

Properties and reactivity of the new $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ clusters, ($\text{PR}_3 = \text{PPh}_x\text{pyl}_{3-x}$, $\text{pyl} = 2\text{-pyridyl}$)

K. Wajda-Hermanowicz, F. Pruchnik*, M. Zuber

Institute of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

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Abstract

The complex $\text{Ir}_4(\text{CO})_{12}$ was shown to react with pyridylphosphines to give $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PPh}_2\text{pyl})(\text{PPh}_2\text{pyl})_2]$ (1) $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PPhyl}_2)(\text{PPhyl}_2)_2]$ (2) and $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-Ppyl}_3)(\text{Ppyl}_3)_2]$ (3) in which one of the phosphine ligands bridges through coordination of P and N atoms. Clusters 1–3 were characterized by ^1H , ^{31}P NMR and IR spectroscopy. Variable-temperature ^1H , ^{31}P and ^{13}C NMR spectra of 1–3 were investigated and the results are discussed. In solution under CO complexes 1–3 are in equilibrium with the clusters $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_6(\text{PR}_3)_3]$.

Keywords: Iridium; Carbonyl; Phosphine; Pyridyl; Clusters; NMR spectroscopy

1. Introduction

The synthesis and reactivity of metal carbonyl clusters is attracting increasing attention [1–3]. These species show a rich substitution, catalytic and structural chemistry. Substitution of the carbonyl groups by other ligands exerts an influence on the reactivity of the clusters [4–8]. Very interesting ligands in this respect could be the potentially multidentate 2-pyridylphosphines of the type $\text{PPh}_x\text{pyl}_{3-x}$ ($x = 0, 1, 2$). It is known that they can act as unidentate terminal ligands [9–11] bridging ligands [12,13] or chelating ligands [14,15]. Changes in coordination on going from the solid to solutions are also known [16]. Recently we made $[\text{Ir}_4(\text{CO})_9(\text{PR}_3)_3]$ -type complexes ($\text{PR}_3 = \text{PPh}_x\text{pyl}_{3-x}$, $\text{pyl} = 2\text{-pyridyl}$, $x = 0, 1, 2$) [17]; in solution under argon the clusters lose one CO ligand and are transformed into complexes $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ ($\text{PR}_3 = \text{PPh}_x\text{pyl}_{3-x}$, $\text{pyl} = 2\text{-pyridyl}$). We report below the results of studies of the synthesis, properties, reactivity and fluxional behaviour of the clusters.

2. Experimental details

2.1. Materials and apparatus

The NMR spectra were recorded on a Bruker AMX-300 spectrometer and IR spectra on Specord M-80 and Bruker IFS 113V spectrometers using KBr pellets. $(\text{NH}_4)_2\text{IrCl}_6$ was purchased from Fluka.

2.2. Preparation of complexes

2.2.1. $[\text{Ir}_4(\text{CO})_{12}]$

The complex was prepared as previously described [18].

2.2.2. $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PPh}_2\text{pyl})(\text{PPh}_2\text{pyl})_2]$ (1)

A sample of $[\text{Ir}_4(\text{CO})_{12}]$ (0.2 g, 0.18 mmol) was placed in a bulb equipped with a reflux condenser, dropping funnel and CO inlet. The apparatus was filled with CO and a KOH/MeOH solution (0.6 M, 20 ml), carefully deaerated with nitrogen, was added. The suspension was stirred at 60–70°C until a clear solution was obtained, and then a solution of PPh_2pyl (0.2 g, 0.76 mmol) $[\text{Ir}_4(\text{CO})_{12}/\text{PR}_3 = 1:4.2]$ in 6 ml of MeOH (carefully deaerated with nitrogen) was added. The mix-

* Corresponding author.

ture was stirred at 70°C for 1 h under a CO atmosphere until the orange product separated out. The precipitate was filtered off, washed with methanol and heptane, and dried under nitrogen. Yield, 87%.

2.2.3. $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PPhpyl}_2)(\text{PPhpyl}_2)_2]$ (2) and $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-Ppyl}_3)(\text{Ppyl}_3)_2]$ (3)

These clusters were prepared analogously using PPhpyl_2 and Ppyl_3 , respectively. Yields of obtained products were similar.

2.3. Spectroscopic data

The IR data 1 (cm^{-1}) in the region 4000–400 cm^{-1} were as follows:

Complex 1: 1769 vs^{**}; 1786 vs^{**}; 1814 w; 1934 vs^{*}; 1950 vs^{*}; 1961 vs^{*}; 1980 vs(sh)^{*}; 2007 vs^{*}; 2040 w^{*}; 3050 m.

Complex 2: 1775 vs^{**}; 1780 vs^{**}; 1842 vw; 1943 vs^{*}; 1972 vs^{*}; 1993 vs^{*}; 2006 s^{*}; 3045 w.

Complex 3: 1771 vs^{**}; 1788 vs^{**}; 1844 vw; 1938 s^{*}; 1974 vs^{*}; 1990 vs^{*}; 2004 s^{*}; 2040 vw^{*}; 2850 vw; 2920 w; 2990 vw; 3040 w; 3435m.

The 121.5 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra 2 (δ , ppm) of $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ in CD_2Cl_2 (with 85% H_3PO_4 as standard) were as follows:

Complex 1: 28.3 [dd, $^3J(\text{P}_r, \text{P}_b) = 48.2$ Hz, $^3J(\text{P}_r, \text{P}_a) = 2.4$ Hz, P_r]; -12.2 [dd, $^3J(\text{P}_b, \text{P}_r) = 48.2$ Hz, $^3J(\text{P}_b, \text{P}_a) = 2.4$ Hz, P_b]; -13.4 [t, $^3J(\text{P}_a, \text{P}_r) = ^3J(\text{P}_a, \text{P}_b) = 2.4$ Hz, P_a] ppm.

Complex 2: 28.9 [dd, $^3J(\text{P}_r, \text{P}_b) = 46.7$ Hz, $^3J(\text{P}_r, \text{P}_a) = 2.2$ Hz, P_r]; -7.4 [dd, $^3J(\text{P}_b, \text{P}_r) = 46.7$ Hz, $^3J(\text{P}_b, \text{P}_a) = 2.2$ Hz, P_b]; -11.2 [t, $^3J(\text{P}_a, \text{P}_r) = ^3J(\text{P}_a, \text{P}_b) = 2.2$ Hz, P_a] ppm.

Complex 3: 31.9 [dd, $^3J(\text{P}_r, \text{P}_b) = 44.0$ Hz, $^3J(\text{P}_r, \text{P}_a) = 2.4$ Hz, P_r]; -3.8 [dd, $^3J(\text{P}_b, \text{P}_r) = 44.0$ Hz, $^3J(\text{P}_b, \text{P}_a) = 2.4$ Hz, P_b]; -9.4 [t, $^3J(\text{P}_a, \text{P}_r) = ^3J(\text{P}_a, \text{P}_b) = 2.4$ Hz, P_a] ppm.

The 300 MHz ^1H NMR spectra 3 (δ , ppm) of $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ in CD_2Cl_2 were as follows:

Complex 1: 8.72 [m(10), $^3J(6,5) = 4.7$ Hz, $J(6,4) = 1.9$ Hz, $J(6,3) = 0.8$ Hz, $J(6,P) = 0.9$ Hz, H6(a)]; 8.55 [m(10), $^3J(6,5) = 4.8$ Hz, $J(6,4) = 1.7$ Hz, $J(6,3) = 1.0$ Hz, $J(6,P) = 0.9$ Hz, H6(a)]; 8.49 [m(10), $^3J(6,5) = 5.4$ Hz, $^4J(6,4) = 1.3$ Hz, $^5J(6,3) = 0.9$ Hz, $J(6,P) = 0.6$ Hz, H6(b)]; 7.15 [m(14), $^3J(5,4) = 7.5$ Hz, $^3J(5,6) = 4.8$ Hz, $^4J(5,3) = 1.3$ Hz, $J(5,P) = 2.7$ Hz, H5(a)]; 7.03 [m(12), $^3J(5,6) = 5.4$ Hz, $^3J(5,4) = 7.2$ Hz, $^4J(5,3) = 1.8$

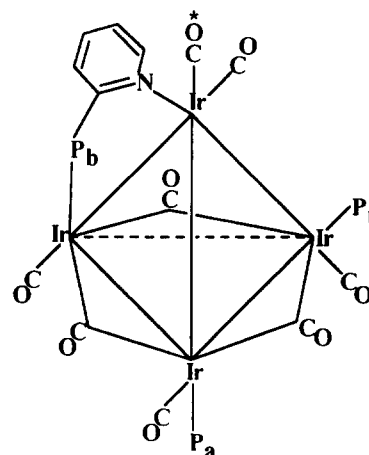


Fig. 1. Schematic structure of the $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ -type clusters.

Hz, $J(5,P) = 2.2$ Hz, H5(b)]; 6.54 [m(16), $^3J(3,4) = 7.8$ Hz, $^4J(3,5) = 1.8$ Hz, $^5J(3,6) = 0.9$ Hz, $J(3,P) = 4.1$ Hz, H3(b)] ppm; Ph and remaining pyl protons overlapped in the range 7.7–7.2 ppm (not resolved).

Complex 2: 8.73 [m(10), $^3J(6,5) = 4.7$ Hz, $^4J(6,4) = 1.7$ Hz, $^5J(6,3) = 1.0$ Hz, $J(6,P) = 0.9$ Hz, H6(a)]; 8.54 [m(10), $^3J(6,5) = 4.7$ Hz, $^4J(6,4) = 1.9$ Hz, $^5J(6,3) = 1.0$ Hz, $J(6,P) = 0.9$ Hz, H6(a)]; 8.51 [m(10), $^3J(6,5) = 4.8$ Hz, $^4J(6,4) = 1.7$ Hz, $^5J(6,3) = 1.0$ Hz, $J(6,P) = 0.9$ Hz, H6(a)]; 8.42–8.36 [H6(b) and H6(a), overlapping, not resolved]; 7.92 [m(12), $^3J(3,4) = 7.8$ Hz, $^4J(3,5) = 1.3$ Hz, $^5J(3,6) = 1.1$ Hz, $J(3,P) = 4.2$ Hz, H3(a)]; 7.83 [m(12), $^3J(4,3) = 7.8$ Hz, $^3J(4,5) = 7.8$ Hz, $^4J(4,6) = 1.7$ Hz, $J(4,P) = 4.2$ Hz, H4(a)]; 6.98 [m(10), $^3J(5,4) = 7.7$ Hz, $^3J(5,6) = 5.3$ Hz, $^4J(5,3) = 1.6$ Hz, $J(5,P) = 2.2$ Hz, H5(b)]; 6.54 [m(12), $^3J(3,4) = 8.0$ Hz, $^4J(3,5) = 1.7$ Hz, $^5J(3,6) = 1.0$ Hz, $J(3,P) = 4.4$ Hz, H3(b)] ppm; Ph and remaining pyl protons overlapped in the range 7.7–7.09 ppm (not resolved).

Complex 3 8.63 [m(10), $^3J(6,5) = 4.8$ Hz, $^4J(6,4) = 1.7$ Hz, $^5J(6,3) = 1$ Hz, $J(6,P) = 0.8$ Hz, H6(a)]; 8.58 [m(10), $^3J(6,5) = 4.8$ Hz, $^4J(6,4) = 1.7$ Hz, $^5J(6,3) = 1$ Hz, $J(6,P) = 0.8$ Hz, H6(a)]; 8.50 [m(10), $^3J(6,5) = 4.7$ Hz, $^4J(6,4) = 1.8$ Hz, $^5J(6,3) = 1.1$ Hz, $J(6,P) = 0.8$ Hz, H6(a)]; 8.41 [H6(b), overlapping, not resolved]; 8.34 [m(10), $^3J(6,5) = 4.8$ Hz, $^4J(6,4) = 1.9$ Hz, $^5J(6,3) = 1.0$ Hz, $J(6,P) = 0.7$ Hz, H6(a)]; 8.03–7.88 (H3 overlapping, not resolved); 7.76 [m(12), $^3J(4,3) = 7.8$ Hz, $^3J(4,5) = 7.6$ Hz, $^4J(4,6) = 1.7$ Hz, $J(4,P) = 4.4$ Hz, H4(a)]; 7.72–7.61 (H4, overlapping, not resolved); 7.49 [m(12), $^3J(4,5) = 7.7$ Hz, $^3J(4,3) = 7.9$ Hz, $^4J(4,6) = 1.7$ Hz, $J(4,P) = 2.6$ Hz, H4(b)]; 7.31 [m(14), $^3J(5,4) = 7.6$ Hz, $^3J(5,6) = 4.6$ Hz, $^4J(5,3) = 1.2$ Hz, $J(5,P) = 2.8$ Hz, H5(a)]; 7.26–7.13 ppm [H5(a), overlapping, not resolved]; 7.00 [m(12), $^3J(5,4) = 7.7$ Hz, $^3J(5,6) = 5.3$ Hz, $^4J(5,3) = 1.5$ Hz, $J(5,P) = 2.2$ Hz, H5(b)]; 6.70 [m(16), $^3J(3,4) = 7.9$ Hz, $^4J(3,5) = 1.6$ Hz, $^5J(3,6) = 0.9$ Hz, $J(3,P) = 3.8$ Hz, H3(b)] ppm.

1 Designation: *, $\nu(\text{CO})$ terminal; **, $\nu(\text{CO})$ bridging.

2 Designation: P_r = radial; P_b = bridging; and P_a = axial phosphine ligand (Fig. 1).

3 Designation: (a) protons of pyridyl ring non-coordinated with iridium; (b) protons of pyridyl ring coordinated with iridium (see Fig. 1).

3. Results and discussion

The $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ clusters ($\text{PR}_3 = \text{PPh}_x\text{pyl}_{3-x}$, $\text{pyl} = 2\text{-pyridyl}$, $x = 0, 1, 2$) were prepared by reaction of $\text{Ir}_4(\text{CO})_{12}$ with the appropriate phosphine in 0.6 M KOH solution in methanol at 75°C under CO with a $\text{Ir}_4(\text{CO})_{12}/\text{PR}_3/\text{KOH}$ ratio of 1:4:10, or from $[\text{Ir}_4(\text{CO})_9(\text{PR}_3)_3]$ in CHCl_3 under argon at 20–50°C. The reactions are shown in Fig. 2.

The clusters of type $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ are very interesting because of their crystal structures and fluxional behaviour in solution. A single-crystal X-ray study of **1** [19] revealed that it contains one phosphine ligand bridging through P and N atoms and two phosphines (radial and axial, see Fig. 1) coordinated through the phosphorus atom only. However $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_6(\text{PPh}_2\text{pyl})_3]$ contains only terminal phosphines. The carbonyl ligands in $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ and in $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_6(\text{PR}_3)_3]$ are present as both terminal and bridging ligands. In both types of clusters there are three carbonyls bridging Ir–Ir bonds in the basal plane of the cluster.

In the IR spectra of **1–3** both the terminal and bridging CO stretching frequencies have lower values than those in $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_6(\text{PR}_3)_3]$ [17]. This is due to the stronger σ -donor and weaker π -acceptor properties of the N atom of pyridyl ring compared with that of the CO ligand. Thus coordination via N atom increases the electron density on Ir atoms in the cluster. This leads to weakening of the C–O bond in coordinated carbonyls and so to a lowering of the $\nu(\text{CO})$ frequencies.

The ^1H NMR spectrum of tris(2-pyridyl)phosphine [20] consists of four well-separated multiplets, assigned to four non-equivalent pyridyl protons (H6, 8.70 ppm; H3, 7.18 ppm; H4, 7.60 ppm; and H5, 7.40 ppm). Four multiplets are also present in the spectrum of tris(2-pyridyl)phosphine oxide or sulphide. Relative to those for the phosphine, the resonances of protons 3, 4 and 6

in the phosphine oxide are shifted towards lower field by about 0.1–0.2 ppm. The resonance of proton 5 is shifted towards lower field by about 0.8 ppm.

For rhodium complexes of the type $[\text{RhCl}(\text{CO})(\text{PR}_3)_2]$ [16] (where $\text{PR}_3 = \text{PPhpyl}_2$ and Ppyl_3) it was found that, because of coordination of phosphine via phosphorus, pyridyl resonances are shifted towards lower fields relative to those for the free phosphine. This is because the electron density on coordinated phosphine is lower (similar to phosphine oxide) than in the free ligand. In contrast, the resonances of the protons of the pyridyl ring coordinated via nitrogen and phosphorus appear at higher field than those for pyridylphosphines coordinated via phosphorus only. This effect is also observed for the iridium clusters $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ considered below.

The 121.5 MHz $^{31}\text{P}\{^1\text{H}\}$ and 300 MHz ^1H NMR spectra of $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ clusters indicate they have the same structure in the solid and in solution. Two pyridylphosphine ligands are coordinated to iridium via P atoms only. The remaining phosphine is coordinated via the phosphorus and the nitrogen of one of pyridyl rings. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in CDCl_3 exhibit two double doublets for the radial and bridging ligands as well as a triplet for the axial phosphine ligand (see NMR data above). The triplet results from overlapping of two doublets with the same $^3J(\text{P}_r, \text{P}_a)$ and $^3J(\text{P}_b, \text{P}_a)$ coupling constants. The ^1H NMR spectra indicate that the chemical shifts of protons of the non-coordinated pyridyl rings are approximately the same for both $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_6(\text{PR}_3)_3]$ and $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ compounds. However, the proton resonances for the pyridyl rings of the P, N-bonded bridging phosphine ligand always appear at the highest fields (see NMR data). The 2D homo- (H, H) and hetero-correlated (H, C) COSY spectra confirm a very characteristic shift of the H3 resonance of the bridging pyridyl ring in $\text{PPh}_x\text{pyl}_{3-x}$ ($x = 0, 1, 2$) ligands. For the bridging Ppyl_3 ligand, the H3 resonance is shifted by ca. 1.15–1.38 ppm towards higher field (in this case the signals of the H3 protons of non-coordinating pyridyls overlap, and the exact values of the chemical shifts were not determined) (see ^1H NMR data). For complexes with PPhpyl_2 and PPh_2pyl ligands, the H3 resonances of the non-bridging phosphines were not resolved. The H4 and H5 resonances undergo analogous shifts of ca. 0.27–0.12 ppm and 0.12 ppm, respectively (as was found for complexes containing the PPh_2pyl ligand). The resonance for H6 proton is shifted only slightly (as in the case of complexes with PPh_2pyl and Ppyl_3 ligands; in the case of the cluster with a PPhpyl_2 ligand this resonance overlaps with the H6 resonance of the uncoordinated pyridyl ring). Thus the most characteristic difference between bridging and non-bridging phosphines in $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ clusters lies in the large shift (towards higher field) of their

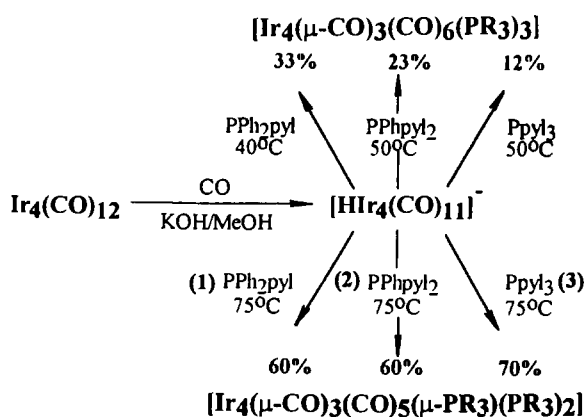


Fig. 2. Preparation of $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ and $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_6(\text{PR}_3)_3]$.

H3 pyridyl protons. It was also found that the lines in resonances of the protons in the pyridyl ring in P,N-bonded phosphine ligands are broader than those for the remaining protons, probably because of the interaction with the iridium atom which possesses a quadrupole moment.

The ^1H and ^{31}P NMR spectra of **1** and **2** are temperature-dependent (Figs. 3 and 4). The ^1H spectra of both compounds in CH_2Cl_2 do not change significantly between $+20^\circ\text{C}$ and -40°C . The only effects observed in this range involve changes in the chemical shifts for some resonances and some broadening of resonance lines at temperatures down to -40°C . This is clearly

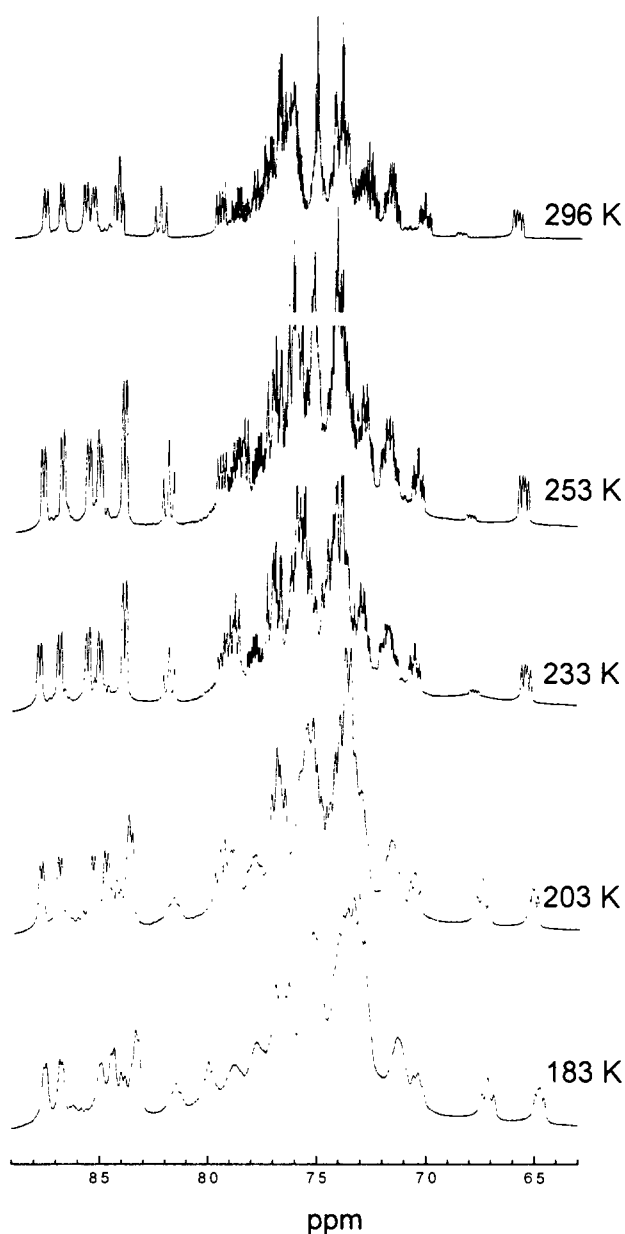


Fig. 3. The 300 MHz ^1H variable-temperature NMR spectra of **2** in CD_2Cl_2 .

seen for **2** in the range 8.2–8.8 ppm (where only signals of the H6 pyridyl protons appear). However at lower temperatures, between -50°C and -90°C , new broad resonances appear. For the cluster with PPh_2pyl [21] the new signals appear at δ 6.7, 7.7 ppm and at δ 6.3, 8.0 ppm. In the case of PPhpyl_2 the new resonances are at δ 6.7 ppm and δ 7.9 ppm (Fig. 3). The ^1H NMR spectra of **3** exhibit no significant changes in the range $+20^\circ\text{C}$ to -90°C . We thus suggest that the observed changes are due to rotation of the ligand around the Ir—P bond or of the phenyl group around the P—C bond.

Complexes **1** and **2** display averaged signals in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra down to about -70°C . The spectra at room temperature, in CD_2Cl_2 or CDCl_3 as solvent, contain three resonances: $\text{P}_r = \text{dd}$, $\text{P}_b = \text{dd}$, $\text{P}_a = \text{t}$ (for designations and values of chemical shifts and coupling constants, see Experimental details). However, the line width depends on the solvent used as well as on the temperature. In $\text{CCl}_4/\text{CDCl}_3/\text{CH}_2\text{Cl}_2$ (13:27:60 volume ratio) (used as a solvent for measurements at temperatures up to -115°C), and also in CD_2Cl_2 and CDCl_3 at temperatures below 0°C , $J(\text{P}_r, \text{P}_a)$ and $J(\text{P}_b, \text{P}_a)$, couplings are not observed. As a result the spectrum consist of a P_r doublet, a P_b doublet and a P_a singlet. At -70°C , collapse of the P_r doublet is observed for the cluster with PPh_2pyl as ligand. In the case of the cluster with PPhpyl_2 , merging of P_r into a singlet takes place at -80°C .

At -90°C , substantial broadening of the P_r resonance at δ 30 ppm is observed for the complex with PPh_2pyl . Below -90°C , two broad signals appear in this region. For **1**, their chemical shifts are δ 33.5 ppm and 29.0 ppm. In the case of the cluster with PPhpyl_2 , the coalescence temperature is lower by about 5°C . At -110°C , resonances for P_r are observed at δ 32.0 and 26.0 ppm. For the bridging phosphine ligand broadening of the P_b doublet is also observed, and this finally merges into a singlet. In the cluster with PPh_2pyl , collapse of the P_b doublet takes place at -90°C (for the corresponding P_r resonance collapse of the doublet occurs at -70°C), while for the complex with PPhpyl_2 the same behaviour is observed at lower temperatures (the P_r doublet becomes a singlet at -80°C while merging of the bridging doublet is observed at about -110°C).

Cluster **3** exhibits dynamic properties only at much lower temperatures. At -113°C , merging of the P_r doublet into a singlet is observed, while the remaining resonances do not essentially change. Because of the sparing solubility of the clusters in solvents with very low freezing points, we were not able to examine the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at lower temperatures.

The temperature-dependent $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for the clusters suggest that the observed changes are due to the change in the coordination sphere of the Ir atom

bound to radial phosphine. It is also noteworthy that the coalescence temperatures depend on the number of pyridyl rings in the phosphine molecules (the larger the number of pyridyl rings, the lower the coalescence temperatures).

The natural abundance ^{13}C NMR spectra of the complexes are very complicated. For illustration, the ^{13}C NMR spectra of **1** in CD_2Cl_2 at $+20^\circ\text{C}$ and -90°C are shown in Fig. 5. The low-field resonances at δ 221.1, 214.3 and 212.7 ppm can be assigned, by analogy with data for known compounds, to the three

bridging carbonyls [22–27]. It is known that in the ^{13}C NMR spectra of Ir_4 clusters the chemical shifts of the ligand resonances decrease in the sequence bridging $>$ radial $>$ axial \approx apical [26]. From the 2D heterocorrelated (H, C) COSY spectra we can also assign the signals in the range δ 179.3–170.0 ppm to the remaining carbonyl groups. The doublet at δ 175.6 ppm can probably be assigned to the apical carbonyl group (designated as * in Fig. 1); the observed $J(\text{C}-\text{P})$ coupling constant for this carbonyl group is 30.5 Hz. Such large coupling constants are observed for analogous com-

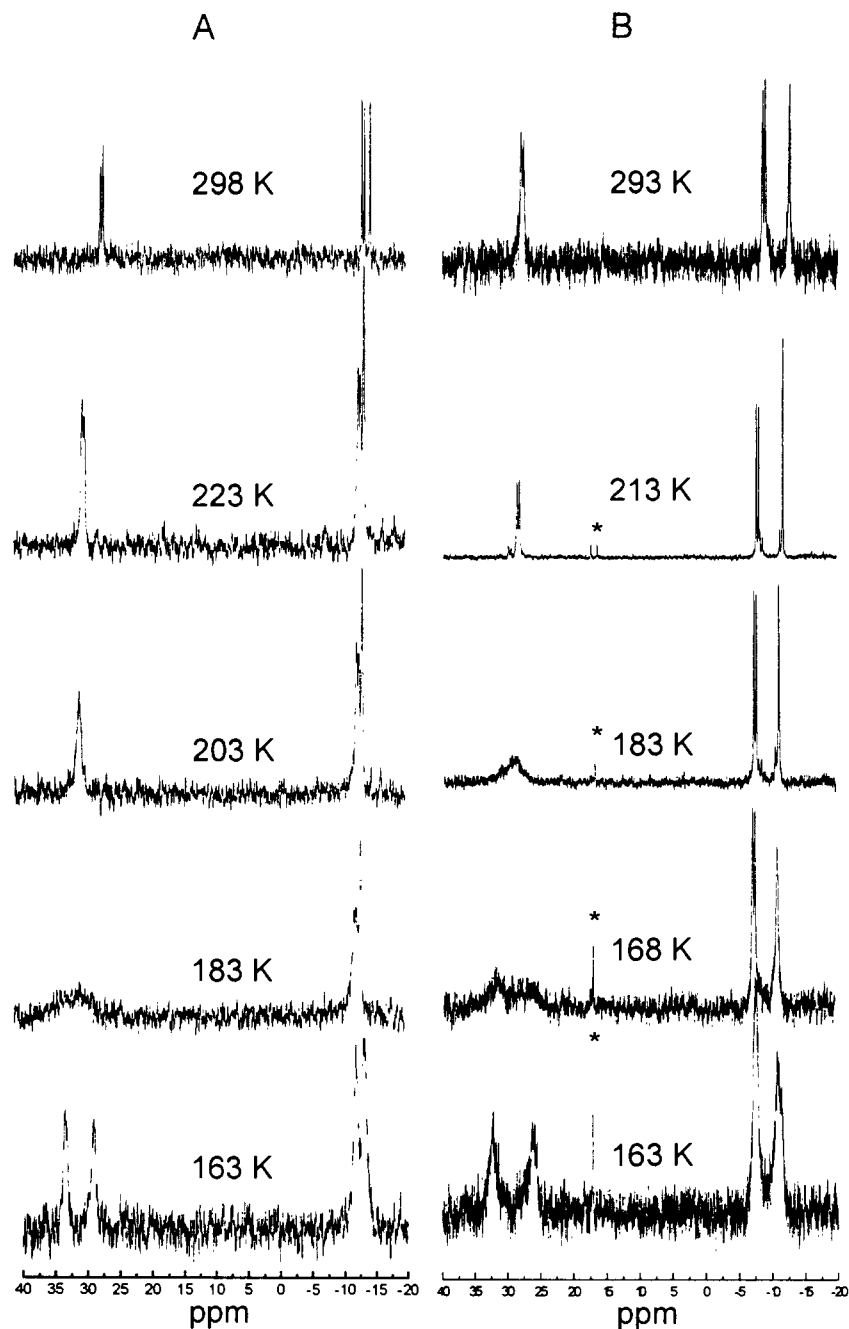


Fig. 4. The 121.5 MHz $^{31}\text{P}\{^1\text{H}\}$ variable-temperature NMR spectra (A) of **1** and (B) of **2** in $\text{CCl}_4/\text{CDCl}_3/\text{CH}_2\text{Cl}_2$ (13:27:60 volume ratio); * = impurity.

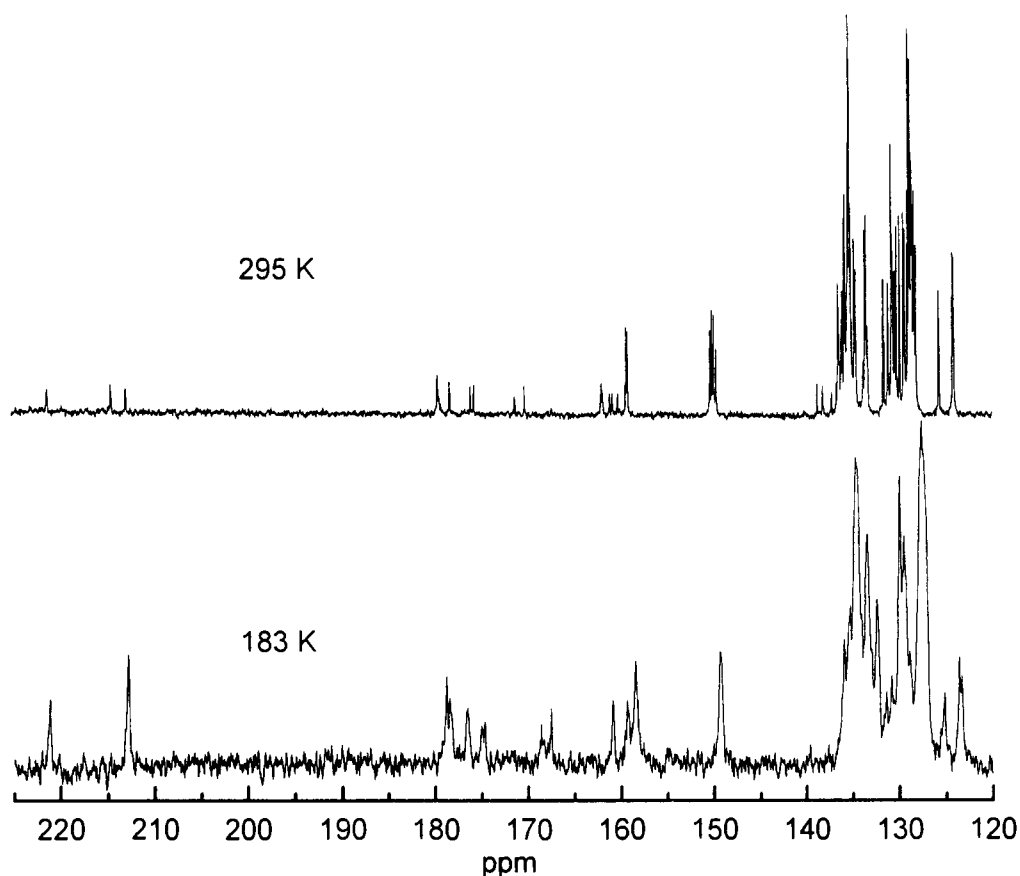


Fig. 5. The 75.5 MHz ^{13}C NMR spectra of **1** in CD_2Cl_2 .

pounds when the ligands are pseudo-*trans* to each other in apical and basal-axial positions [8,22,24]. The remaining carbonyl resonances proved more difficult to assign. The signals in the range δ 161.7–120 ppm belong to the carbons of the phenyl and pyridyl rings. They are coupled with P atoms and were not resolved.

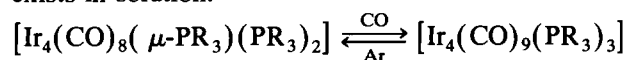
As is shown in Fig. 5, lowering of the temperature causes only slight changes in $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in the carbonyl region. At -90°C the lines are broader and there is some change in the chemical shifts of some resonances. However at -90°C only two resonances are observed above δ 210 ppm (δ 221.1 and 212.8 ppm, intensity ratio 1:2). Taking account of the nature of the changes with temperature, we suggest that the two bridging carbonyl resonances observed at -90°C are due to coincidental overlapping of signals at δ 214.3 and 212.7 ppm as a result of a shift of the first of these signals.

In the light of the ^1H , $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, and of the temperature-dependent spectra, we conclude that:

1. The $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ -type clusters have the same geometry in the solid state and in solution, since the ^{31}P NMR spectrum of **1** at room temperature is consistent with the X-ray structure.

2. Carbonyl scrambling is not observed in the temperature range $+90^\circ\text{C}$ to -115°C .
3. The 2-pyridyl rings (both coordinated and non-coordinated) are not involved in the exchange process and their resonances do not coalesce. Therefore the dynamic properties at low temperatures are due to rotation of the ligand around the Ir—P bond or of the phenyl group around the P—C bond.

There is a very interesting reaction of the $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ clusters with CO [21]. Even with only a stoichiometric amount of CO splitting of the Ir—N bond is observed and a carbonyl ligand is coordinated to the apical iridium atom. These reactions can be monitored by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy. The rate of consumption of a stoichiometric amount of CO is slow at room temperature. The reverse processes were also observed. In solution under argon, the $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_6(\text{PR}_3)_3]$ clusters one carbonyl ligand at the apical iridium atom is substituted by the N atom of one of the pyridyl groups. Thus the following equilibrium exists in solution:



Similar behaviour was observed for $[\text{Ir}_2\text{Rh}_2(\text{CO})_{10}(\eta^4\text{-COD})]$ [25]. Displacement of the second carbonyl

ligand at the apical iridium atom was not observed by use of NMR spectroscopy even at 90°C. No displacement of a CO ligand in $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_5(\mu\text{-PR}_3)(\text{PR}_3)_2]$ to give $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_4(\mu\text{-PR}_3)_2(\text{PR}_3)]$ was observed also in a basic medium.

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References

- [1] D. Braga and F. Grepioni, *J. Organometal. Chem.*, **336** (1987) C9.
- [2] J.D. Atwood, *Coord. Chem. Rev.*, **83** (1988) 93.
- [3] B.C. Gates, L. Guzzi and H. Knözinger, *Metal Clusters in Catalysis*, Elsevier Amsterdam, 1986.
- [4] J.P. Kennedy, P. Selz, A.L. Rheingold, W.C. Trogler and F. Basolo, *J. Am. Chem. Soc.*, **111** (1989) 3615.
- [5] G.F. Holland, D.E. Ellis, D.R. Tyler, H.B. Gray and W.C. Trogler, *J. Am. Chem. Soc.*, **109** (1987) 4276.
- [6] K. Dahlinger, F. Falcone and A.J. Poë, *Inorg. Chem.*, **25** (1986) 2654.
- [7] J.D. Atwood, *J. Organometal. Chem.*, **383** (1990) 59.
- [8] B.E. Mann, M.D. Vargas and R. Khadar, *J. Chem. Soc., Dalton Trans.*, (1992) 1725.
- [9] K. Wajda, F. Pruchnik and T. Lis, *Inorg. Chim. Acta*, **40** (1980) 207.
- [10] K. Wajda-Hermanowicz and F.P. Pruchnik, *Transition Metal Chem.*, **13** (1988) 22.
- [11] J.P. Farr, M.M. Olmstead and A.L. Balch, *J. Am. Chem. Soc.*, **102** (1980) 6654.
- [12] A. Maisonnat, J.P. Farr and A.L. Balch, *Inorg. Chim. Acta*, **53** (1981) L217.
- [13] A.J. Deeming and M.B. Smith, *J. Chem. Soc., Chem. Commun.*, (1993) 844.
- [14] M.M. Olmstead, A. Maisonnat, J.P. Farr and A.L. Balch, *Inorg. Chem.*, **20**, (1981) 4060.
- [15] J.P. Farr, M.M. Olmstead, F.E. Wood and A.L. Balch, *J. Am. Chem. Soc.*, **105** (1983) 792.
- [16] K. Wajda-Hermanowicz and F.P. Pruchnik, *Transition Metal Chem.*, **13** (1988) 101.
- [17] K. Wajda-Hermanowicz, M. Koralewicz and F.P. Pruchnik, *Appl. Organomet. Chem.*, **4** (1988) 73.
- [18] F.P. Pruchnik, K. Wajda-Hermanowicz and M. Koralewicz, *J. Organometal. Chem.*, **381** (1990) 384.
- [19] E. Gałdecka, Z. Gałdecki, K. Wajda-Hermanowicz and F.P. Pruchnik, *J. Chem. Crystallogr.*, in press.
- [20] G.E. Griffin and W.A. Thomas, *J. Chem. Soc. B*, (1970) 477.
- [21] K. Wajda-Hermanowicz, F. Pruchnik, M. Zuber, G. Rusek, E. Gałdecka and Z. Gałdecki, *Inorg. Chim. Acta*, **232** (1995) 207.
- [22] G.F. Stuntz and J.R. Shapley, *J. Am. Chem. Soc.*, **99** (1977) 607.
- [23] P.E. Cattermole, K.G. Orrell and A.G. Osborne, *J. Chem. Soc., Dalton Trans.*, (1974) 328.
- [24] B.E. Mann, B.T. Pickup and A.K. Smith, *J. Chem. Soc., Dalton Trans.*, (1989) 889.
- [25] G. Bondietti, G. Suardi, R. Ros, R. Roulet, F. Grepioni and D. Braga, *Helv. Chim. Acta*, **76** (1993) 2913.
- [26] R. Ros, A. Scrivanti, V.G. Albano, D. Braga and L. Garlaschelli, *J. Chem. Soc., Dalton Trans.*, (1986) 2411.
- [27] A. Strawczynski, G. Suardi, R. Ros and R. Roulet, *Helv. Chim. Acta*, **76** (1993) 2210.