- EXPERIMENT AIM

  The aim of this experiment was to synthesize one isomer of $[Mo(CO)_4(pip)_2]$ and both possible isomers of $[Mo(CO)_4(PPh_3)_2]$, and explore stereochemistry of these compounds through IR spectroscopic studies.

- PRODUCT YIELD

Product		Mass/g	yield	Literature yield
$[Mo(CO)_4(pip)_2]$ (1)		0.961	$\frac{0.961}{(\frac{0.998}{264}) \times 378.28} = 67.2\%$	91%
$[Mo(CO)_4(PPh_3)_2]$ (2)		0.48	$\frac{0.48}{(\frac{0.500}{378.28}) \times 732.55} = 49.6\%$	≥50%
$[Mo(CO)_4(PPh_3)_2]$ (3)	Crude	0.27	$\frac{0.270}{0.300} = 90\%$	55%
	Pure	0.16	$\frac{0.16}{0.270} = 59.3\%$	

  (Due to poor yield of step 2, only 0.3g of (2) was used to in step 3.)

  (reference[1])

  Yields obtained were lower than those of literature, and that might be caused by inaccurate apparatus and small quantities of starting materials.

- IR SPECTRA

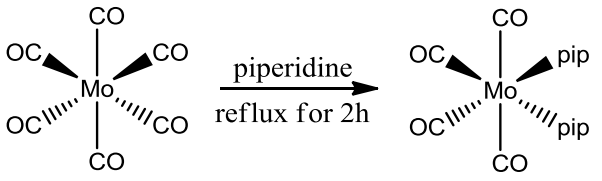
  (Spectra of the three products seen in APPENDIX)

Product	CO stretching / cm^{-1}	Stereochemistry	Point group
$[Mo(CO)_4(pip)_2]$ (1)	2011.94, 1889.91, 1839.13, 1777.82	Cis-	C_{2v}
$[Mo(CO)_4(PPh_3)_2]$ (2)	2013.77, double peaks at 1884.06	Cis-	C_{2v}
$[Mo(CO)_4(PPh_3)_2]$ (3)	1890.17	Trans-	D_{4h}

  Number and positions of peaks of each product in CO stretching region match those of literature, though two stretches at 1884.06 cm^{-1} in the second spectrum were rather close to each other and hence could be hardly observed.

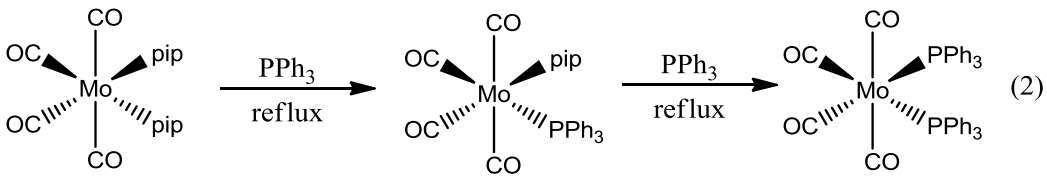
- REACTION SCHEME

  (i) Formation of $[Mo(CO)_4(pip)_2]$ (1)



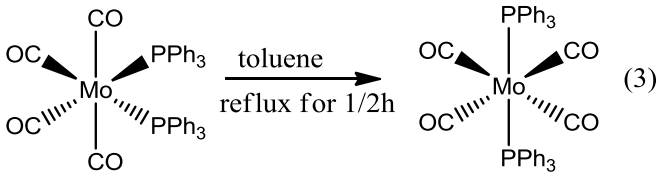
(1)

  (ii) Formation of $[Mo(CO)_4(PPh_3)_2]$ (2)



(2)

  (iii) Formation of $[Mo(CO)_4(PPh_3)_2]$ (3)



(3)

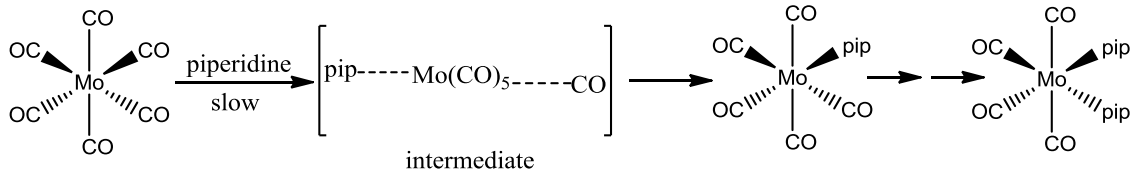
- MELTING POINTS

	1st drop appeared /°C	completely molten /°C	literature M.P. /°C
$[Mo(CO)_4(pip)_2]$ (1)	125	129	98
$[Mo(CO)_4(PPh_3)_2]$ (2)	156	158	160
$[Mo(CO)_4(PPh_3)_2]$ (3)	168	170	168

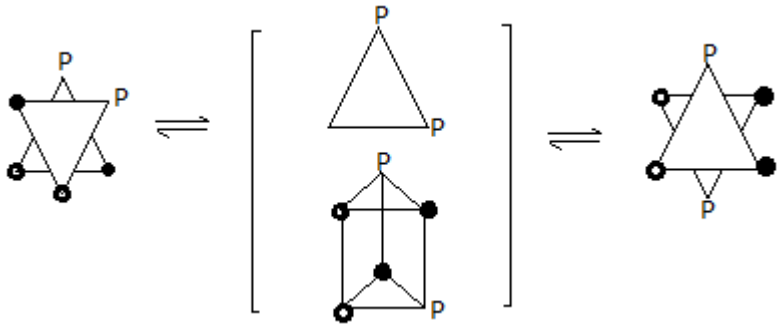
(reference[4])

Melting points obtained were similar to those of literature.

- Metal carbonyl substitution reactions undergo S_{N2} substitution, that is, associative mechanism. For example, formation of $[Mo(CO)_4(pip)_2]$ from $[Mo(CO)_6]$:



- Instead of breaking Mo-P bonds, $[Mo(CO)_4(PnBu_3)_2]$ transforms to a trigonal-prismatic intermediate or transition state in order to achieve lowest energy mechanism of isomerisation.



Where ○ and ● represent equatorial and axial CO ligands respectively.

As shown above, the two triangular octahedral faces rotate 60° anticlockwise to form another isomer. However, PPh_3 ligands are too bulky to undergo this kind of mechanism, and cleavage of Mo-P bonds is more favourable.

- According to assays examing the isomerisation equilibrium of $[Mo(CO)_4(PR_3)_2]$ derivatives, reaction to the right is more favourable. That is, the trans- isomer of $[Mo(CO)_4(PR_3)_2]$ is thermodynamically more stable.

$$\textbf{cis-}[Mo(CO)_4(PR_3)_2] \rightleftharpoons \textbf{trans-}[Mo(CO)_4(PR_3)_2]$$

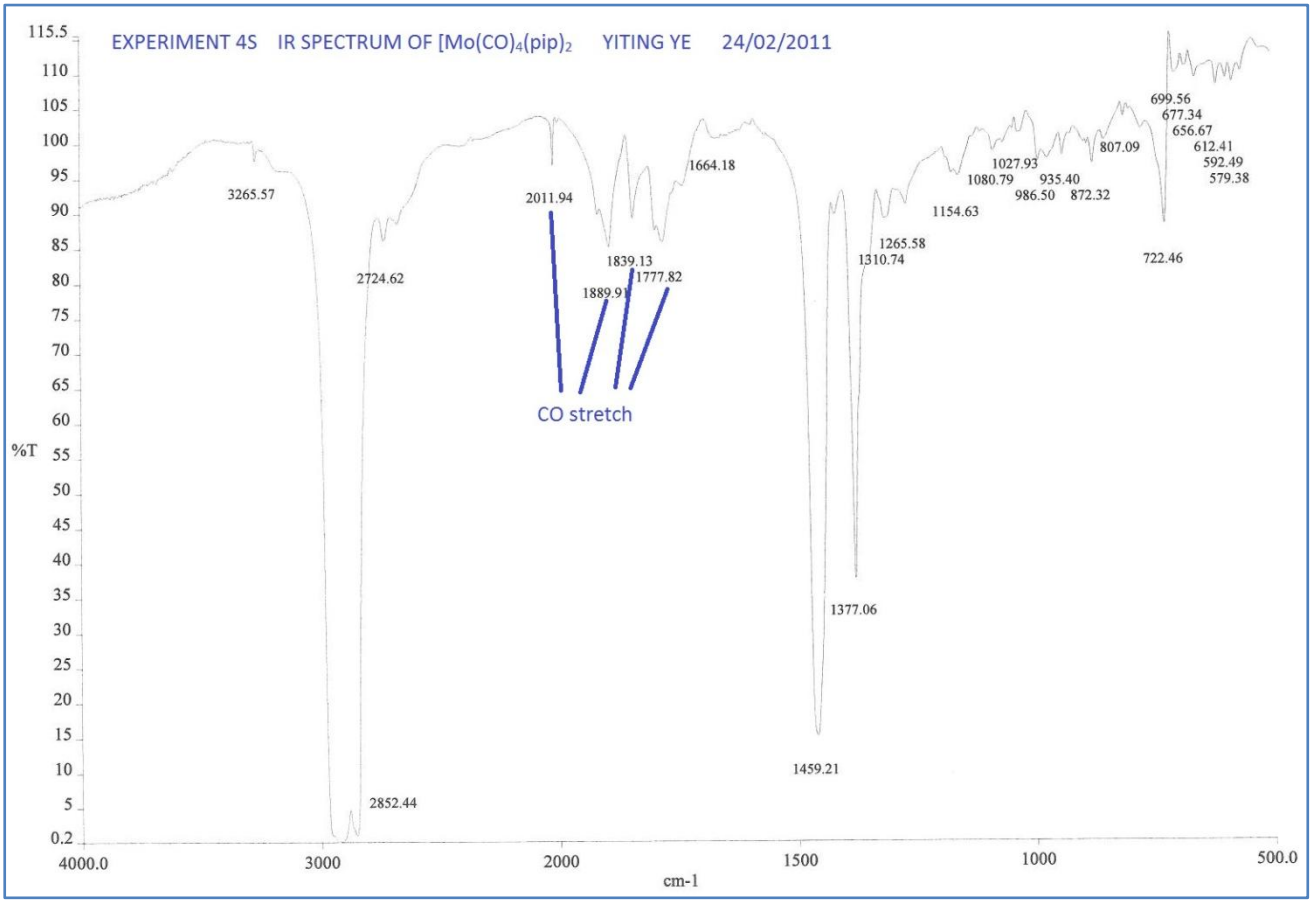
- CONCLUSION

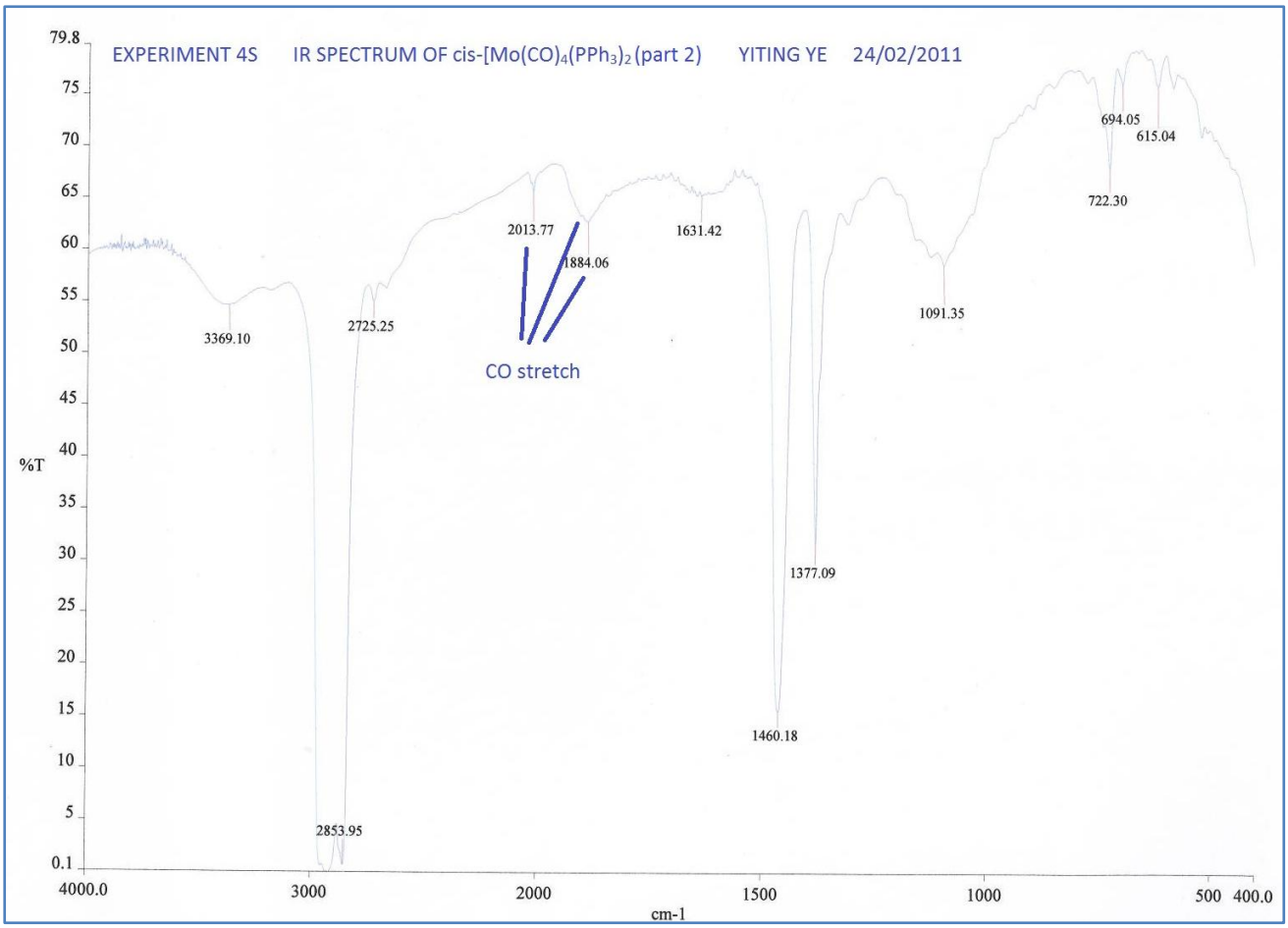
In this experiment, a bright yellow powder, a pale yellow powder and an off-white powder were obtained as cis-$[Mo(CO)_4(pip)_2]$, cis-$[Mo(CO)_4(PPh_3)_2]$ and trans-$[Mo(CO)_4(PPh_3)_2]$ respectively. Molecular structures were observed by analysing IR spectra of these compounds, and the results were similar to the literature ones. Also, physical properties of the three complexes (e.g. melting point, colour) were as expected. However, the yields were relatively poor due to small amount of starting materials as well as inaccuracy caused by apparatus.

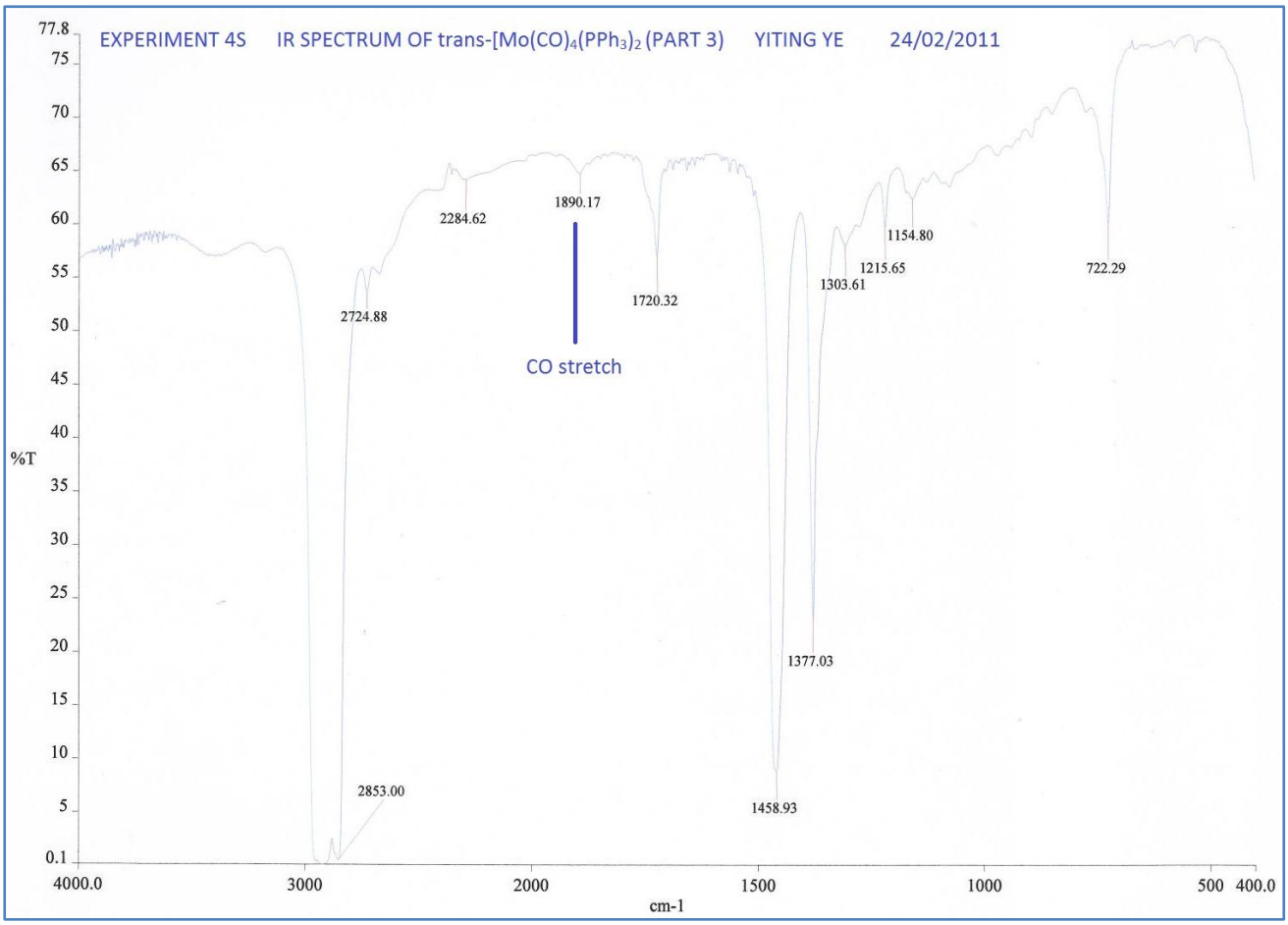
- REFERENCE

1. **A Convenient Synthesis of cis-$Mo(CO)_4L_2$ Derivatives (L = Group 5A Ligand) and a Qualitative Study of Their Thermal Reactivity toward Liggand Dissociation**, Donald J. Darensbourg and Robin L. Kump, 1978
2. **Phosphine-substituted carbonyl halide complexes of chromium and molybdenum**, A.D. Allen and P.F. Barrett, 1967
3. **Intramolecular Isomerization of and Octahedral Complex: Bis(tri-n-butylphosphine) molybdenum Tetracarbonyl**, Donald J. Darenbourg, 1978
4. **Dinuclear group VIB metal carbonyl complexes bridged by bis(diphenykphosphino) aklkanes**, Mohammad Elkhateeb, Khalil J. Asali and Musa M.Musa, 2001

- APPENDIX




EXPERIMENT 4S IR SPECTRUM OF cis-[Mo(CO)4(PPh3)2 (part 2) YITING YE 24/02/2011
%T
cm-1
3369.10
2725.25
2853.95
2013.77
1884.06
CO stretch
1631.42
1460.18
1377.09
1091.35
722.30
694.05
615.04


EXPERIMENT 4S IR SPECTRUM OF trans-[Mo(CO)4(PPh3)2 (PART 3) YITING YE 24/02/2011
77.8
75
70
65
60
55
50
45
40
%T
35
30
25
20
15
10
5
0.1
4000.0
3000
2000
1500
1000
500
400.0
cm-1
2724.88
2284.62
1890.17
1720.32
CO stretch
1303.61
1215.65
1154.80
722.29
1377.03
2853.00
1458.93