

An NMR study of some seven-coordinate organophosphine carbonyl iodide derivatives of molybdenum(II) and tungsten(II)

Paul K. Baker, Michael A. Beckett* and Lisa M. Severs

Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW (UK)

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Abstract

The seven-coordinate complexes $[MI_2(CO)_3L_2]$ ($M = Mo$, $L = PMe_2Ph$; $M = W$, $L = PMe_2Ph$, $PMePh_2$ or PPh_3) have been studied by variable temperature $^{31}P\{-^1H\}$ NMR spectroscopy; a fluxional process is observed and activation energies ($\Delta G^\ddagger = 52\text{--}57 \text{ kJ mol}^{-1}$) have been calculated from coalescence temperatures. Low temperature $^{13}C\{-^1H\}$ and $^{31}P\{-^1H\}$ spectra suggest that the lowest energy configuration of $[WI_2(CO)_3(PMe_2Ph)_2]$ is based on that of a carbonyl ligand face-capped octahedron with overall C_s symmetry with the PMe_2Ph ligands *trans*, and the two remaining carbonyl ligands presumably *cis*.

Introduction

The solid state molecular geometry of a seven-coordinate transition-metal complex is usually based upon that of a capped octahedron, a pentagonal bipyramid, or a capped trigonal prism (Fig. 1) with the metal atom situated at the polyhedron's centre and a ligand donor atom at each of the seven vertices [1]. There is no strong energy preference for any one of these three common structures, and in solution, theory suggests that interconversions can occur without difficulty, so that in general

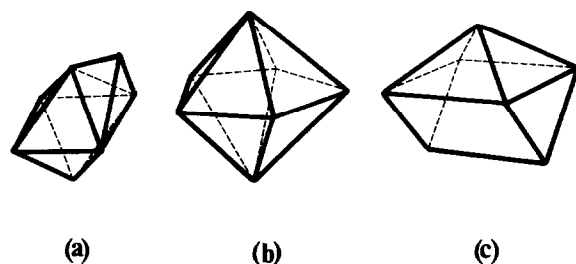


Fig. 1. Ligand geometries encountered in seven-coordinate complexes: (a) capped octahedron (b) pentagonal bipyramid (c) capped trigonal prism.

seven-coordinate complexes should be stereochemically nonrigid. Activation energies for the interconversion of these seven-coordinate molecular geometries are likely to fall within the range which is suited to study by dynamic NMR [2], and this paper examines the stereochemical behaviour of some seven-coordinate organophosphine carbonyl iodide derivatives of molybdenum(II) and tungsten(II) by this technique.

Results and discussion

The reaction of $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ with two equivalents of L in CH_2Cl_2 at room temperature affords the previously reported complexes $[\text{MI}_2(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mo}$ or W , $\text{L} = \text{PMe}_2\text{Ph}$; $\text{M} = \text{W}$, $\text{L} = \text{PPh}_3$) [3,4] and the new compound $[\text{WI}_2(\text{CO})_3(\text{PMePh}_2)_2]$ in good yields.

Variable temperature $^{31}\text{P}\{-^1\text{H}\}$ and ^1H experiments were performed on CDCl_3 solutions of $[\text{WI}_2(\text{CO})_3(\text{PMe}_2\text{Ph})_2]$ to see whether any fluxional process could be observed. The $^{31}\text{P}\{-^1\text{H}\}$ spectrum of $[\text{WI}_2(\text{CO})_3(\text{PMe}_2\text{Ph})_2]$ is temperature dependent and data obtained at -40°C and $+50^\circ\text{C}$ are reported in Table 1. At -40°C the $^{31}\text{P}\{-^1\text{H}\}$ spectrum appears as an AB quartet (with ^{183}W satellites), which broadens upon warming to produce a coalesced signal at $+40^\circ\text{C}$ and then sharpens to yield a singlet at $+50^\circ\text{C}$. These spectral changes indicate that either the seven-coordinate complex is stereochemically nonrigid, or that metal-organophosphine dissociation/recombination occurs. To determine which is the case, an equivalent of PMe_2Ph was added to the NMR sample of $[\text{WI}_2(\text{CO})_3(\text{PMe}_2\text{Ph})_2]$ and its spectrum recorded at $+50^\circ\text{C}$. This spectrum clearly showed two singlets present at chemical shifts corresponding to those of uncomplexed PMe_2Ph and of the seven-coordinate tungsten complex. This evidence implies that some form of ligand

Table 1
NMR data for seven-coordinate complexes ^a

Compound	$\delta(^{31}\text{P})$ (ppm)		$^2J(^{31}\text{P}^{31}\text{P})$ (Hz) ^d	Coalescence temperature ($^\circ\text{C}$)	Activation energy ΔG^* ^e (kJ mol^{-1})
	-40°C ^b	$+40^\circ\text{C}$ ^c			
$[\text{WI}_2(\text{CO})_3(\text{PMe}_2\text{Ph})_2]$ ^g	-35.0 -44.1	-39.5 ^f	170.8	+40	56.9 ± 1.0
$[\text{MoI}_2(\text{CO})_3(\text{PMe}_2\text{Ph})_2]$ ^h	-23.6 -33.9	-28.8	189.2	+18	52.4 ± 1.0
$[\text{WI}_2(\text{CO})_3(\text{PMePh}_2)_2]$ ⁱ	-33.0 -28.9	-30.9	172.5	+25	56.1 ± 1.0
$[\text{WI}_2(\text{CO})_3(\text{PPh}_3)_2]$	-36.1 -45.1	-41.9	171.1	+33	55.7 ± 1.0

^a In CDCl_3 solution at room temperature unless otherwise stated. ^b AB quartet. ^c Singlet. ^d At -40°C . ^e Calculated from $\Delta G^* = -RT \ln(\pi\Delta\nu h/kT\sqrt{2})$. ^f At $+50^\circ\text{C}$. ^g $\delta(^{13}\text{C})$ (ppm) at -70°C in CD_2Cl_2 : 15.4 (d), $^1J(^{31}\text{P}^{13}\text{C})$ 35.5 Hz; 17.1 (d), $^1J(^{31}\text{P}^{13}\text{C})$ 39.6 Hz (P-CH₃); 132.8 (d), $^1J(^{31}\text{P}^{13}\text{C})$ 47.8 Hz, Ci; 134.3 (d), $^1J(^{31}\text{P}^{13}\text{C})$ 45.5 Hz, Ci; 128.2 (d), $^2J(^{31}\text{P}^{13}\text{C})$ 9.7 Hz, Co; 127.9 (d), $^2J(^{31}\text{P}^{13}\text{C})$ 9.8 Hz, Co; 130.8 (d), $^3J(^{31}\text{P}^{13}\text{C})$ 8.0 Hz, Cm; 129.6 (d), $^3J(^{31}\text{P}^{13}\text{C})$ 8.0 Hz, Cm; 130 (q) Cp (P-C₆H₅); 209.9 (d), $^2J(^{31}\text{P}^{13}\text{C})$ 18.2 Hz, $^2J(^{31}\text{P}^{13}\text{C})$ 4.0 Hz; 232.3 (CO ligands). $\delta(^1\text{H})$ (ppm): 2.38 (d) (6H), $^2J(^{31}\text{P}^1\text{H})$ 8.8 Hz, P-Me; 7.4-7.8 (m) (5H), P-Ph. ^h $\delta(^1\text{H})$ (ppm): 2.47 (d) (6H), $^2J(^{31}\text{P}^1\text{H})$ 8.8 Hz, P-Me; 7.2-7.9 (m) (5H), P-Ph. ⁱ $\delta(^1\text{H})$ (ppm): 2.38 (d) (3H), $^2J(^{31}\text{P}^1\text{H})$ 8.4 Hz, P-Me; 7.4-7.65 (m) (10H), P-Ph.

scrambling is responsible for the temperature variant NMR spectra of $[\text{WI}_2(\text{CO})_3(\text{PMe}_2\text{Ph})_2]$. The activation energy for this ligand scrambling process can be calculated to be 56.9 kJ mol^{-1} from the coalescence temperature ($+40^\circ\text{C}$) and from data taken from the low temperature limiting $^{31}\text{P}\{-^1\text{H}\}$ spectrum [5].

Dynamic behaviour was also observed in the ^1H spectrum of $[\text{WI}_2(\text{CO})_3(\text{PMe}_2\text{Ph})_2]$ where the P-methyl protons are observed as a doublet at room temperature. On cooling the sample the signals broaden and unresolved multiplets are detected indicating the freezing out of the P-methyl protons into different environments.

Analogous $^{31}\text{P}\{-^1\text{H}\}$ spectral changes to those discussed above are also observed for solutions of $[\text{MI}_2(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mo}$, $\text{L} = \text{PMe}_2\text{Ph}$; $\text{M} = \text{W}$, $\text{L} = \text{PMePh}_2$ or PPh_3). The activation energies for the ligand scrambling process of these complexes are reported in Table 1. The energy barrier to ligand scrambling in the molybdenum(II) complex, $[\text{MoI}_2(\text{CO})_3(\text{PMe}_2\text{Ph})_2]$, is significantly lower (by 5 kJ mol^{-1}) than that of the corresponding tungsten(II) complex. Varying the steric bulk of the organophosphine ligands, L, about the tungsten(II) centre of $[\text{WI}_2(\text{CO})_3\text{L}_2]$ ($\text{L} = \text{PPh}_3$, PMePh_2 , PMe_2Ph) has a small effect on ΔG^\ddagger for this ligand scrambling process with the complex containing the largest organophosphine having the smallest value for ΔG^\ddagger . This effect is small however, and may not be significant. Recently, the seven-coordinate complexes $[\text{M}(\text{CO})_2(\text{pyS})_2(\text{PMe}_2\text{Ph})]$ ($\text{M} = \text{Mo}$, W) have been synthesized and are reported to be fluxional with ΔG^\ddagger for the tungsten(II) compound being estimated to be ca. 50 kJ mol^{-1} [6]. The nature of this fluxionality, which may be relevant to the iodo compounds presented in this paper, has been discussed and as in our case, conclusive evidence concerning the exact mechanism of the ligand scrambling process was not obtained.

Close examination of the $^{13}\text{C}\{-^1\text{H}\}$ and $^{31}\text{P}\{-^1\text{H}\}$ low temperature spectra of $[\text{WI}_2(\text{CO})_3(\text{PMe}_2\text{Ph})_2]$ enables its lowest energy molecular geometry to be determined. The NMR data are fully consistent with their structure shown in Fig. 2 where the molecule has overall C_s symmetry and the ligand arrangement about the tungsten(II) centre is based upon that of a capped octahedron. The structure shown in Fig. 2 is based upon the following four NMR structural indicators.

(i) The CO resonance at $\delta 232.3 \text{ ppm}$ in the $^{13}\text{C}\{-^1\text{H}\}$ spectrum has a chemical

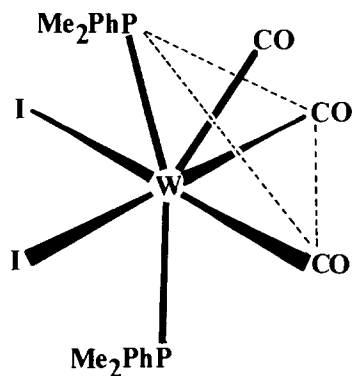


Fig. 2. Proposed low temperature molecular geometry of $[\text{WI}_2(\text{CO})_3(\text{PMe}_2\text{Ph})_2]$. The capping CO ligand is drawn capping the $[(\text{CO})_2(\text{PMe}_2\text{Ph})]$ face on the basis of steric demands. The alternative position would be capping the $[(\text{I})_2(\text{PMe}_2\text{Ph})]$ face of the octahedron.

shift typical of those generally observed for a CO ligand in a face-capping position of an octahedron [7].

(ii) The more intense CO resonance centered at δ 209.9 in the $^{13}\text{C}\{-^1\text{H}\}$ spectrum shows a small splitting (18 Hz and 4 Hz) due to $^2J(^{31}\text{P}^{13}\text{C})$ coupling. Larger $^2J(^{31}\text{P}^{13}\text{C})$ coupling are generally observed when organophosphines are *trans* to CO ligands and the magnitude of the splitting is consistent with the PMe_2Ph ligands being *cis* to the CO ligands [8,9] and therefore, mutually *trans*.

(iii) Further evidence that the PMe_2Ph ligands are *trans* to one another is obtained from $^{31}\text{P}\{-^1\text{H}\}$ spectrum where the $^2J(^{31}\text{P}^{31}\text{P})$ splitting for the AB quartet of 171 Hz is typical for such a configuration [9].

(iv) The P-methyl region of the $^{13}\text{C}\{-^1\text{H}\}$ spectrum contains two doublet resonances which is as to be expected when both prochiral phosphorus centres are in the molecular mirror plane.

Further studies of the fluxionality of other related seven-coordinate halocarbonyl complexes of molybdenum(II) and tungsten(II) are currently being investigated.

Experimental

General

Reactions were carried out by standard Schlenk techniques under N_2 . The CH_2Cl_2 was dried over CaH_2 and distilled under nitrogen before use. $[\text{Ml}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}$ or W) were prepared by standard methods [10]. PPh_3 , PMePh_2 and PMe_2Ph were obtained commercially and were used without further purification. The complexes $[\text{Ml}_2(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mo}$, $\text{L} = \text{PMe}_2\text{Ph}$; $\text{M} = \text{W}$, $\text{L} = \text{PMe}_2\text{Ph}$, PPh_3) have been previously reported [3,4] and were prepared in a similar manner to that given below for $[\text{Wl}_2(\text{CO})_3(\text{PMePh}_2)_2]$. Elemental analysis, melting points and IR data for the known compounds were in agreement with the literature data.

Preparation of $[\text{Wl}_2(\text{CO})_3(\text{PMePh}_2)_2]$

$[\text{Wl}_2(\text{CO})_3(\text{NCCH}_3)_2]$ (0.33 g, 0.53 mmol) was dissolved in dry CH_2Cl_2 (15 cm^3). To this solution was added, under a flow of nitrogen, and with constant stirring, PMePh_2 (0.22 g, 1.07 mmol). An immediate colour change from brown to green was observed, and after 10 min stirring the reaction mixture was filtered before the solvent was removed to yield the crude product as a green/yellow solid, which was recrystallised from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ as yellow crystals (0.33 g, 65%) m.pt. 160–165 °C. Elemental analysis for $\text{C}_{29}\text{H}_{26}\text{I}_2\text{O}_3\text{P}_2\text{W}$: found (calc.), C 37.8 (37.8); H 3.0 (2.8); N 0.0 (0.0)% $\nu(\text{C}=\text{O}) = 2017 \text{ cm}^{-1}$, 1944 cm^{-1} , 1914 cm^{-1} .

NMR studies

^1H , ^{13}C and ^{31}P experiments were performed on a Bruker AC 250 FT spectrometer at 250, 62.8, and 101.25 MHz, respectively. Solutions and conditions are specified in Table 1. Chemical shifts (δ) are given in ppm to high frequency (low field) of SiMe_4 for ^1H and ^{13}C , and of 85% H_3PO_4 for ^{31}P . Variable temperature ^{31}P and ^1H experiments were obtained with the aid of a standard variable temperature accessory. Coalescence temperatures are accurate to $\pm 5^\circ\text{C}$.

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