4</sub> <sup>+</sup>		
	26.1(s)		PPh <sub>3</sub>		
[PPh <sub>4</sub> ][Mo(S <sub>2</sub> COC <sub>2</sub> H <sub>5</sub> )(CO) <sub>3</sub> (CEP)]	11.2(s)		CEP		
	24.5(s)		PPh <sub>4</sub> <sup>+</sup>		
[PPh <sub>4</sub> ][W(S <sub>2</sub> COC <sub>2</sub> H <sub>5</sub> )(CO) <sub>3</sub> (PPh <sub>3</sub> )]	24.8(s)		PPh <sub>4</sub> <sup>+</sup>	23.3(s)	
	30.9(s)	205	PPh <sub>3</sub>	29.5(s)	199
[PPh <sub>4</sub> ][W(S <sub>2</sub> COC <sub>2</sub> H <sub>5</sub> )(CO) <sub>3</sub> (CEP)]	11.1(s)	214	CEP		
	24.4(s)		PPh <sub>4</sub> <sup>+</sup>		
[PPh <sub>4</sub> ][W(2-pic)(CO) <sub>3</sub> (PPh <sub>3</sub> )]			PPh <sub>4</sub> <sup>+</sup>	23.3(s)	
			PPh <sub>3</sub>	29.5(s)	243
[PPh <sub>4</sub> ][W(2-pic)(CO) <sub>3</sub> (CEP)]			CEP	12.8(s)	219
			PPh <sub>4</sub> <sup>+</sup>	23.3(s)	
[Et <sub>4</sub> N][W(2-Spy)(CO) <sub>3</sub> (PPh <sub>3</sub> )]			PPh <sub>3</sub>	33.7(s)	194

same solvent containing the PR<sub>3</sub> and the (X,Y)-donor ligand. When the PR<sub>3</sub> is added to a solution of M(CO)<sub>3</sub>L<sub>3</sub> and the (X,Y)-ligand the main product is the [M(X,Y)(CO)<sub>4</sub>]<sup>-</sup> complex. However, if the (X,Y)-ligand is added to the suspension containing the other two reactants, a mixture of M(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>3</sub> and [M(X,Y)(CO)<sub>4</sub>]<sup>-</sup> can be isolated. The relative concentration of the reagents does not dictate the nature of the product, since when a 1/2 molar ratio (M complex/(X,Y) ligand) was used there was no evidence for the formation of the species [M(X,Y)<sub>2</sub>(CO)<sub>*n*</sub>L<sub>*m*</sub>]<sup>2-</sup>.

The [M(S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)(CO)<sub>3</sub>(PR<sub>3</sub>)]<sup>-</sup> derivatives could not be obtained pure.

The new anionic complexes isolated are soluble in polar solvents and behave as 1/1 (PPh<sub>4</sub><sup>+</sup>, Et<sub>3</sub>NH<sup>+</sup> and Et<sub>4</sub>N<sup>+</sup> derivatives) or 2/1 ([Ni(phen)<sub>3</sub>]<sup>2+</sup> derivatives) electrolytes in freshly prepared solutions. They decompose gradually even when stored at low temperature under an inert atmosphere and in the absence of light. The stability is much lower in solution; e.g., [Mo(2-pic)(CO)<sub>3</sub>(PPh<sub>3</sub>)]<sup>-</sup> readily decomposes into *trans*-Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> and MoO(2pic)<sub>2</sub> · 3H<sub>2</sub>O [8] in acetone/diethylether. The substitution of the PPh<sub>3</sub> by a phosphine of lower basicity, such as P(CH<sub>2</sub>CH<sub>2</sub>CN)<sub>3</sub>, does not increase the stability of the tricarbonyl species.

Analytical, infrared, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectral data are summarized in Tables 1-4.

The IR spectra of the [M(X,Y)(CO)<sub>3</sub>(PR<sub>3</sub>)]<sup>-</sup> complexes in the CO stretching region are similar to those of several *fac*-tricarbonyl derivatives [12-14]. Depending on the cation used, small changes in the  $\nu$ (CO) vibrations are observed, this type of behaviour has been previously noted [15]. The values of the  $\nu$ (C-OR) stretching frequencies of xanthate ligands are indicative of a (*S,S*)-chelating coordination of the ligand to a zerovalent metal in an octahedral environment [8,10]. In the [W(2-Spy)(CO)<sub>3</sub>(PR<sub>3</sub>)]<sup>-</sup> complex the deprotonated ligand acts as a (*N,S*)-chelate in spite of its small bite [10,16] to form a four membered ring similar to that formed by the xanthate ligands. A (*N,O*)-bidentate coordination such as was previously described for 2-pic and 2-quin [9,17,18] is suggested for these tricarbonyl complexes.

The  $^1\text{H-NMR}$  spectra (see Table 2) of the new complexes are consistent with the proposed formulae. The  $^{13}\text{C-}$  and  $^{31}\text{P-NMR}$  spectra of only a selection of products were recorded owing to their low stability in solution. These spectra are consistent with the presence in solution, as in solid state, of the *facial* isomer, although sometimes traces of the *meridional* isomer are also detected.

The assignments of the carbon resonances are based on the intensity ratios and the magnitude of the phosphorus coupling constant, in a manner consistent with assignments for other carbonyl derivatives [7,14,19,20]. The anionic carbonyl complexes possess two different types of carbonyl ligands whose signals couple to the phosphorus-31 nucleus. However, no coupling to  $^{183}\text{W}$  nucleus is observed. The resonance with  $^2J(\text{C-P}) = 4.5\text{--}9.2$  Hz is assigned to the two CO groups *cis* to  $\text{PR}_3$ , and the signal with  $^2J(\text{C-P}) = 27.8\text{--}43.5$  Hz is due to the CO group *trans* to the phosphine ligand. The  $^{13}\text{C-NMR}$  spectrum for  $[\text{PPh}_4][\text{Mo}(\text{S}_2\text{COC}_2\text{H}_5)(\text{CO})_3(\text{PPh}_3)]$  shows an additional peak at 224.1 ppm ( $J = 4.5$  Hz) but we suspect that this arises from an impurity even though there is nothing in the other data to suggest this.

As expected, the  $\delta(\text{CO})$  values are higher for the molybdenum complexes than for the analogous tungsten derivatives owing to the more basic character of tungsten.

The  $^2J(\text{C-P})$  coupling constant data presented in Table 3 show several features of interest. First, the magnitude of the *cis* and *trans*  $^2J(\text{C-P})$  coupling increases in the order  $\text{Mo} > \text{W}$ . Second, the *trans* coupling constant is significantly larger than the *cis* coupling constant; the presence of both types of coupling confirms the presence of the *fac*- $[\text{M}(\text{X},\text{Y})(\text{CO})_3(\text{PR}_3)]^-$  complexes. Third, it appears that the absolute magnitude of both coupling constants increases with the increasing electronegativity of the substituents on phosphorus, as noted previously [19,20].

The signal at lowest field can be assigned to carbon atom of the  $\text{OCS}_2$  group of the xanthate ligand.

The  $^{31}\text{P}$  NMR spectra contain one signal for the coordinated phosphine, which for the tungsten derivatives show coupling to  $^{183}\text{W}$  nucleus, with  $^1J(\text{W-P}) = 194\text{--}243$  Hz. These values for coupling constants are similar to those found for other carbonylphosphine complexes of tungsten(0) [13]. When the cation is  $[\text{PPh}_4]^+$  there is also a singlet signal at  $\delta = 24.4$  ppm (in acetone- $d_6$ ) or 23.3 ppm (in  $\text{CDCl}_3$ ). Sometimes the presence of free phosphine can be observed, owing to low stability in solution of these tricarbonyl species. A very weak resonance at lower field ( $\delta > 34$  ppm), can be assigned to the presence in the solution of traces of the *meridional*-isomer.

## Experimental

All manipulations were performed under oxygen-free dry nitrogen. Analytical grade solvents were used.

**Reagents.** The  $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$ ,  $\text{Mo}(\text{CO})_3(\text{C}_7\text{H}_8)$ ,  $\text{M}(\text{CO})_3(\text{py})_3$  ( $\text{M} = \text{Mo}$ ,  $\text{W}$ ) and  $[\text{Ni}(\text{phen})_3]\text{Cl}_2$  complexes were prepared as previously described [21–25], as were sodium cyclohexylxanthate and potassium 2-picolinate [26,9]. Molybdenum and tungsten hexacarbonyl, potassium ethylxanthate, pyridine-2-thiol and 2-picolinic or 2-quinaldinic acids were used as purchased.

**Analysis and physical measurements.** C,H,N analyses were carried out by Elemental Micro-Analysis Ltd. Laboratories, Amberley, Bearworthy, (Devon, UK).

Infrared spectra in the 4000–200  $\text{cm}^{-1}$  region were recorded on a Perkin–Elmer 100 spectrophotometer, with KBr disks. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Varian VXR-300 spectrometer operating in the FT mode, and chemical shifts are relative to  $\text{Me}_4\text{Si}$  for  $^1\text{H}$  and  $^{13}\text{C}$ , and to 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$  spectra in deuterodimethylsulphoxide, deuteriochloroform or deuterioacetone solutions.

*Preparation of complexes.* Due to the difficulty to isolate these complexes as solids, yields are very dependent on the work-up procedure used, and can vary from 50 to 80%.

*[Cat][Mo(S<sub>2</sub>COR)(CO)<sub>3</sub>(PR'<sub>3</sub>)] complexes* ( $R = \text{C}_2\text{H}_5$ ,  $R' = \text{Ph}$ ,  $\text{Cat}^+ = \text{PPh}_4$ ,  $\text{Et}_4\text{N}$ ;  $R' = \text{CH}_2\text{CH}_2\text{CN}$ ,  $\text{Cat}^+ = \text{PPh}_4$ ;  $R = \text{C}_6\text{H}_{11}$ ,  $R' = \text{Ph}$ ,  $\text{Cat}^+ = \text{PPh}_4$ )

A solution of  $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$ ,  $\text{Mo}(\text{CO})_3(\text{C}_7\text{H}_8)$  or  $\text{Mo}(\text{CO})_3(\text{py})_3$  (1 mmol) in acetone was added with stirring to a solution of  $\text{PR}'_3$  (1 mmol) and the salt of the xanthate (1 mmol) in acetone. The solution was stirred until a colour change was observed and  $\text{PPh}_4\text{Br}$  or  $\text{Et}_4\text{NCl}$  (1 mmol) was then added. After some minutes stirring the mixture was filtered through Celite. Addition of cold diethyl ether gave an orange solid, which was filtered off, washed with n-hexane and dried *in vacuo*.

*[Et<sub>3</sub>NH][Mo(N,O)(CO)<sub>3</sub>(PPh<sub>3</sub>)] complexes* ( $\text{N}$ ,  $\text{O} = 2\text{-pic}$ ,  $2\text{-quin}$ )

$\text{Mo}(\text{CO})_3(\text{C}_7\text{H}_8)$  (1 mmol) was added to a stirred suspension of equimolecular amounts of the picolinic or quinaldinic acid,  $\text{PPh}_3$  and  $\text{Et}_3\text{N}$  in  $\text{CH}_2\text{Cl}_2$ . After 20 min (2-pic<sup>-</sup>) or 5 min (2-quin<sup>-</sup>) stirring a few ml of cold diethyl ether were added and the mixture was filtered. The solvent was removed under reduced pressure and the residual oil was crystallized as a orange (2-pic) or deep red (2-quin) solid by addition of cold diethyl ether and vigorous stirring.

*[PPh<sub>4</sub>][W(S<sub>2</sub>COC<sub>2</sub>H<sub>5</sub>)(CO)<sub>3</sub>(P(CH<sub>2</sub>CH<sub>2</sub>CN)<sub>3</sub>)] complex*

A solution of  $\text{W}(\text{CO})_3(\text{Rpy})_3$  (0.4 mmol) in acetone was added to a stirred suspension of  $\text{KS}_2\text{COC}_2\text{H}_5$  (0.4 mmol) and  $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$  (0.4 mmol) in the same solvent. The mixture was stirred for 1 h and 20 min and an equimolecular quantity of  $\text{PPh}_4\text{Br}$  and several drops of cold diethyl ether were added. The solution was filtered then treated with diethyl ether to give an oil. The supernatant solution was decanted off and the residual oil was dissolved in acetone and the solution filtered through Celite. The solvent was removed under reduced pressure and the residual oil was crystallized as described above.

*[PPh<sub>4</sub>][W(S<sub>2</sub>COC<sub>2</sub>H<sub>5</sub>)(CO)<sub>3</sub>(PPh<sub>3</sub>)] complex*

The procedure was similar to that described for  $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$  derivative, but the initial filtrate was treated with diethyl ether to give an orange solid, which was filtered off, washed with the same solvent, and dried *in vacuo*.

*[PPh<sub>4</sub>][W(2-pic)(CO)<sub>3</sub>(PPh<sub>3</sub>)] complex*

A solution of  $\text{W}(\text{CO})_3(\text{Rpy})_3$  (0.4 mmol) in 20 ml of acetone was added to a stirred suspension of equimolecular amounts of  $\text{PPh}_3$ , 2-picH acid and  $\text{KOH}$  in 5 ml of ethanol. The mixture was stirred for 15 min and then evaporated to dryness under reduced pressure. The residual oil was dissolved in acetone and the solution filtered through Celite then treated with  $\text{PPh}_4\text{Br}$  (0.4 mmol) and 3 ml of diethyl



ether. The mixture was stirred for 1 or 2 min then filtered. Addition of diethyl ether gave a reddish-brown solid, which was filtered off, washed with diethyl ether, and dried *in vacuo*.

*[Ni(phen)<sub>3</sub>][W(N,O)(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> complexes (N,O = 2-pic, 2-quin)*

A solution of W(CO)<sub>3</sub>(Rpy)<sub>3</sub> (0.2 mmol) in acetone (10 ml) was added to a suspension of PPh<sub>3</sub> (0.2 mmol) and potassium 2-picolinate (0.2 mmol) in acetone (10 ml) with stirring. After ca. 10 min, the mixture was filtered and a solution of [Ni(phen)<sub>3</sub>]<sup>2+</sup> (0.1 mmol) in 20 ml of distilled, degassed water was added. The addition of more distilled water gave a brown (2-pic) or deep red (2-quin) solid which was filtered off, washed with diethyl ether, and dried *in vacuo*.

*[Cat][W(X,Y)(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>3</sub> complexes (X,Y = 2-pic, R = CH<sub>2</sub>CH<sub>2</sub>CN, Cat<sup>+</sup> = PPh<sub>4</sub>, Et<sub>3</sub>NH; X,Y = 2-Spy, R = Ph, Cat<sup>+</sup> = Et<sub>3</sub>NH, Et<sub>4</sub>N)*

A solution of W(CO)<sub>3</sub>(Rpy)<sub>3</sub> (0.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was added to a suspension of equimolecular amounts of 2-picH or 2-SpyH and Et<sub>3</sub>N. Stirring was continued for 1 h (2-pic) or 15 min (2-Spy), and then PPh<sub>4</sub>Br (0.4 mmol) (when Cat<sup>+</sup> = PPh<sub>4</sub>) and a few ml of diethyl ether were added. The solution was filtered and addition of cold diethyl ether gave an oil. The supernatant solution was decanted and the oily residue was dissolved in acetone, filtered, and precipitated as an orange solid by addition of cold n-hexane. The compound was filtered off, washed with n-hexane and dried *in vacuo*.

## Acknowledgements

Financial support for this work from Comisión Interministerial de Investigación is gratefully acknowledged (Projet PS87-0028). We thank D. J.A. Campo for recording the NMR spectra.

## References

- 1 (a) S. Trofimenko, *J. Am. Chem. Soc.*, 91 (1969) 588; (b) S. Trofimenko, *Inorg. Chem.*, 9 (1970) 2493.
- 2 G.H. Barnett, M.K. Cooper, M. McPartlin and G.B. Robertson, *J. Chem. Soc., Dalton Trans.*, (1978) 587.
- 3 (a) G. Doyle, *J. Organomet. Chem.*, 61 (1973) 235; (b) *idem, ibid.*, 84 (1975) 323; (c) *idem, ibid.*, 101 (1975) 85.
- 4 D. Sellmann and J. Schwarz, *J. Organomet. Chem.*, 241 (1983) 343.
- 5 M.R. Houchin and K. Mitsios, *Inorg. Chim. Acta*, 64 (1982) L 147.
- 6 E.C. Alyea and A. Somogyvari, *Inorg. Chim. Acta*, 83 (1984) L49.
- 7 D.J. Darensbourg, K.M. Sanchez, J.H. Reibenspies and A.L. Rheingold, *J. Am. Chem. Soc.*, 111 (1989) 7094.
- 8 A.E. Sánchez-Peláez, M.F. Perpiñán and A. Santos, *J. Organomet. Chem.*, 296 (1985) 367.
- 9 J.A. Campo, M. Cano, M.F. Perpiñán and A.E. Sánchez-Peláez, *J. Organomet. Chem.*, 345 (1988) 299.
- 10 A.E. Sánchez-Peláez, M.F. Perpiñán, E. Gutiérrez-Puebla, A. Monge and C. Ruiz-Valero, *J. Organomet. Chem.*, 384 (1990) 79.
- 11 H. Friedel, I.W. Renk and H. tom Dieck, *J. Organomet. Chem.*, 26 (1971) 247.
- 12 R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim.*, (1962) 1301.
- 13 M.K. Cooper, P.A. Dunkworth, K. Henrick and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, (1981) 2357.
- 14 D.J. Darensbourg, K.M. Sanchez and J. Reibenspies, *Inorg. Chem.*, 27 (1988) 3636.
- 15 H. Behrens, E. Linder and G. Lehner, *J. Organomet. Chem.*, 22 (1970) 665.

- 16 S.G. Rosenfield, S.A. Swedberg, S.K. Aora and P.K. Mascharak, *Inorg. Chem.*, 25 (1986) 2109.
- 17 T.E. Dorsett and R.A. Walton, *J. Chem. Soc., Dalton Trans.*, (1976) 347.
- 18 M.F. Perpiñán, L. Ballester, A. Santos, A. Monge, C. Ruiz-Valero and E. Gutiérrez-Puebla, *Polyhedron*, 6 (1987) 1523.
- 19 G.M. Bodner, *Inorg. Chem.*, 14 (1975) 2694.
- 20 G.M. Bodner, M.P. May and L.E. McKinney, *Inorg. Chem.*, 19 (1980) 1951.
- 21 D.P. Tate, W.R. Knipple and J.M. Angle, *Inorg. Chem.*, 1 (1962) 433.
- 22 A. Pidcock and B.W. Taylor, *J. Chem. Soc. (A)*, (1967) 878.
- 23 W. Hieber and F. Mühlbauer, *Z. Anorg. Allg. Chem.*, 221 (1935) 337.
- 24 L. Westland and N. Muriithi, *Inorg. Chem.*, 12 (1973) 10.
- 25 R.B. Petersem, J.A. Ragosta, G.E. Whitwell and J.M. Burlitch, *Inorg. Chem.*, 22 (1983) 325.
- 26 G. Bulmer and F.G. Hansm, *J. Chem. Soc.*, (1945) 666.