Experiment 4S

Identification of Stereochemical (Geometrical) Isomers of $[Mo(CO)_4(L)_2]$ by Infrared Spectroscopy

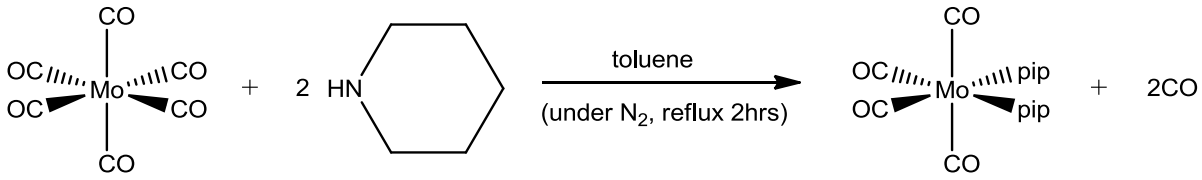
Introduction and aims

In this experiment, molybdenum carbonyl complexes were prepared and their stereochemistry identified by the use of infrared spectroscopy. The first prepared was $[Mo(CO)_4(pip)_2]$ which can be made relatively conveniently and inexpensively and is a useful route to deriving other $[Mo(CO)_4(L)_2]$ complexes by ligand displacement.[1] The other compounds prepared were expected to be stereoisomers, the first being prepared by displacement of the piperidine (NHC_5H_{10}) ligands by triphenylphosphine (PPh_3) to give $[Mo(CO)_4(PPh_3)_2]$ and the second prepared by thermal isomerisation of this product.

Experimental

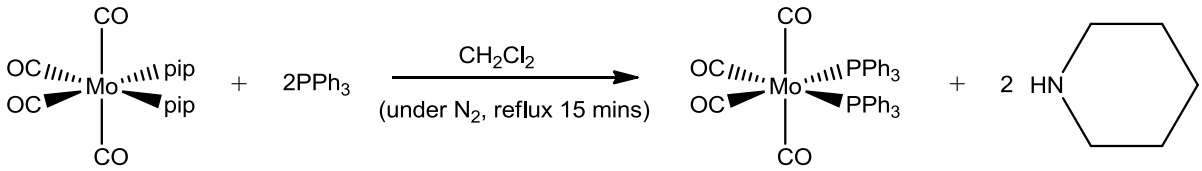
(The stereochemistry of the complexes was determined by use of the IR spectra obtained, as discussed below)

1) Preparation of cis-$[Mo(CO)_4(pip)_2]$



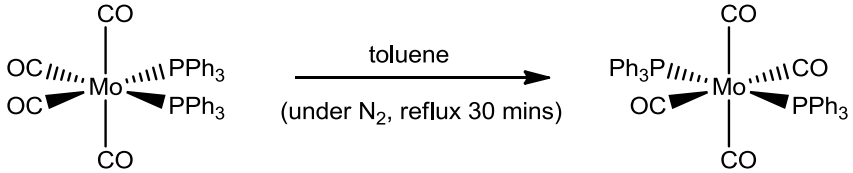
This part was repeated once as a result of an unsuccessful attempt to obtain the PPh_3 complex in the second part of the experiment. The product initially obtained after filtration and drying was a bright yellow solid composed of fine crystals. After the second attempt, the product was slightly darker in colour but otherwise very similar. The IR spectra for both were identical in terms of the relevant regions so it is reasonable to assume that they were the same compound despite different appearances. The yields obtained in the first and second attempts respectively were 58.9% and 74.5%. These compare with a literature value of 78%.[2] This is very close to what was obtained the second time, although a different method was used in the literature. A similar method using heptanes and a longer reflux yielded 91%.[1]

2) Preparation of cis-$[Mo(CO)_4(PPh_3)_2]$



This part resulted in the isolation of a quantity of pale yellow flaky crystals in an overall yield of 65.4%. The yield reported in literature was 61%[2] although again a slightly different method involving microwave assisted reflux was used.

3) Preparation of trans-$[Mo(CO)_4(PPh_3)_2]$



The product after isomerisation was an off-white powdery solid in 49.7% yield. This again compares favourably with the product obtained from the microwave assisted method in literature which was reported to give 42% yield[2] and a very similar method to the one used which resulted in a 55% reported yield.[1]

Results and Discussion

Looking at the C=O stretching regions of the IR spectra obtained, it was possible to determine the stereochemistry of the complexes. For $[Mo(CO)_4(pip)_2]$ prepared in part one, there are four peaks clearly visible at 2011.9cm^{-1},

1890.0cm^{-1}, 1839.4cm^{-1} and 1777.9cm^{-1}. This shows that the complex is unsymmetrical resulting in the C=O stretches absorbing at different energies. It is therefore reasonable to conclude that this is the cis-isomer for which four peaks would be expected corresponding to the different vibrations. If piperidine is considered a point ligand, the cis-complex has C_{2v} point group (see **Fig 1** for symmetry elements).[3]

For the $[Mo(CO)_4(PPh_3)_2]$ complex produced in part two, there are two clear peaks in the C=O stretching region at 2013.2cm^{-1} and at 1889.6cm^{-1}. However the peak at 1889.6cm^{-1} is very broad and it is likely that this is the result of overlapping signals, as there is a slight shoulder visible at about 1800cm^{-1}. In addition, it is expected that the ligand displacement reaction to convert $[Mo(CO)_4(pip)_2]$ to$[Mo(CO)_4(PPh_3)_2]$ would result in a product of the same stereochemistry as it is more facile for the ligands to undergo a direct substitution reaction under the relatively mild conditions and short reaction time.[1] Therefore it is also reasonable to conclude that product two is the cis-isomer. This also has C_{2v} point group if the PPh_3 ligands are regarded as point ligands.

The isomerisation product in part three would be expected to have only one peak for C=O stretching as all the carbonyl groups should be identical in the symmetrical trans-product. This does appear to be the case as there is one very sharp peak at 1890cm^{-1}. However some very small peaks are also visible on either side of this main peak which indicates that there may be some remaining cis-geometry product meaning that the isomerisation was not entirely complete. This is only a very small proportion of the product as the intensity of these peaks is tiny. In contrast to the cis-isomers, the trans-product has D_{4h} symmetry when PPh_3 is considered a point ligand.[3] It has a much higher symmetry (see **Fig 2** for symmetry elements).

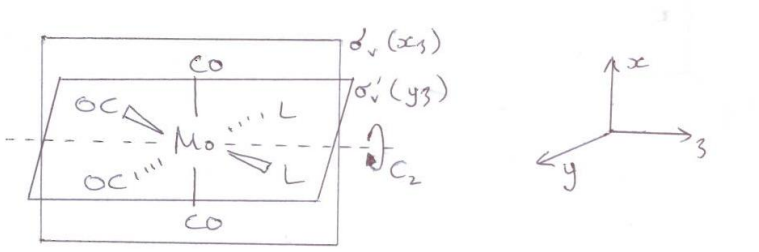


Fig 1: Symmetry elements of the cis-isomers where L=pip or L=PPh_3

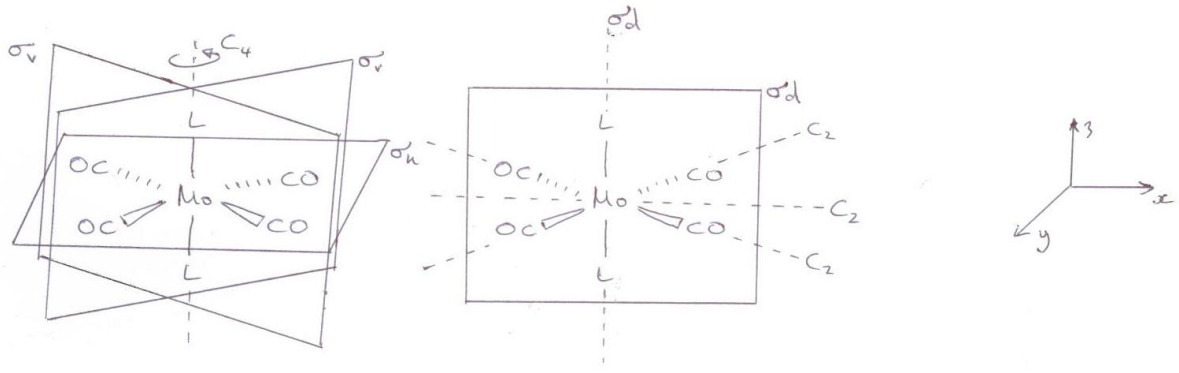


Fig 2: Symmetry elements of the trans-isomer where L=PPh_3

Decomposition points

It was found that none of the products obtained in this experiment melted upon heating but they did appear to decompose.

For $[Mo(CO)_4(pip)_2]$ the solid was heated and appeared to start darkening in colour at about 105°C. From 125°C there appeared to be no further change in colour and the compound remained a light brown colour until about 160°C when it again began darkening, turning black and tarry in appearance at about 196°C. From this it seems that the decomposition temperature was around 120-125oC when the colour had changed fully prior to extreme heating. The literature value given is 120°C[4] which is in some agreement with the findings.

For the cis-$[Mo(CO)_4(PPh_3)_2]$ complex, the solid began to darken in colour around 100°C and between 137 and 144°C it clumped together in a mass. At 207°C it had become black and tarry as above. The decomposition point was taken

to be between 137°C and 144°C when there appeared to be little more change in the appearance of the compound. The literature value given is 148-150°C[5] which shows the value obtained to be slightly lower than expected. This may be due to the presence of some impurities.
The decomosition point for trans-$[Mo(CO)_4(PPh_3)_2]$ was difficult to determine as it began to darken in colour from 160°C before appearing to melt at 185-191°C. The reported literature value for decomposition is 210-220°C[2] which is significantly higher than observed but this is very likely to be due to incomplete isomerisation resulting in a mixture of the cis- and trans- isomers. This is supported by the evidence in the C=O stretching region of the IR spectrum for this compound.

Substitution mechanism
The substitution mechanism for the metal carbonyl is likely to be dissociative as all the complexes are electronically saturated. This means that they satisfy the 18-electron rule and an associative mechanism requiring the co-ordination of another ligand and addition of further electrons would be unfavourable.

Isomerisation of $[Mo(CO)_4L_2]$
When L=PPh3, the isomerisation reaction occurs dissociatively with Mo-P bond cleavage results in trans-$[Mo(CO)_4(PPh_3)_2]$ being the exclusive product. When L=P^nBu_3 then it is found that a 15%:85% mixture of cis-:trans-$[Mo(CO)_4(P^nBu_3)_2]$ results. This was produced without any bond breaking which implies that this is the lower energy mechanistic pathway. This can be explained by concluding that the complex must pass through a trigonal prismatic transition state which allows an interconversion with no bond cleavage. This rotational movement is very sterically hindered for more bulky ligands such as PPh_3 so they must undergo a dissociative mechanism.[6]

Relative stability of isomers
The trans- isomer is more thermodynamically stable than the cis-isomer due to the steric interactions between the bulky PPh_3 ligands. They therefore prefer to be further apart to reduce this effect. This explains why the isomerisation reaction of $[Mo(CO)_4(PPh_3)_2]$ occurs with almost 100% conversion. The cis-isomer is the kinetic product due to the lower energy barrier for bonding of the incoming PPh_3 ligand to the square pyramidal 5-coordinate intermediate species produced by the dissociative mechanism.[7] In the 5-coordinate species, the PPh_3 ligand prefers to take an axial position.[6]

Conclusion
Using the information provided by the IR spectra of the products, it can be concluded that the $[Mo(CO)_4(pip)_2]$ complex synthesised in this experiment has cis- geometry, as does the $[Mo(CO)_4(PPh_3)_2]$ substitution product. This complex can undergo thermal isomerisation to afford the trans- product which is also easily identified by examining the IR spectrum. The trans-isomer is the thermodynamic product and hence more stable but has a higher activation energy to overcome than the cis-isomer due to the dissociation mechanism of isomerisation.

References

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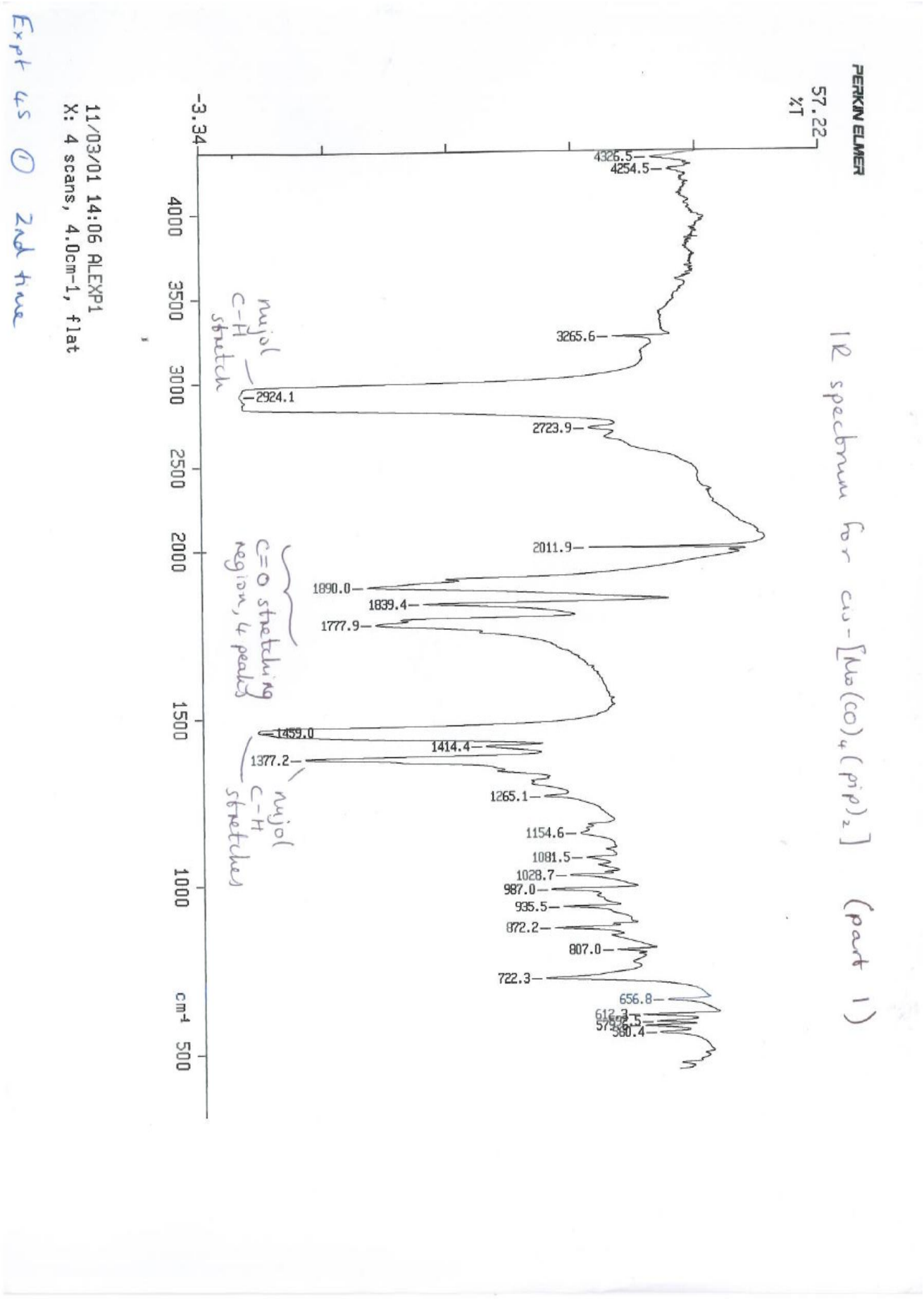
2) Ardon M., Hayes P. D., Hogarth G., *J. Chem. Ed.*, 2002, 79(10), pp1249-1251
3) Darensbourg M. Y., Darensbourg D. J., *J. Chem. Ed.*, 1970, 47(1), pp33-35
4) Strohmeier W., Gerlach K. and Hobe D. V., *Chem. Ber.*, 1961, 94, pp164
5) Allen A. D., Barrett P. F., *Can. J. Chem*., 1968, 46, pp1649
6) Darensbourg D. J., *Inorg. Chem*., 1979, 18(1), pp14-17
7) Darensbourg D. J., Graves A. H., *Inorg. Chem.*, 1979, 18(5), pp1257-1260


PERKIN ELMER
57.22
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4254.5
3265.6
2924.1
2723.9
2011.9
1890.0
1839.4
1777.9
1459.0
1414.4
1377.2
1265.1
1154.6
1081.5
1028.7
987.0
935.5
872.2
807.0
722.3
656.8
612.3
580.4
4000
3500
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500
cm-1
nujol C-H stretch
C=O stretching region, 4 peaks
nujol C-H stretches
IR spectrum for cis-[Mo(CO)4(pip)2] (part 1)
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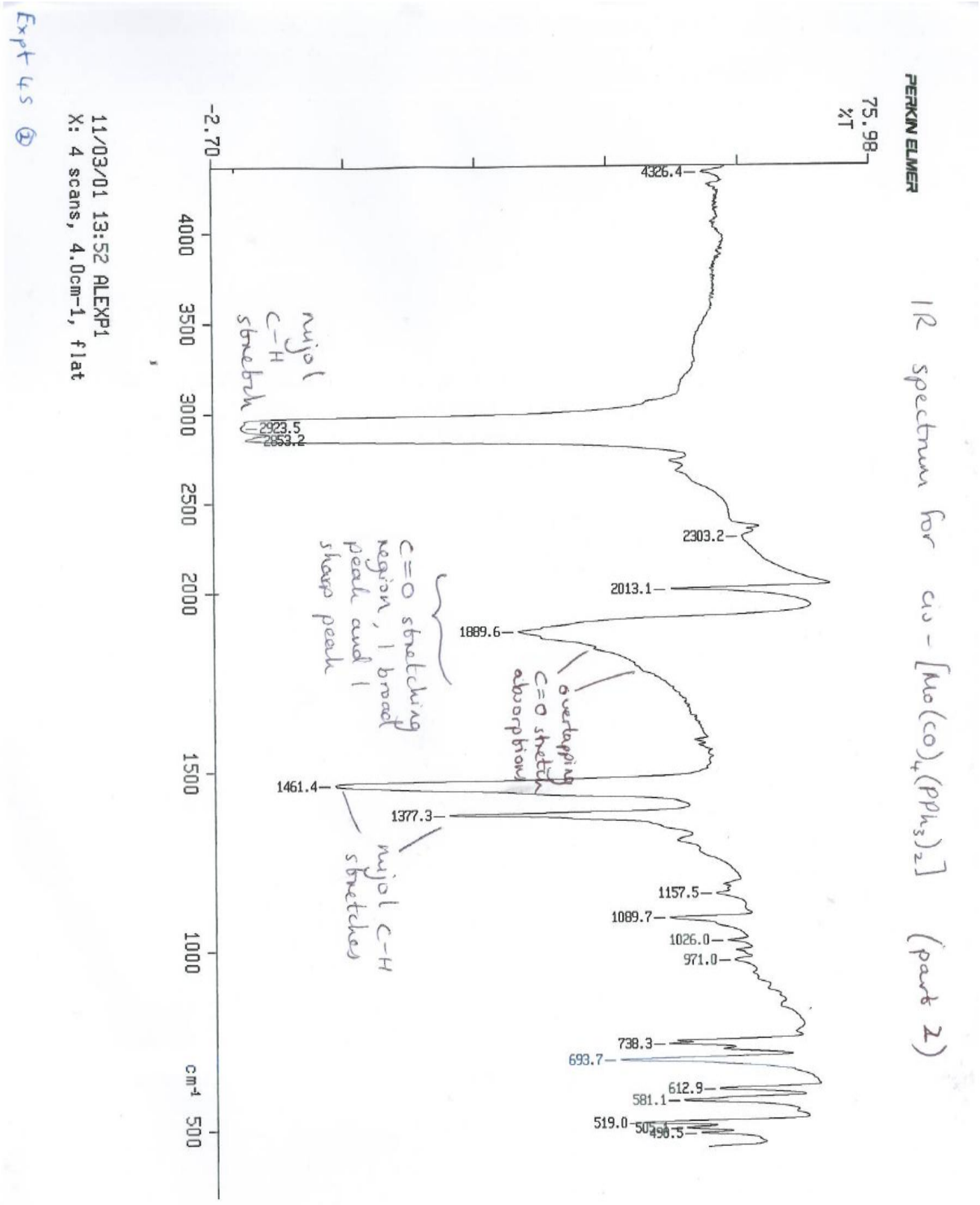
X: 4 scans, 4.0cm-1, flat
Expt 45 ① 2nd time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11/03/01 13:52 ALEXP1
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-2.70
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1157.5
1089.7
1026.0
971.0
738.3
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612.9
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4000
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cm-1
nujol C-H stretch
C=O stretching region, 1 broad peak and 1 sharp peak
overlapping C=O stretch absorptions
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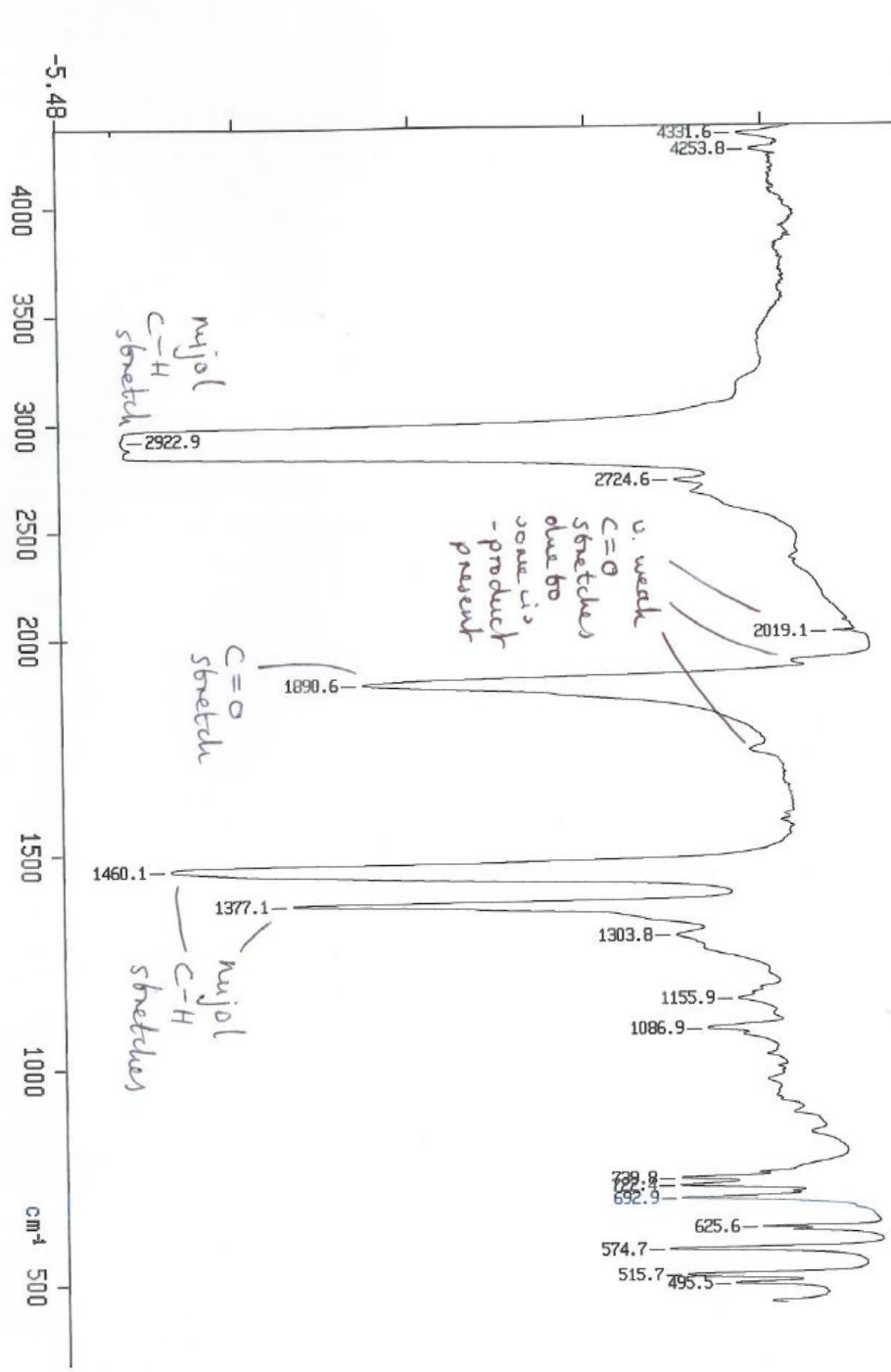
IR spectrum for cis - [Mo(CO)4(PPh3)2] (part 2)



IR spectrum for trans-[Mo(CO)$_4$(PPh$_3$)$_2$] (part 3)

Expt 45 (3)

11/03/01 15:54 ALEXP1
X: 4 scans, 4.0cm-1, flat