

INTRODUCTION

- Conformation rearrangements are well known in five coordinate species, involving interconversion between square pyramid and trigonal bipyramidal geometries. See *R. R. Holmes, Acc. Chem. Res., 1979, 12, 257* and *R. R. Holmes and J. A. Deiters, J. Am. Chem. Soc, 1977, 99, 3318*.
- Four coordinate metals have a tendency to adopt one of two geometries: square planar or tetrahedral. However, these geometries can be affected by external factors, e.g. substituents, and thus not all metal complexes have idealised conformations. The geometries can be described using the four cis-ML₂ angles as well as the two trans-ML₂ angles. Clearly these would be expected to be around 90° and 180° respectively for square planar complexes while all angles would be around 109.5° for tetrahedral complexes.
- The 3D search facility available in *ConQuest* can be used to facilitate the study of such systems and potential interconversion ‘transition states’.

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This module is divided into the following sections:

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OBJECTIVES

- Search for 4-coordinate transition metal complexes in the CSD and for each hit structure retrieve the values of the ML_2 angles (four 'cis' and two 'trans').
- Determine the preferred geometries adopted by 4-coordinate transition metal complexes by analysing the collected geometric data.
- Investigate some structures with non-idealised coordination geometries.

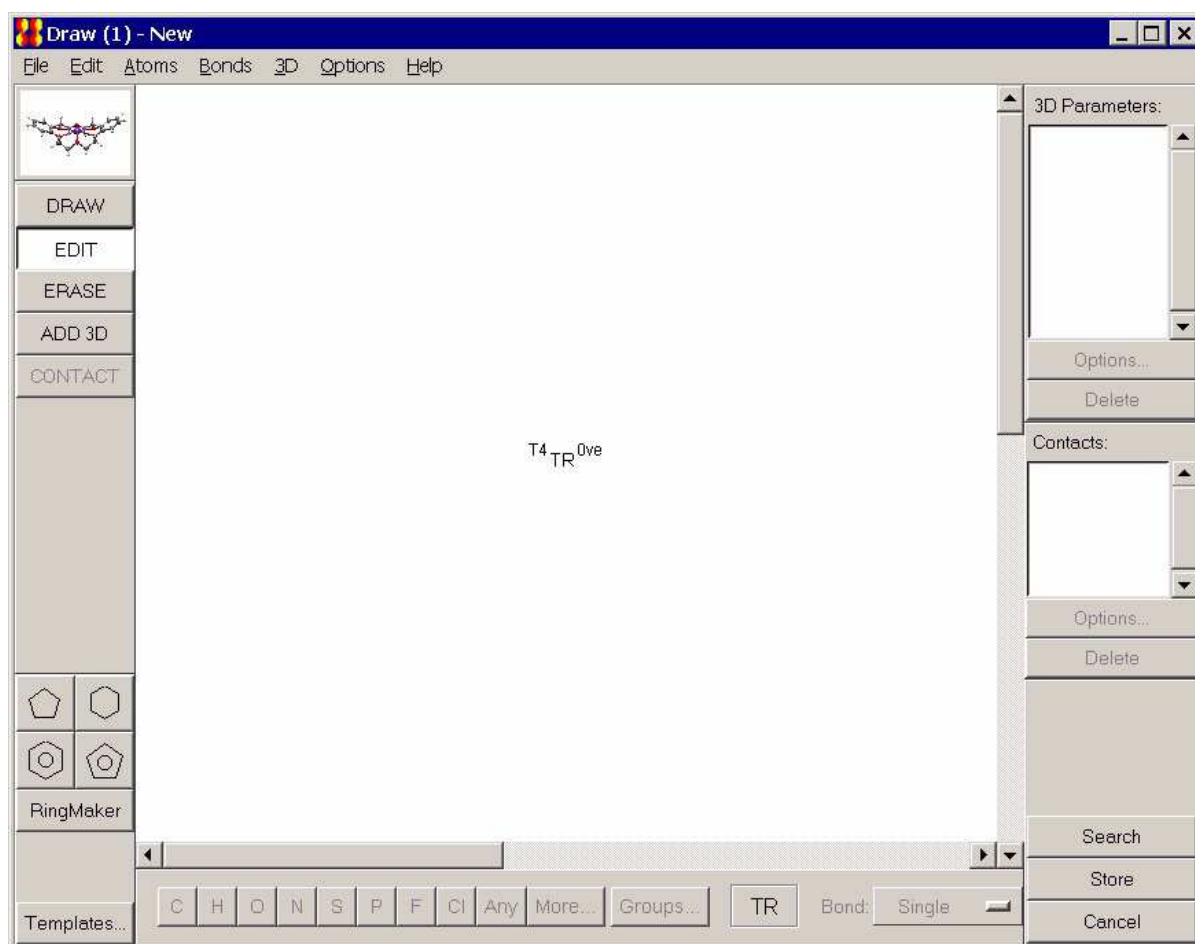
GETTING STARTED

- This module requires full access to the Cambridge Structural Database System. Specifically, the following software components will be used:
 - *ConQuest*, for search and retrieval of crystal structure data.
 - *Vista*, for numerical analysis of ConQuest search results.

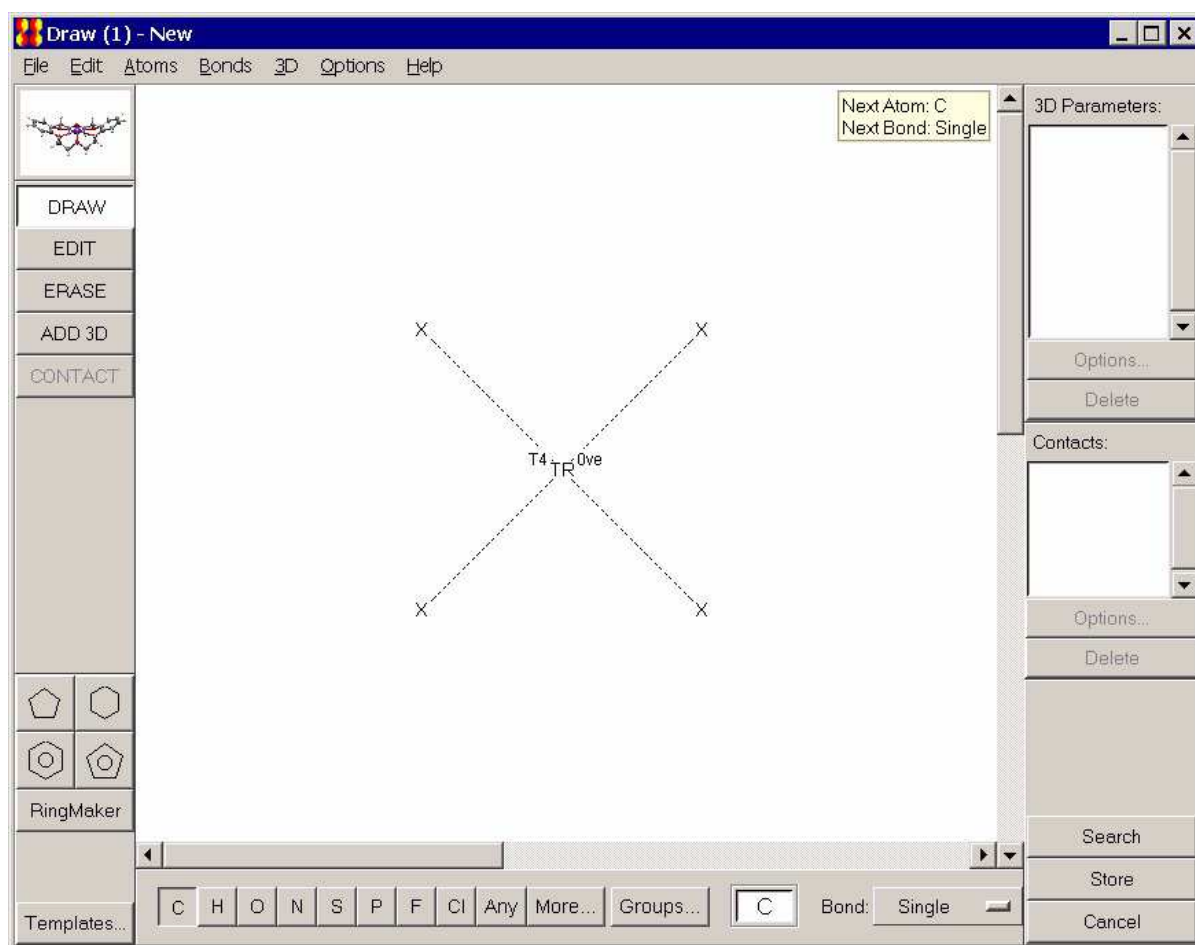
1 STEPS REQUIRED

1.1 Find 4-coordinate transition metal complexes in the CSD

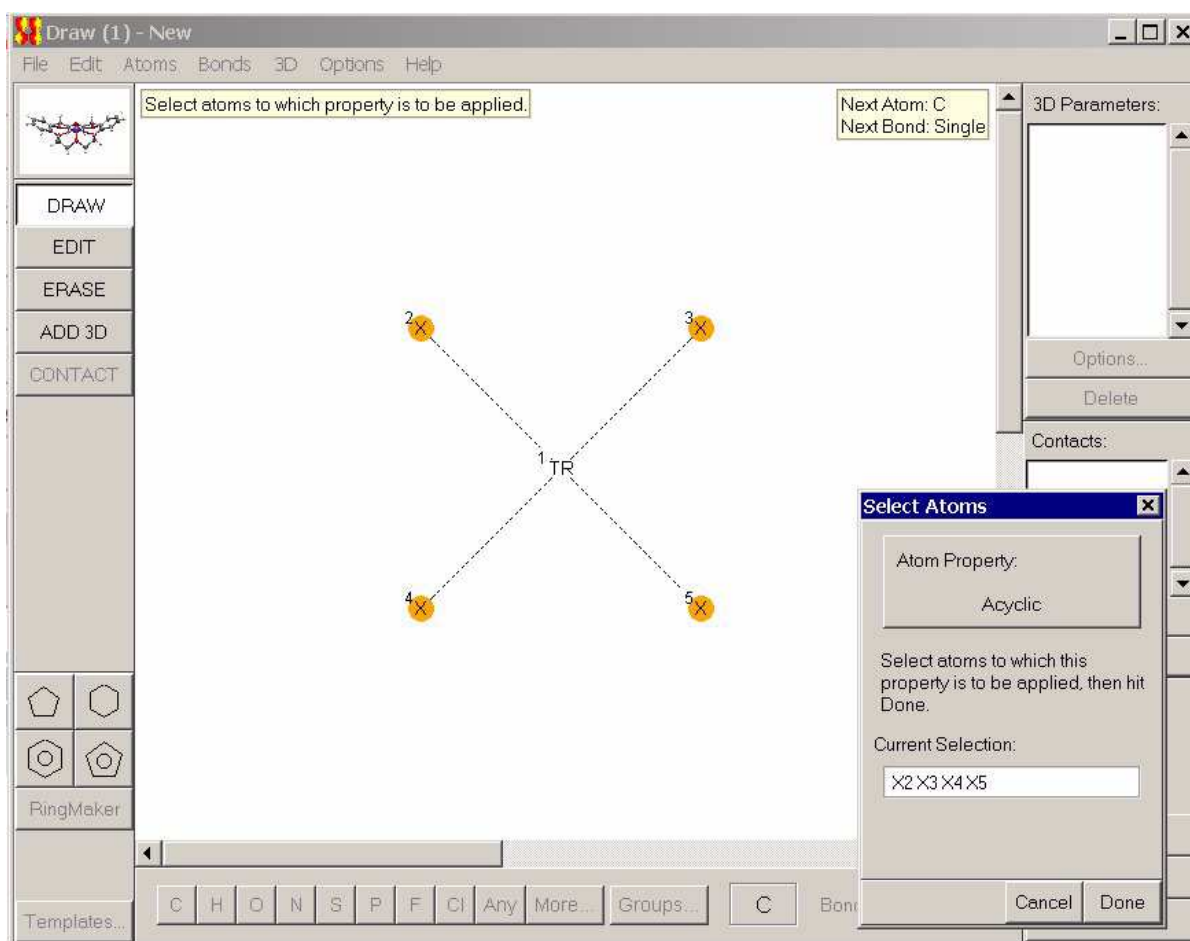
- Start ConQuest and hit the **Draw** button to open the *Draw* window.
- Click on the **More...** button at the bottom of the *Draw* window and select **Any Transition Metal** from the resulting menu. Then click in the display area to draw the transition metal *TR* atom.
- To specify that the transition metal must be uncharged right click on *TR* and select **Charge** followed by **Zero** from the resulting menus. This will produce a superscript *0ve* on the right hand side of the *TR*.
- To specify that the metal must have 4 bonded atoms (i.e. be 4 coordinate) right click on *TR* and select **Number of Bonded Atoms**, followed by **4** from the resulting menus. This will create a label *T4* which should appear on the left hand side of *TR*.



- To specify that the transition metal can be bound to four ligands of *any* type click on the **Bond** button at the bottom of the *Draw* window and select **Any** from the resulting menu. Next, click on the atom type **Any** button at the bottom of the *Draw* window. Then, draw four *Any* atoms, which are represented by the letter *X*, and connect them to the metal with the bond type *Any*.



- In this example we are only interested in monodentate ligands which are not connected or linked, therefore to specify that the *X* atoms must be acyclic click on **Atoms** in the main menu, then **Cyclic** followed by **Acyclic** from the resulting menus. Select all four *X* atoms by clicking on them in the *Draw* window.



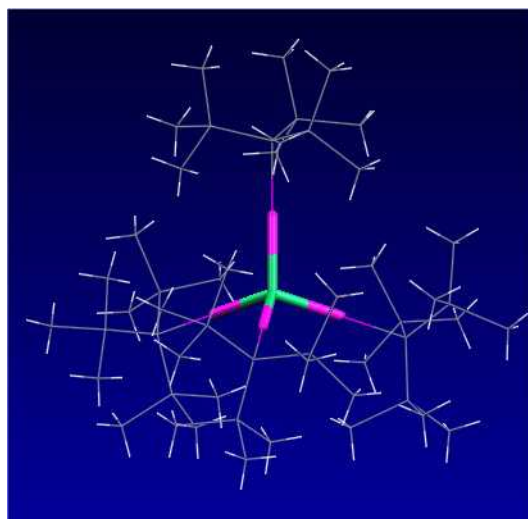
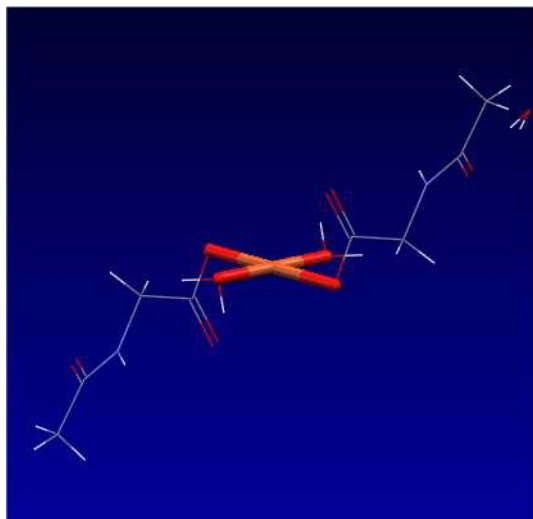
- Once you have identified all of the acyclic atoms, click **Done**.
- Next, to specify that the *X* atoms must have no direct cyclic links click on **Bonds** in the main menu and select **Exclude**. Click on the *Direct Links* tab, then once again select all of the ligand *X* atoms. Doing this means that none of the *X* atoms will be directly linked to one another. Once you have selected all of the *X* atoms, click on **OK**.

1.2 Run the search

- Hit the **Search** button at the bottom right-hand corner of the drawing window.
- A *Search Setup* window will pop up which allows you to specify which database you wish to search and also allows you to add filters to your search. For the purposes of this search, this will be left as it is. Hit **Start Search** at the bottom left of the screen to begin the search.
- As soon as you start the search, the ConQuest interface moves to the *View Results* pane. After a few moments, the reference codes (*refcodes*) of hit structures will start to appear in the list on the right-hand side. How many hits are found?
- Click on any structures refcode to see its chemical diagram, the transition metal substructure will be highlighted in red. Alternatively, use the << and >> buttons to scroll through some of the hits.

Select *3D Visualiser* from the tabs on the right hand side of the *View results* pane and inspect some of the hits. What metal coordination geometries are observed?

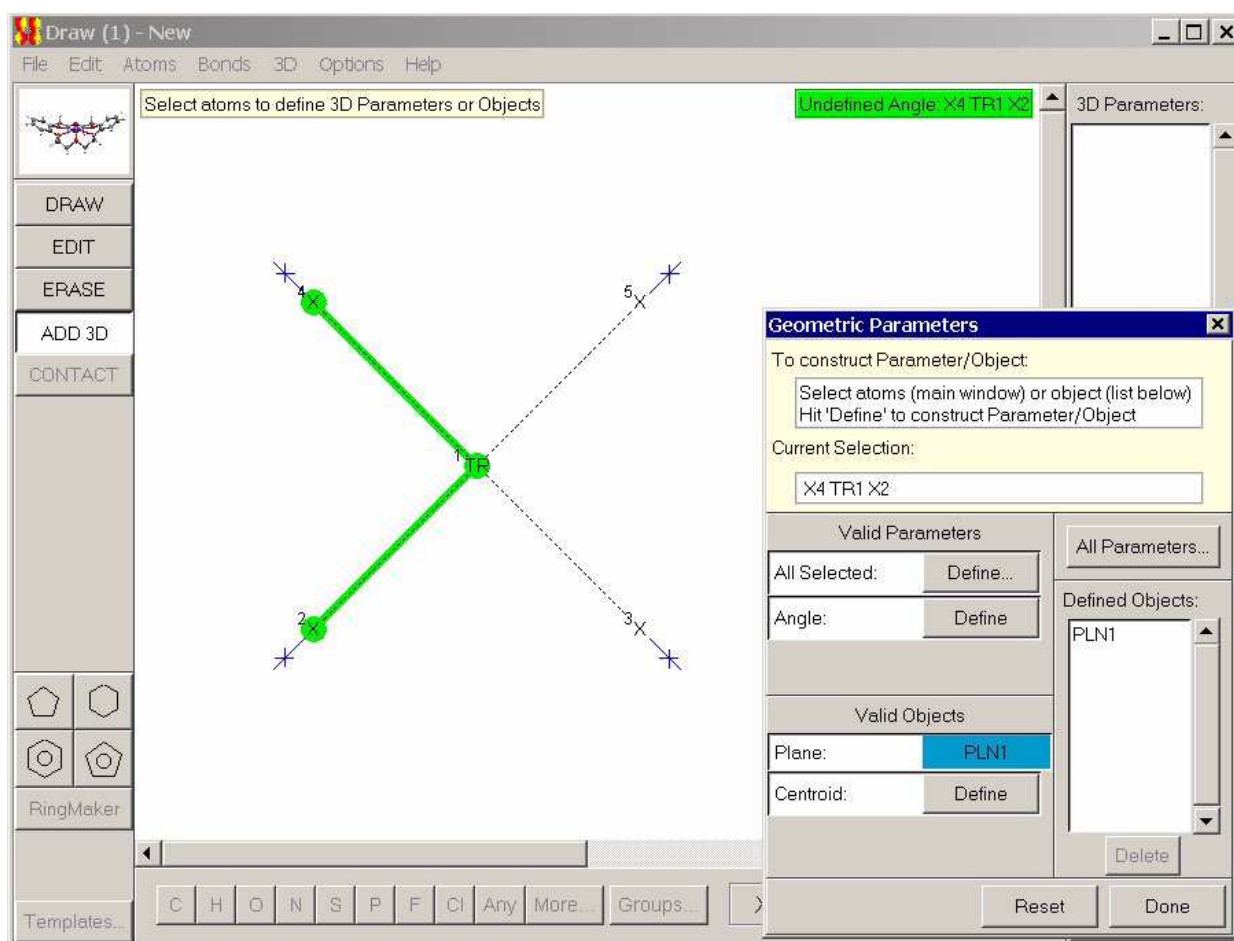
- You should notice that the hits predominantly contain structures with square planar (e.g. *AGLCUD* and *BDMIUP*) and tetrahedral (e.g. *CETXOO* and *FOJBUB02*) geometries.



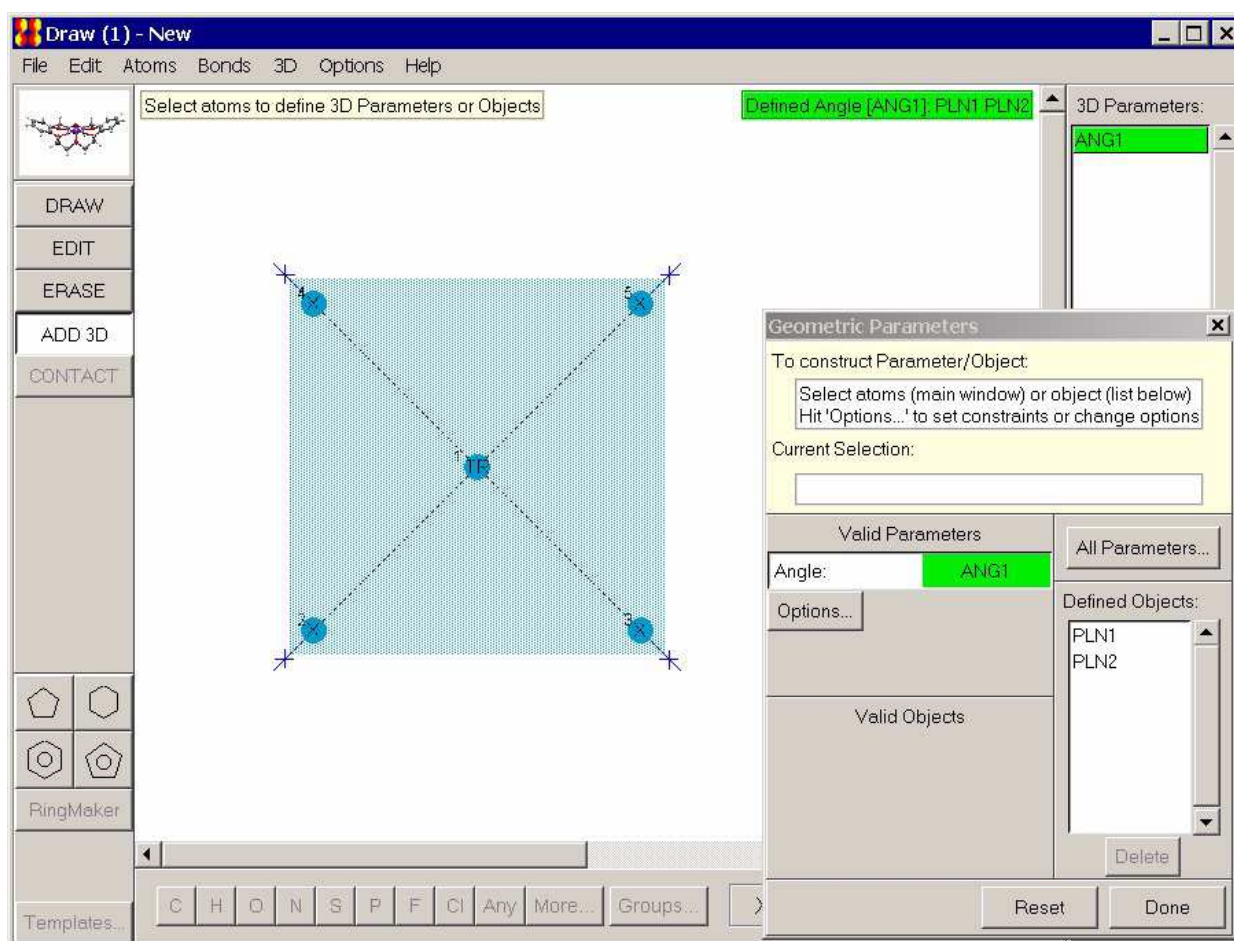
left: square planar geometry in AGLCUD; right: tetrahedral geometry in CETXOO

1.3 Define geometric parameters

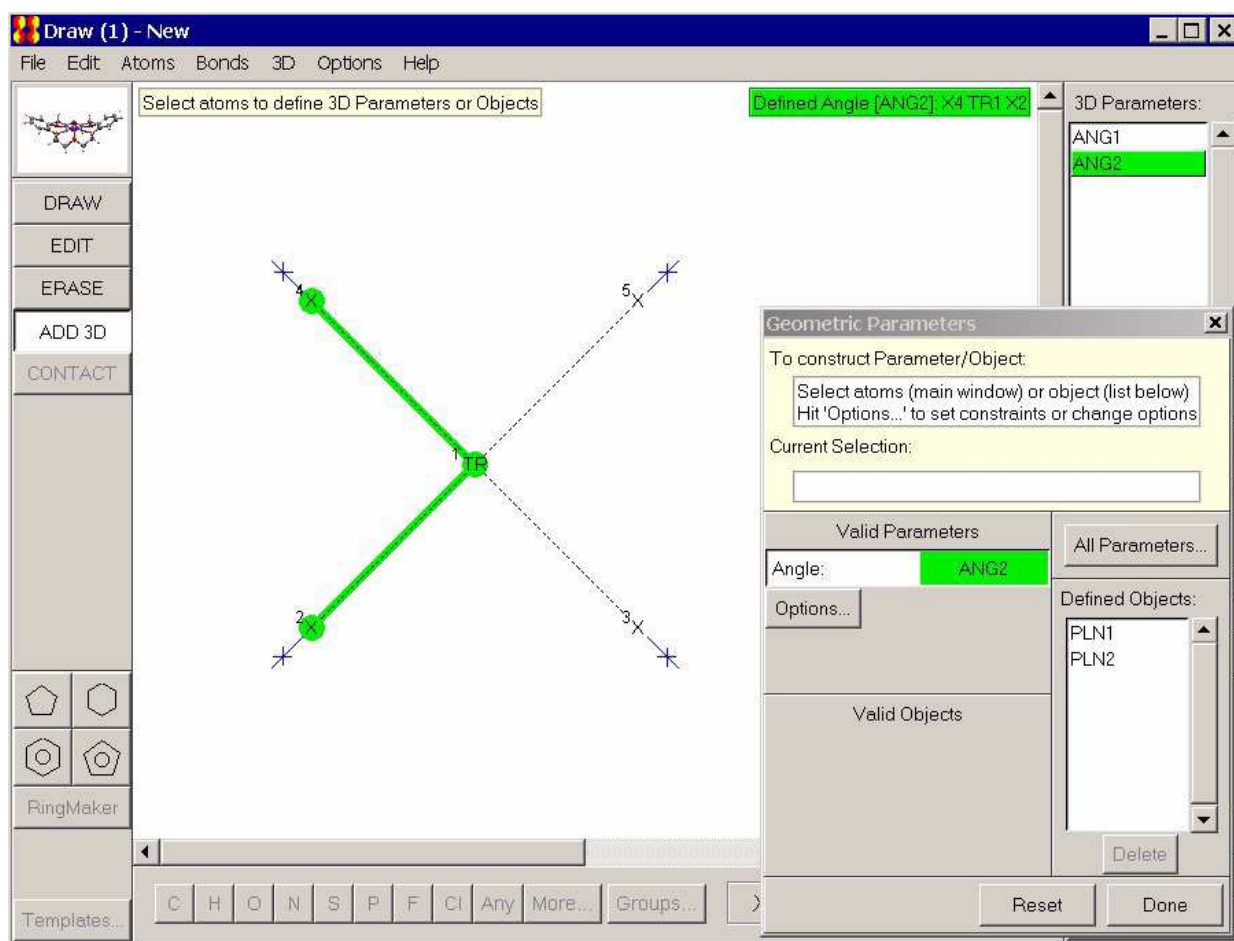
- In order to analyse the 3D geometry of our 4-coordinate transition metal complexes we need to define some geometric parameters. The values of defined parameters can then be retrieved for each hit structure and analysed collectively.
- We will start by defining the angle between two unique ML_2 planes. Return to the *Build Queries* pane and click on **Edit** next to the query you just submitted. This should take you back to the *Draw* window. Click on the **ADD 3D** button on the left of the *Draw* window then select one of the *X* atoms, then the *TR*, then the next *X* atom, and finish by hitting the **Define** button next to *Plane* in the *Geometric Parameters* window.



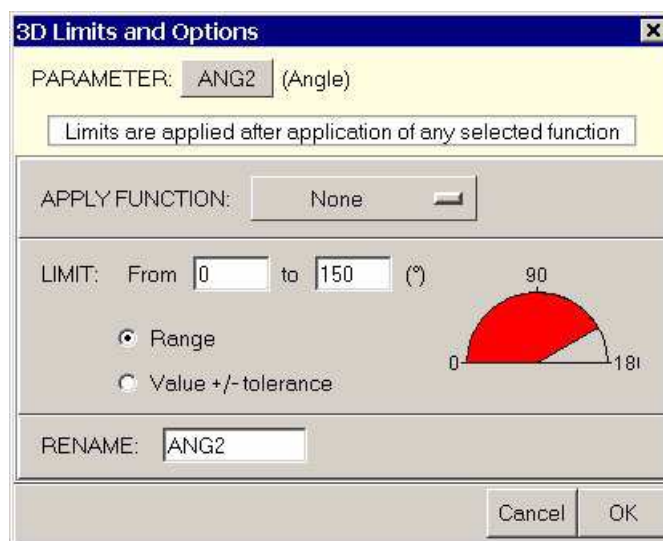
- Repeat with the remaining two ligand atoms and the transition metal to define the second plane in the same way. *PLN1* and *PLN2* should now have appeared in the *Defined Objects* box in the *Geometric Parameters* window.
- Click on both *PLN1* and *PLN2*. This should allow you to define the angle between the two planes by clicking on the **Define** button next to *Angle* in the *Geometric Parameters* window.



- We will now define the ML_2 angles: four 'cis' ones and two 'trans' ones. Click on one of the X atoms, then the TR , then the next X atom, similarly to the previous angle between the plane definition, except this time hit the **Define** button next to *Angle*.



- Now click the **Options...** button underneath *Angle* and specify that the angle must lie between 0 and 150°. This will restrict the ‘*cis*’ angles to less than 180 degrees, meaning that they must be ‘*cis*’ angles, not ‘*trans*’.



- Click **OK** to close the *Limits and Options* window.
- Define the other three ‘*cis*’ angles in the same way.
- Finally, define the two ‘*trans*’ angles with no angle constraints, then click on **Done** in the *Geometric parameters* window.

1.4 Run the search and export the data

- Hit the **Search** button at the bottom right-hand corner of the drawing window (when prompted with the *Overwrite query* pop-up screen, select **Yes** - this will replace the initial query with the edited one).
- Inspect some of the resultant hits. The angles you defined earlier should be given in the top right hand corner of the 2D visualiser.
- Geometric parameters retrieved from a *ConQuest* search can be exported to *Vista* for analysis. Click on the **Analyse Hitlist** button in the *View Results* pane and select **View in Vista**, then in the resulting window click on the **View in Vista** button. The main *Vista TABLE SPREADSHEET* window should appear:

Quest File : C:\DOCUME-1\battle\CSDS_D-1\searches\temp\cq_temp0

Test : 1 of 1

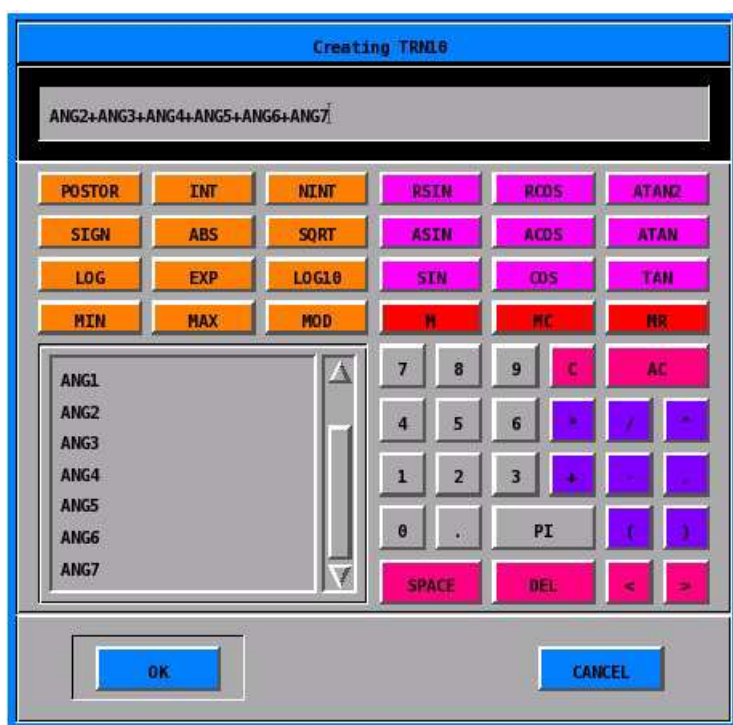
	Total	Selected	Suppressed
Parameters	9	0	n/a
Refcodes	6828	n/a	n/a
Fragments	8115	0	0

REFCD	PARAMS	1	2	3	4	5	6	7	8	9	10	11
1	ABAKEU	1	ABAKEU	90.000	116.492	116.486	100.964	100.965	116.429	100.971		
2	ABAMIA	2	ABAMIA	4.260	85.508	97.164	90.089	87.361	175.419	172.568		
3	ABANDH	3	ABANDH	4.954	90.032	92.941	87.611	89.207	175.696	175.948		
4	ABANUN	4	ABANUN	4.530	89.299	89.887	92.608	88.166	175.439	177.431		
5	ABANUN	5	ABANUN	8.506	89.718	92.946	88.812	88.758	176.980	171.507		
6	ABAIIE	6	ABAIIE	5.076	89.962	92.194	86.724	91.129	174.493	178.908		
7	ABAQOK	7	ABAQOK	10.467	88.831	93.064	88.000	89.592	176.300	169.782		
8	ABAYOR	8	ABAYOR	86.023	109.712	105.680	106.093	111.404	125.586	93.536		
9	ABAYOS	9	ABAYOS	83.824	90.988	97.321	136.105	90.669	82.903	126.273		
10	ABEPOM	10	ABEPOM	89.684	108.966	109.726	110.556	109.363	109.509	108.693		
11	ABINEF	11	ABINEF	84.910	127.532	112.344	114.494	99.833	90.143	111.023		
12	ABIWIR	12	ABIWIR	89.909	107.677	111.860	110.214	107.754	108.526	110.666		
13	ABIWUD	13	ABIWUD	6.782	90.073	87.715	91.014	91.198	177.654	178.728		
14	ABOOOY	14	ABOOOY	8.931	107.248	135.743	95.186	146.998	116.958	41.615		
15	ABULAL	15	ABULAL	85.779	114.077	103.774	107.266	107.744	109.534	114.139		
16	ABULAL	16	ABULAL	87.533	111.620	109.121	105.610	107.164	110.986	112.182		
17	ABUPIX	17	ABUPIX	89.126	108.502	109.683	111.061	110.173	108.363	109.017		

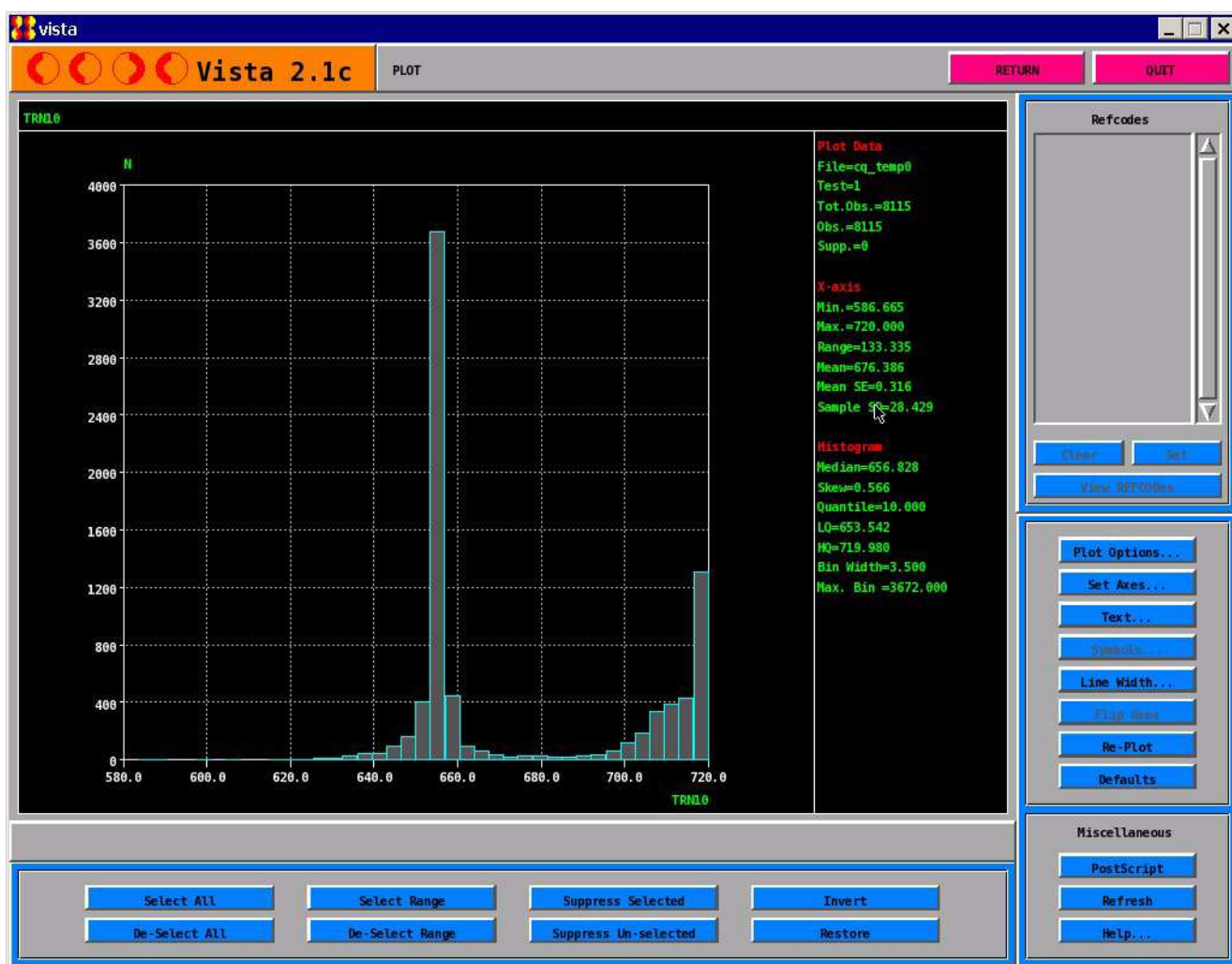
- *Vista* displays the defined angles i.e. the angle between the planes, *ANG1*, and the TRX₂ angles, *ANG2...ANG7*, for each entry in the database matching the substructure.

1.5 Analyse the geometric data

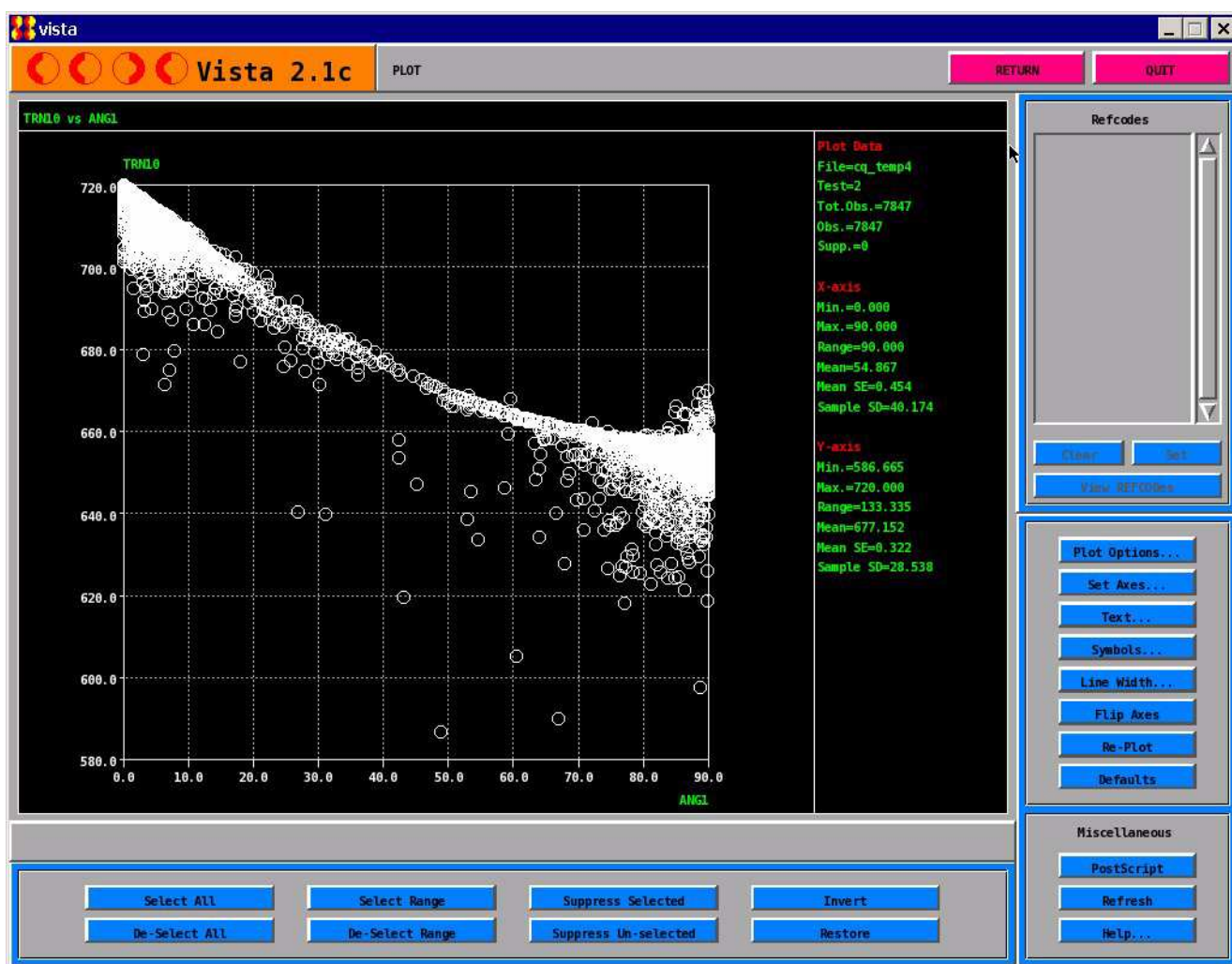
- Sum the TRX₂ angles by selecting **Create...** in the *Parameters* box on the left side of the *Vista* interface. This will generate a *creating TRN10* window. Click on *ANG2*, then the + button, then *ANG3* etc. Once you have done this for all of the TRX₂ angles, i.e. summed all of the TRX₂ angles, press **OK**.



- This will create a new column in the table, labelled *TRN10*.
- To plot the summed angle data as a histogram select the parameter *TRN10* by clicking on the grey numbered button at the top of the relevant column, then select **Histogram** from the *Data Visualization* options on the right hand side of the window.



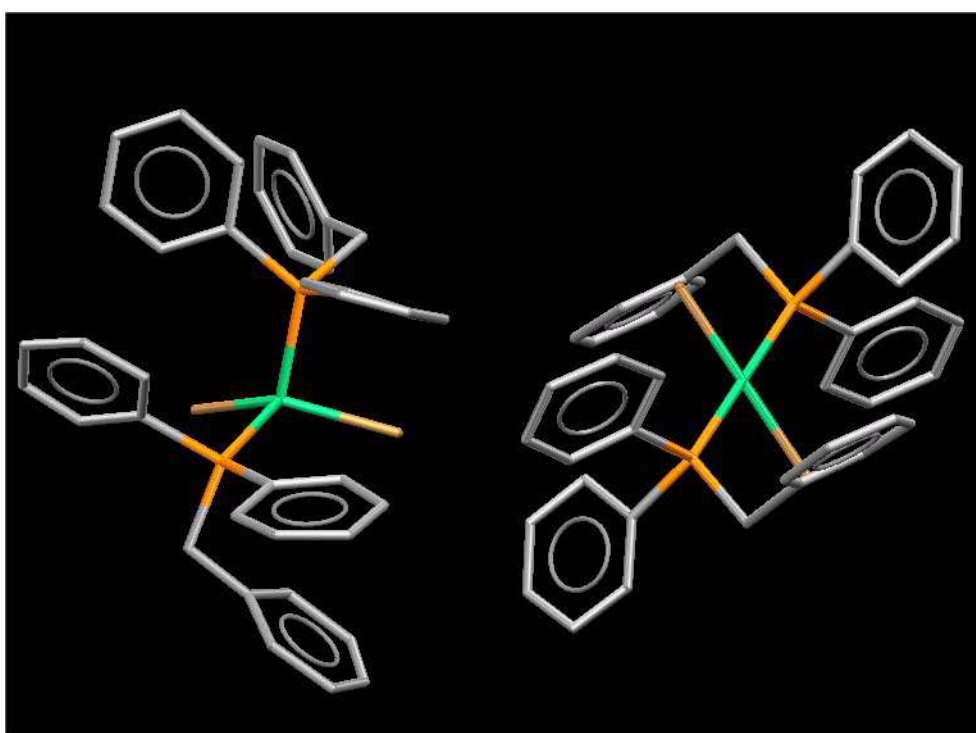
- Inspect the histogram, what does this tell you about the preferred geometries of 4-coordinate transition metal complexes?
- Structures with tetrahedral geometries can be found around 660 degrees in the histogram ($6 \times 109.5^\circ$) while the square planar structures are found close to 720 degrees ($4 \times 90^\circ$ plus $2 \times 120^\circ$).
- Return to the spreadsheet window by clicking on **RETURN**.
- To plot a scattergram of the summed angles versus *ANG1* (the angle between the two TRX_2 planes) click on the grey buttons above *TRN10* and *ANG1*. This should highlight the appropriate columns. Then, select **Scattergram**, within the **Data visualisation** section on the right of the screen.



- It is possible to link back to the original CSD entries by selecting data points in the scattergram then clicking on **View Refcodes**. What conclusions can you draw?
- The scattergram shows that most four coordinate complexes are either square planar (in the top left of the scattergram) or tetrahedral (bottom right). However this is not always clear cut, exemplified by the fact that there are many database entries linking the two geometries resulting in a continuum. Closer inspection of the structures which are neither square planar nor tetrahedral represent the interconversion between the two geometries e.g. *CCXAPT*, *COBZAU*, *CMTUCU10*.

SUMMARY OF KEY CONCEPTS

- Four coordinate metals (ML_4) predominantly adopt one of two geometries: square planar or tetrahedral.
- In some complexes the energy difference between these two preferred geometries is small. Indeed, in a few specific complexes the difference in stability of the two possible stereochemical forms (square planar or tetrahedral) is so small that each can exist in the same crystal structure.
- Dibromo-bis(benzylidiphenylphosphine) nickel(ii) (CSD refcode *DBBZPN*) is one such structure. The term *allogons* (Greek: *allos*, other, different; *andgonia*, angle) is used to describe such isomers. This crystal is thus an *interallogon* compound.



Both square planar and tetrahedral forms exist together in dibromo-bis(benzylidiphenylphosphine) nickel(ii) (CSD refcode DBBZPN)

- The preferred square planar and tetrahedral geometries can be affected by e.g. the nature of the substituents, and thus not all metal complexes have idealised conformations. In fact there are many database entries linking the two idealised geometries resulting in a continuum.
- The structures which are neither square planar nor tetrahedral can be regarded as snapshots of transition states along the interconversion pathway. i.e. proceeding along the continuum in the *Vista* distribution and viewing successive entries will allow the pathway for the interconversion between the square planar and tetrahedral geometries to be mapped out.