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SHORT PAPER

Iridium carbonyl clusters with pyridylphosphines: $[Ir_4(CO)_9(PPh_xpyl_{3-x})_3]$

K Wajda-Hermanowicz, M Koralewicz and F P Pruchnik
Institute of Chemistry, University of Wrocław, 14 Joliot-Curie, 50 383 Wrocław, Poland

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$[Ir_4(CO)_9(PR_3)_3]$ type complexes were obtained in the reaction between $Ir_4(CO)_{12}$ and the 2-pyridylphosphines: diphenyl(2-pyridyl)phosphine (PPh_2pyl), phenylbis(2-pyridyl)phosphine ($PPhpyl_2$), tris-(2-pyridyl)phosphine ($Ppyl_3$) (pyl = 2-pyridyl) in methanol in basic medium, in the presence of carbon monoxide. The reaction conditions were determined and the products were spectroscopically characterized.

Keywords: Iridium, carbonyl clusters, pyridylphosphines, catalysis

INTRODUCTION

Interest in the high catalytic activity of transition metal carbonyls was followed by analogous growing interest in polynuclear complexes. In many cases, however, under catalytic reaction conditions oxidation, fragmentation or aggregation of clusters is facilitated. Substitution of the carbonyl groups by some other ligands could influence these processes. Quite promising in this respect could be the potentially multidentate 2-pyridylphosphine ligands, containing the donor atoms nitrogen and phosphorus. They could act as monodentate terminal ligands,[1] bridging ligands[2,3] or as chelate ligands.[4,5] Changes in coordination following transition from the solid state to the solution state are also known.[6] In the presence of certain metals, pyridylphosphine may undergo oxidation, with formation of phosphine oxide complexes, with chelate coordination by phosphorus and oxygen atoms.[7] Formation of complexes with pyridylphosphide bridges, produced in an elimination reaction of one of the substituents of pyridylphosphine, has also been reported.[8]

The subject of our paper is the reactions of $Ir_4(CO)_{12}$ with 2-pyridylphopshines: PPh_2pyl, $PPhpyl_2$ and $Ppyl_3$ (pyl = 2-pyridyl).

EXPERIMENTAL

$Ir_4(CO)_{12}$ was obtained in quantitative yield by the reaction of $IrCl_3 \cdot 3H_2O$ or $(NH_4)_2IrCl_6$ with formic acid (HCOOH).[9] All substitution reactions in $Ir_4(CO)_{12}$ were carried out under a carbon monoxide (CO) atmosphere.

$[Ir_4(CO)_9(PR_3)_3]$

To $Ir_4(CO)_{12}$ (0.1 g) a solution of potassium hydroperoxide (0.25 g) in methanol (10 cm^3) was added. After about 10 min a clear yellow–orange solution was obtained to which a solution of 2-pyridylphosphine (0.1 g) in methanol was added; 6 cm^3 for PPh_2pyl and 8 cm^3 for $PPhpyl_2$, $Ppyl_3$ and PPh_3. The reactions were carried out at 40 °C for PPh_2pyl, at 50 °C for $PPhpyl_2$ and $Ppyl_3$ and at 75 °C for PPh_3. After about 2 h, the yellow crystalline precipitates settled. These were filtered off, washed with methanol and heptane and dried *in vacuo*. Yields: $[Ir_4(CO)_9(PPh_3)_3]$ 98%, $[Ir_4(CO)_9(PPh_2pyl)_3]$ 33%, $[Ir_4(CO)_9(PPhpyl_2)_3]$ 23%, $[Ir_4(CO)_9(Ppyl_3)_3]$ 12%.

^{31}P NMR spectra were recorded on a JEOL JNM-ES-100 spectrometer at 40.5 MHz. IR spectra were measured on a Perkin–Elmer 180 spectrometer.

RESULTS AND DISCUSSION

$Ir_4(CO)_{12}$ in basic medium is known to be capable of transformation into the monohydride anion $[Ir_4H(CO)_{11}]^-$,[13] stable in methanol/potassium hydroxide (KOH) solution at a ratio of $[Ir_4H(CO_{11}]^-$: KOH = 1:8.[14] Under carbon monoxide atmosphere the $[Ir_4H(CO)_{11}]^-$ anion readily reacts with phosphines to yield the $[Ir_4(CO)_{10}(PR_3)_2]$- and

Table 1 Selected IR bands for $[Ir_4(CO)_9(PR_3)_3]$ (cm^{-1})

	PPh$_3$		PPh$_2$pyl		PPhpyl$_2$		Ppyl$_3$	
PR$_3$	KBr	CHCl$_3$	KBr	CHCl$_3$	KBr	CHCl$_3$	KBr	CHCl$_3$
ν_{CO}	2042vs	2047s	2040vs	2047s	2040s	2045s	2040vs	2046s
				2008sh	2009vs	2012s	2012sh	2014s
	1995sh	1992vs	1998sh					
						1989vs		1990vs
	1985sh		1985vs	1986vs	1980vs		1984vs	
		1972sh		1976sh	1772sh			
	1965vs		1965sh					
	1840w	1840vw	1840w	1840w	1850vw	1852vw	1851vw	1852vw
	1790sh		1790vs	1790vs	1798vs	1794s	1796vs	1795s
		1786s						
	1778vs		1778vs	1772s	1782vs	1780s	1780vs	1780s
ν_{C-C}			1563sh		1565sh		1568sh	
			1572m		1573m		1575m	

$[Ir_4(CO)_9(PR_3)_3]$-type complexes, depending on reaction conditions.

Substitution reactions were carried out in the presence of PPh$_3$, PPh$_2$pyl, PPhpyl$_2$ and Ppyl$_3$ at a molar ratio $[Ir_4H(CO)_{11}]^-:PR_3 = 1:3$.

Within the temperature range 50–75 °C, in the presence of triphenylphosphine the only product was the trisubstituted complex $[Ir_4(CO)_9(PPh_3)_3]$. The reaction yield increases with temperature and at 75 °C it is almost quantitative (at 50 °C, yield = 80%).[15]

For 2-pyridylphosphine, the products of the CO group substitution reaction are temperature-dependent. At 30 °C, diphenylpyridylphosphine (PPh$_2$pyl) yields a mixture of the bi- and tri-substituted products, $[Ir_4(CO)_{10}(PR_3)_2]$ and $[Ir_4(CO)_9(PR_3)_3]$ (R = generic; Ph or pyl). The IR spectrum in the ν_{CO} vibration range displayed bands at 1817 and 2070 cm^{-1}, indicative of $[Ir_4(CO)_{10}(PPh_2pyl)_2]$-type complexes.[16] Elevation of the temperature to 40 °C results in the formation of the yellow, trisubstituted complex $[Ir_4(CO)_9(PPh_2pyl)_3]$. The trisubstituted complexes arise also in reactions with phenyldipyridylphosphine and tripyridylphosphine at 50 °C. The yield of $[Ir_4(CO)_9(PR_3)_3]$-type complexes decreases with increasing number of pyridyl substituents on phosphine and for PPh$_2$pyl, PPhpyl$_2$ and Ppyl$_3$ is equal to 33%, 23% and 12% respectively. Temperature increase to 75 °C leads to the formation of a new group of compounds, being the subject of continued studies.

All the trisubstituted pyridylphosphine derivatives are yellow-coloured, stable in air, soluble in chloroform and in methylene chloride, but less easily than the triphenylphosphine analogues, which prevented recording of the ^{13}C NMR spectra. They are insoluble in carbon tetrachloride, benzene, methanol, acetone and water.

Like the majority of known compounds of that type,[15,17] they incorporate bridging groups, as well as CO terminal groups (Table 1). Pyridylphosphines are coordinated with iridium only via phosphorus, indicated by the frequency of the $\nu(C-C)$ vibration of the pyridyl ring. In compounds where a metal-pyridyl nitrogen bond is formed, the $\nu(C-C)$ of the free ligand at 1573 cm^{-1} is shifted upwards by *ca* 10–15 cm^{-1}. If the nitrogen atom of the pyridyl ring is not coordinated, the $\nu(C-C)$ remains unchanged.[7] In chloroform the structure of the compounds was retained. The ^{31}P {^{1}H} NMR spectra exhibit two singlets of intensity ratio 2 : 1 (Table 2), similar to the complex with PPh$_3$.[18] It was found that, with increase of the number of the pyridyl rings in PPh$_{3-x}$pyl$_x$, the difference in chemical shifts of the free and the

Table 2 ^{31}P{^{1}H} NMR spectra of $[Ir_4(CO)_9(PR_3)_3]$-type complexes in CDCl$_3$ (ppm); external reference 85% H$_3$PO$_4$

	PR$_3$			
	PPh$_3$	PPh$_2$pyl	PPhpyl$_2$	Ppyl$_3$
δ_L	−5.6	−4.1	−2.9	−1.3
$\delta_{L_{rad}}$	20.0 (2)	16.3 (2)	18.8 (2)	21.9 (2)
$\delta_{L_{ax}}$	−17.4 (1)	−19.5 (1)	−15.6 (1)	−12.9 (1)
Δ_{comp}(rad)^a	25.6	20.4	21.7	23.2
Δ_{comp}(ax)^a	−11.8	−15.4	−12.7	−11.6

[a] $\Delta_{comp} = \delta_{comp} - \delta_L$ (ppm).

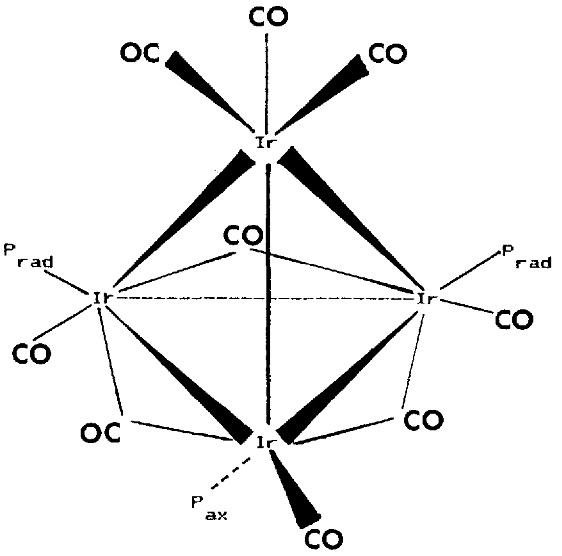

Figure 1 Structure postulated for the pyridylphosphine complexes $Ir_4(CO)_9(PPh_xpyl_{3-x})_3$.

coordinated ligand also increases (Table 2). The coordination shift Δ of phosphorus depends on the nature and oxidation state of the metal, on the nature of the other ligands, on the metal–phosphorus σ-bond strength and upon the C – P – C angle in the phosphine. Increase of the M – P bond strength as well as increase of the C – P – C bond angle result in a downfield chemical shift.[19] It could thus be postulated that in the transition from PPh_2pyl to $PPhpyl_2$ to $Ppyl_3$ the Ir—P bond strength grows slightly, assuming an unchanged angle between substitutents in phosphine.

From the position and intensity of ^{31}P NMR signals, it follows that two phosphines occupy a radial and one an axial position, as in $[Ir_4(CO)_9(PPh_3)_3]$, whose X-ray structure has been determined.[20] Thus, we postulate for the complexes with the pyridylphosphines PPh_2pyl, $PPhpyl_2$ and $Ppyl_3$ obtained by us the structure outlined in Fig. 1.

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REFERENCES

1. Wajda, K, Pruchnik, F and Lis, T *Inorg. Chem. Acta*, 1980, 40:207; Wajda-Hermanowicz, K and Pruchnik, F P, *Trans. Met. Chem.*, 1988, 13:22
2. Farr, J P, Balch, A L *Inorg. Chem. Acta*, 1981, 53:C217
3. Farr, J P, Olmstead, M M and Balch, A L *J. Am. Chem. Soc.*, 1980, 102:6654
4. Olmstead, M M, Maisonnat, A, Farr, J P and Balch, A L *Inorg. Chem.*, 1981, 20:4060
5. Farr, J P, Olmstead, M M, Wood, F E and Balch, A L *J. Am. Chem. Soc.*, 1983, 105:792.
6. Wajda-Hermanowicz, K and Pruchnik, F P *Trans. Met. Chem.*, 1988, 13:101
7. Phenylbis(2-pyridyl)phosphine reacts with nickel(II) chloride in a normal atmosphere to give a nickel(II) complex with phosphine oxide: $NiCl_2(OPPhpyl_2)_2$ CH_3OH. The crystal structure has been determined and is to be submitted for publication.
8. Lugan, N, Lavigne, G and Bonnet, J J *Inorg. Chem.*, 1987, 26:585
9. Pruchnik, F P, Wajda-Hermanowicz, K and Koralewicz, M, *J. Organometal. Chem.*, in press
10. Plażek, E and Tyka, R *Zeszyty Naukowe Politechniki Wrocławskiej* Chem., 1957, 4:79
11. Davies, W C and Mann, F G *J. Chem. Soc.*, 1944, 276; Mann, F G and Watson, J *J. Org. Chem.*, 1948, 13:502
12. Maisonnat, A, Farr, J P, Olmstead, M M, Hunt, C T and Balch, A L *Inorg. Chem.*, 1982, 21:3961
13. Malatesta, L and Caglio, G *Chem. Commun.*, 1967, 420; Angoletta, M, Malatesta, L and Caglio, G *J. Organomet. Chem.*, 1975, 94:99
14. Bau, R, Chiang, M Y, Wei, C, Garlaschelli, L and Martinengo, S *Inorg. Chem.*, 1984, 23:4759
15. Drakesmith, A J and Whyman, R *J. Chem. Soc., Dalton Trans.*, 1973:362
16. Stuntz, F G and Shapley, J R *Inorg. Chem.*, 1976, 15:1994
17. Orlewski, J, Santi, C C and Basset, J M *Inorg. Chem.*, 1986, 25:4322
18. Stuntz, G F and Shapley, J R *J. Am. Chem. Soc.*, 1977, 99:607
19. Pregosin, P S and Kunz, R W ^{31}P and ^{13}C NMR of Transition Metal Phosphine complexes, in *NMR Basic Principles and Progress*, eds. P. Diehl, E. Fluck, R. Kosfeld, vol. 16, Springer-Verlag, Berlin, 1979
20. Albano, V G, Bellon, P and Scatturin, V *J. Chem. Soc., Chem. Commun.*, 1967, 730