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Chemical Bonding in Methylidyne Complexes:

Neutron diffraction study on single crystal of $\text{BrW}\equiv\text{CH}(\text{dmpe-d}_{12})_2$

at 100 K and 293 K.

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INTRODUCTION

Our studies of metal-alkylidyne complexes are directed at developing a thorough understanding of the nature of the metal-carbon triple bond¹. Elucidation of the molecular structure (table 1) and bonding of complexes of the type *trans*-W(CH)(dmpe)₂X (dmpe=1,2-bis(dimethylphosphino)ethane, X=halide or alkynyl, compounds **1** to **12**) or *trans*-W(CH)(PMe₃)₄X (X=halide or alkynyl, compounds **13** to **16**), especially of the geometry of the M ≡ C - H group, is particularly important, since these are the simplest carbyne derivatives²⁻⁸ known up to now, and especially conjugation and hyperconjugation effects^{9,10} are absent in these structures. Another interesting feature of this series is due to the fact that the hydrogen atom is much smaller than alkyl and aryl substituents. The steric effects are negligible and the bending or the linearity of the carbyne group can be due to only the chemical effects, either electronic or hydrogen bonding.

The first attempt, by Churchill *et al.*⁷, at determining the X-ray crystal structure of **13** was inconclusive due to disorder within the crystal. The tungsten atom lies on a crystallographic C₂ axis, such that the methylidyne and chloride atoms overlap each other in the electron density map, making an accurate determination of the W ≡ C and W - Cl distances difficult. Recently, we have obtained ordered crystals of **2b** whose X-ray structure has been determined³. Interestingly, the molecules are arranged such that the W ≡ C - H ···· H - C ≡ W moieties are in a parallel configuration, a peculiarity which has been observed for all the methylidyne compound (complexes **1** to **15** in table 1). The W ≡ C - H bond angle of the former series varies apparently from 158(8)° for **4b**⁴ to 173(3)° for **15**³ according to the X-ray data (table 1). The distribution of the M ≡ C - R bond angles for the Cr, Mo and W compounds in Fischer-type either Schrock type carbyne complexes (figure 1) shows that a little number of compounds presents a bent conformation. This bending is explained with sterical considerations as reported by the authors^{13b,f,g,l,p} or with an unusual very long metal - carbyne bond^{13t,w} (W ≡ C = 1.90 Å). However, for the pure methylidyne compounds the linearity does not seem to be verified. As the position of the methylidyne hydrogen is uncertain due to the presence of the heavy metal and the relatively small scattering factor of hydrogen for the X-ray diffraction, a neutron diffraction structure determination is essential to establish the methylidyne-hydrogen position.

This study relates the results obtained by neutron diffraction of an isotopomer of **2**: to avoid excessive absorption due to the presence of hydrogen atoms in the structure, P(CD₃)₂ groups were preferred to the P(CH₃)₂ for the neutron diffraction study, since the crystal structures of the isotopomers are known to be identical. For this reason, W(CH)((CD₃)₂PCH₂CH₂P(CD₃)₂)₂Br, **1** was synthesised for this study. We performed two neutron experiments: one at low temperature (100 K) to increase the quality of the data and the other at room temperature to study any behaviour as a function of the temperature.

EXPERIMENTAL SECTION

Synthesis of W(CH)(dmpe-*d*₁₂)₂Br (**1**)

All manipulations were performed under inert atmosphere using standard glovebox and Schlenk techniques. The ligands dmpe and (CD₃)₂PCH₂CH₂P(CD₃)₂ (dmpe-*d*₁₂) were prepared by treating Cl₂PCH₂CH₂PCl₂ with Li(CH₃)₃ and Li(CD₃), respectively. Lithium bromide (99+%; 0.074 g, 0.85 nmol) was added to a stirred solution of W(CH)(dmpe)₂(OTf) (0.500 g, 0.77 nmol) in 30 mL of THF at room temperature. The reaction was shown to be complete after 2 days, at which point the solvent was removed *in vacuum* and the remaining yellow solid was extracted into a solution of 3:1 pentane/toluene (60 mL) and filtered. The pentane was then recrystallized from a concentrated 3 mL toluene solution at 233 K, yielding, after 1 day, 0.413 g (92% yield) of large, yellow block-shaped crystals.

Data collection and data reduction at 100 K and 293 K

The single crystal of **1** used for the neutron diffraction experiment at low temperature is cylindrical shaped (diameter of 5 mm, height of 1.2 mm) and was glued with an araldite glue inside an aluminium cylindrical box filled with helium. The crystal was kept at 100(1) K with a closed-cycle cryorefrigerator¹⁴. A second single crystal was used at room temperature for the neutron diffraction experiment, it is roughly hexagonal shaped (diameter of 4.5 mm, height of 3 mm) and was also glued and stored in similar conditions.

The neutron diffraction data were collected using the 6T2 four-circle diffractometer (thermal source $\lambda_{100\text{ K}} = 1.51 \text{ \AA}$ and $\lambda_{298\text{ K}} = 1.54 \text{ \AA}$) of the Orphée Reactor, Saclay, France. The orientation matrix

and the lattice parameters were refined using the space group $P2_1/n$. Partial data collection have been performed in order to check this space group determined by preliminary X-ray diffraction experiment³ at 213 K. The neutron parameters are at 100 K: $a = 8.98(3) \text{ \AA}$, $b = 18.23(8) \text{ \AA}$, $c = 12.57(7) \text{ \AA}$ and $\beta = 100.548(6)^\circ$, $V = 2022(15) 10^9 \text{ \AA}^3$ and at 293K: $a = 9.12(3) \text{ \AA}$, $b = 18.42(6) \text{ \AA}$, $c = 12.77(3) \text{ \AA}$ and $\beta = 101.228(5)^\circ$, $V = 2104(12) 10^9 \text{ \AA}^3$ compared to the X-ray values³ (213 K) $a = 9.138(2) \text{ \AA}$, $b = 18.468(4) \text{ \AA}$, $c = 12.793(3) \text{ \AA}$ and $\beta = 101.07(3)^\circ$, $V = 2119(1) 10^9 \text{ \AA}^3$.

At low temperature, the intensity data were collected for one complete quadrant of the reciprocal sphere up to 0.57 \AA^{-1} and equivalent reflections were measured for some low order Bragg peaks. Intensities of two reflections (0 4 0) and (2 4 0), monitored every 100 reflections, have a variation inferior to 3%. The ω -step, ω/θ , and $\omega/2\theta$ -step - scan methods were used for the intensity recording, depending of the θ values. The intensities were calculated using the Lehman and Larsen algorithm¹⁵, COLL5 program. Finally 3267 reflections were recorded, of which 2486 reflections uncontaminated from the aluminium sheet or from overlapping at high order, leading to 1880 independent reflections of which 1053 were such as $I \geq 3\sigma$ with an internal reliability factor¹⁶ $R_{int}(F^2) = 0.029$. This experiment will be referenced as **1a**.

At room temperature, the intensity data were collected for all the reciprocal sphere up to 0.35 \AA^{-1} and for one complete quadrant of the reciprocal sphere between 0.35 \AA^{-1} and 0.57 \AA^{-1} . Intensities of two reflections (0 4 0) and (2 4 0), monitored every 200 reflections, have a variation inferior to 3%. The ω -step, ω/θ , and $\omega/2\theta$ -step - scan methods were used for the intensity recording, depending of the θ values leading to 4179 recorded reflections. A first rough integration was done using the Lehman and Larsen algorithm¹⁵ in order to facilitate a precise examination of each profile. After a precise determination of the number of points belonging to the background, and an elimination of the reflections contaminated by the aluminium sheet, a simple integration (peak – background) was performed. Thus 2216 reflections were kept, leading to 1034 averaged independent reflections for whom 982 show an intensity higher than 3σ with an internal reliability factor $R_{int}(F^2) = 0.060$ (experiment **1b**).

RESULTS AND DESCRIPTION OF THE STRUCTURE

Full matrix least - square refinements were performed using the CRYSTAL program¹⁷ and the SHELX93 program¹⁸ package. Coherent scattering lengths for W, P, C, O, H and D were taken from Sears¹⁹. For the low temperature experiment, the refinement converged to $R_I(F) = 0.054$ and G.O.F. = 1.17 for 1053 reflections with $I \geq 2\sigma$ and 470 parameters (consisting of scale factor, nuclear position, anisotropic thermal parameters and extinction parameter). At room temperature the refinement converged to $R_I(F) = 0.059$ and G.O.F. = 1.05 for 982 reflections with $I \geq 2\sigma$ and 470 parameters. A preliminary convergence of the refinement was obtained with constraints applied on the 51 bond distances, and has been suppressed for the final solution. Extinction correction was found negligible at room temperature. Taking into account the experimental parameters (wavelength, aluminium sample holder, size of the unit cell...) the main difficulty of this work has consisted in the elimination of the contaminated reflection by the aluminium diffraction peaks. Despite, the low number of used reflections the model fits a stable and reliable solution.

Tables 2 and 3 give the nuclear positions and the isotropic thermal parameters for the two temperatures. Figure 2 shows the molecular structure of the complex and figure 3 the arrangement of two neighbored molecules respectively at low temperature. The main interatomic distances, bond angles are given in Table 4 and 5. In a general manner, the results obtained by neutron diffraction confirm in a more precise way the preliminary structure determined previously by X-ray diffraction³. Indeed, all the hydrogen or deuterium atoms are localised and the averaged distances C - H or C - D are very satisfying ($d_{C-H} = \langle 1.113(4) \text{ \AA} \rangle$, $d_{C-H} = \langle 1.10(2) \text{ \AA} \rangle$ and $d_{C-D} = \langle 1.072(1) \text{ \AA} \rangle$, $d_{C-D} = \langle 1.05(1) \text{ \AA} \rangle$) respectively at 100 and 293 K.

The general features of the structure can be briefly described as following: i) The metal lies in a pseudooctahedral environment. ii) The $W \equiv C$ bond distance is one of the shortest distance reported ($1.750(12) \text{ \AA}$ at 100 K and $1.769(15) \text{ \AA}$ at 293 K). iii) The four phosphorous atoms are globally situated on the equatorial plane. The P - W - P intra-angles ($\langle P - W - P = 81.1(2)^\circ \rangle$ at 100 K, $\langle P - W - P = 80.9(4)^\circ \rangle$ at 293 K) differ significantly from the P - W - P inter-angle ($\langle P - W - P = 98.5(2)^\circ \rangle$ at 100 K, $\langle P - W - P = 98.7(4)^\circ \rangle$ at 293 K) as observed for other similar complexes¹⁹. In a first approximation these dmpe ligands are bent toward the bromium atom ($\langle C1 - W - P = 93.3(1)^\circ \rangle$ at 100 K, $\langle C1 - W - P = 93.2(3)^\circ \rangle$ at 293 K). Kostic and Fenske²³ have demonstrated that the *cis* carbonyl ligands are oriented towards the groups with the weakest π -acceptor, i.e. that

carbyne ligand are among the best π -acid ligands. These theoretical results have been already observed experimentally for octahedral chromium carbyne complexes^{10,24}. In order to extend this trend to the phosphine ligand, the behaviour of some octahedral tungsten carbyne complexes containing phosphine and carbonyl *cis* ligand has been studied (complexes presenting sterical effects have been excluded). One can find that for four complexes^{13e,h,q,r} the $\langle C \equiv W - P \rangle = 96,8^\circ$ while $\langle C \equiv W - C(CO) \rangle = 88,0^\circ$, therefore the phosphine ligand seems to be a more flexible ligand than the carbonyl groups. Taking into account the complexes of table 1 and some other octahedral tungsten carbyne complexes¹³ⁱ, one obtains $\langle C \equiv W - P \rangle = 93,3^\circ$ over 54 bond angles. A finest analysis of the behaviour of the dmpe in *trans*-W(\equiv CH)(dmpe)₂X will be discussed later.

iv) The most significant result of this work, is the precise determination of the W \equiv C - H bond angle ($178.0(7)^\circ$ at 100 K, $177.8(18)^\circ$ at 293 K).

DISCUSSION

Effect of the temperature

A fine observation of tables 4 and 5 for the three experiments let us to conclude in the following way : i) Despite the small number of used reflexions, the neutron experiment at low temperature is of the same quality level than the X-ray experiment except evidently for the hydrogen and deuterium atom for which one can obtain in this work a very good determination. ii) As expected, the accuracy decrease strongly from 100 K to room temperature (about one digit on the interatomic distances). Nevertheless, examination of the repartition of similar distances or angles shows that results at room temperature are still reliable. iii) No effect of the temperature (except thermal motions) has been detected. The molecule keeps the same electronic properties in the range 100 \times 300 K.

Specific behaviour of the dmpe ligand

The behaviour of the dmpe ligand presents some specific characteristics that are necessary to emphasise. i) The C1 - W - P angles are not equals. Three of them give an average value of

$\langle 92.3(2)^\circ \rangle$ at 100 K and $\langle 92.4(3)^\circ \rangle$ at 293 K compared to the fourth value ($96.4(3)^\circ$ at 100 K and $95.6(6)^\circ$ at 293 K). ii) A disordered character of one of the two dmpe has been modelised in this work by abnormally large U_{eq} values (the ratio of the averaged U_{eq} value of the carbon atoms of each dmpe is 1.32 at 100 K and 1.48 at 293 K)²⁵. iii) The disordered dmpe ligand is the one which does not contain the phosphorous atom which is more bent toward the bromium ligand.

For all the complexes except for **11**, one phosphorous atom presents the specific behaviour (point i) described above. One of the two dmpe is disordered in all the complexes for which the structure can be simply determined, i.e. except for **3** and **4**. This disorder (point ii) is described by two branches (case of **2b**, **8**, **9**, **10a** and **12a**) or by using abnormally large U_{eq} values (case of **1a**, **1b**, **2a**, **5**, **6** and **7**). (the ratio of the averaged U_{eq} value of the carbon atoms of each dmpe is 1.33 for **2a**, 1.76 for **5** and 1.32 for **6** and **7**).

We have been able to explain the special position of one phosphorous atom by an accurate quantitative examination of the packing arrangement. We have eliminated two compounds (**11** and **12**) for which the *trans* ligand presents a great steric bulk and two complexes for which the determination of the dmpe ligands was uncertain (**3** and **4**). Therefore we have worked with 10 structures (7 compounds). A modelised structure has been defined by performing a 180° rotation of the dmpe which presents the shorter C1 – W – P angles. The C...C intermolecular contacts have been determined. The C...C shortest distance in the real molecules have been reported (Table 6) compared to the C1...C1 intermolecular distance (C1 is the carbynic atom). In order to modelise a steric effect, we have arbitrarily fixed a value (3.9 \AA) above which the intermolecular distance have no more influence on the steric bulk. We have estimated quantitatively the relative influence of each intermolecular distance inferior to 3.9 by the quantity define as the summation of $(3.9 - d_{C...C})$ over all the C...C distance shorter than 3.9; this parameter will be called the steric parameter (SP)²⁶. It can give an estimation of the constraints in the molecule. The greater this parameter is, the bigger the steric constraints are. One can observed (Table 6) that except for **7** where SP is similar in the real and in the modelised structure, all the steric effects are minimised in the real molecule. In other words, that means that one phosphorous atom kicked out from the equatorial plane (C1 – W - P $\approx 96^\circ$) give less steric effects than all four phosphorous atoms presenting a similar C1 – W – P value ($\approx 92^\circ$).

In order to explain the disorder of only one dmpe and for the compounds (**2b**, **8** and **10a**) where the disorder is modelised in the refinement by two dmpe (named A and B branch) at 50 % occupation each other, we have calculated two modelised structures containing two A dmpe or two B dmpe²⁷. As previously done a steric parameter has been calculated in the real molecule and in the two modelised conformations. The calculations show also that steric constraints are responsible of the disorder of one dmpe ligand.

Therefore, in order to minimise the unfavourable Van der Waals interaction between carbon atoms in the dmpe ligands in adjacent molecules, one of the phosphorous atoms is kicked out of the equatorial plane while the carbon atoms of the other dmpe sit alternatively on two different positions. This is true for almost all the isostructural compounds, the exceptions being some structures the accuracy of which was not sufficient.

Nature of the $W \equiv C - H$ bond angle

Now we want to focus on the question of the different $W \equiv C - H$ bond angle values in methylidyne complexes. As observed in Table 1, half of the previous $W \equiv C - H$ bond angle values reported from classical X-ray diffraction experiments is between 158(8) and 169(5) °, leading to a bent carbyne (**2b**, **6**, **9** and **14**) whereas the others present a $W \equiv C - H$ bond angle values between 173(3) and 177(4) ° leading to a linear carbyne (**4**, **7**, **8**, **10a**, **11** and **15**).

In order to obtain a tentative explanation of these different behaviours, it is important to remind the following parameters which influence the $M \equiv C$ chemical bond in such compounds: i) The nature of the ligand *trans* to the carbyne carbon (i.e. the strength of the *trans* effect); ii) The nature of the organic substituent of the carbyne atom (i.e. an organic moiety able to generate a conjugation effect); these two factors lead to slight modifications in the $M \equiv C$ bond distance (i.e. longer for a soft ligand²⁸ or a conjugated R); iii) The nature of the *cis* ligand. For example, substituting four PMe_3 by two dmpe change the conformation and lead to a lowering of the local symmetry of the metal from C_{4v} to C_{2v} . Moreover, the *cis* ligand can slightly move away from the equatorial plane and modify the metal orbitals. The interatomic distance $M - L_{cis}$ is also important, as shown by *ab initio* calculations^{10a,29} and experimental works based on Raman spectroscopy³⁰ or density

deformation study^{10a,10c} of a methylmethylidyne complex; iv) The intermolecular bonding. All these parameters can induce a dissymmetry in the π -orbital of the carbyne bond, and a relative contribution of the $M \equiv C$ resonant form.

Some commonly explanations for the bending of methylidyne ligand are based either on a packing effect hypothesis or on electronic considerations. Concerning crystallographic considerations, compounds of Table 1 display a «head-to-head» packing features. Manna *et al*⁵ has made the hypothesis that a short $C_{\text{carbyne}} \cdots C_{\text{carbyne}}$ distance between two adjacent molecules may be responsible of the bent linkage. Moreover, Jorgensen³¹ has studied the influence of a ligand *trans* to the $M \equiv C - H$ fragment using the Extended Hückel method. He has established that soft ligands which are *trans* to the alkylidyne carbon cause more bending than hard ligands.

Before a precise examination of the behaviour of complexes of Tables 1, function of these two hypothesis, one have to remind that X-ray data concerning the geometry of the carbyne groups are to be considered with care when H-atom positions are concerned. One can notice, for exemple, that two experiments were performed with classical X-ray diffraction for **10** at 209 K (experiment **10a**)³ and an other at 225 K (experiment **10b**)⁶. The results of these experiments are not in agreement concerning the determination of the $W \equiv C - H$ bond angle: for **10a** the axis $W \equiv C - H$ is bent whereas for **10b** the axis is linear. Therefore, as expected, the geometry of the $W \equiv C - H$ moiety can only be determined accurately from a neutron experiment.

Nevertheless, the hypothesis of Manna *et al*⁵ which states that a short $C_{\text{carbyne}} \cdots C_{\text{carbyne}}$ distance between two adjacent molecules suggests the presence of hydrogen bonding thus implying a bent linkage is to be reconsidered. Indeed, in the present case of the simple bromine carbyne complexes (compounds **1a**, **1b**, **2a**, **2b**) the $C_{\text{carbyne}} \cdots C_{\text{carbyne}}$ bond is measured significantly shorter for the neutron experiments and nevertheless the $W \equiv C - H$ axis remains linear. So the link geometry is not a consequence of the packing effect.

The hypothesis of Jorgensen³¹ which states that soft ligands *trans* to the carbyne carbon create more bending than hard ligands is valid for our results (experiments **1a**, **1b**, **2a**): that compound possesses a *trans* hard ligand (Br) and experimental observations indicate a linear linkage. The behaviour of the complexes **5**, **7** and **8** (hard ligand) and **6**, **9** and **10a** (soft ligand) seems consistent with this interpretation while **2b**, **4b**, **10b** and **11** does not verify this hypothesis. However, we have

previously demonstrated for **2b** and **10b** that the ambiguity was due to the accuracy expected with a classical X-ray measurement. Therefore, it is not possible to validate the Jorgensen's hypothesis even though for the compounds (**5**, **6**, **7**, **8**, **9** and **10a**) for which it seems consistent. The only solution for validate or infirm Jorgensen's hypothesis is to perform an experiment by neutron diffraction or a precise synchrotron experiment² on a simple carbyne complex with a soft ligand.

The situation of **14** seems to be different because it presents a short intramolecular $C_{\text{carbyne}} \cdots \text{Al}$ bond distance which can induce a bending.

In earlier works¹⁰, we have experimentally studied the bonding of a $\text{Cl}(\text{CO})_4\text{Cr}\equiv\text{C}-\text{C}_6\text{H}_5$ (**17**) and $\text{Cl}(\text{CO})_4\text{Cr}\equiv\text{C}-\text{CH}_3$ (**18**) methylidyne complexes. A conjugation effect has been clearly demonstrated for **17** from the electron deformation density maps. The same trend has not been established for the methyl compound **18**. Thus, these results has shown the strong influence of the R substituent for the contribution of the $\text{M}\equiv\text{C}-\text{R}$ resonant form. Concerning the $\text{M}\equiv\text{C}-\text{H}$ moiety, simple chemical considerations should lead to a total *sp* character, and therefore to a linear behaviour, with a shorter $\text{M}\equiv\text{C}$ bond distance. These trends are effectively observed for **1a** and **1b**.

CONCLUSION

The structure of a methylidyne compound possessing a hard ligand have been studied by neutron diffraction at low and room temperature. Despite the low number of used reflexions in the refinements the two structures has been solved and gave consistent results. The main characteristics of the complexe are similar to those observed for other simple methylidyne complexes. No specific electronic effect due to the temperature has been demonstrated. The specific behaviour of the dmpe ligands (one phosphorous atom strongly out of the *cis* plane, and the second dmpe exhibiting a disorder) has been precisely studied for 10 compounds. The steric bulk of the dmpe in the head to head packing arrangement is responsible of this behaviour. The linearity of simple methylidyne has been proved without ambiguity, which was expected for a total *sp* character of the $\text{M}\equiv\text{C}$. The bent linkage observed previously for some compounds seems an artefact of the classical X-ray

measurements. Nevertheless, it will be interesting study a methylidyne compound possessing a soft ligand, experimentally (by neutron diffraction) or theoretically (ab initio calculations) in order to increase the understanding of the behaviour of the metal carbyne moiety.

FIGURES CAPTIONS

FIGURE 1

Distribution of the $W \equiv C - H$ bond angles for the carbyne complexes of Cr^{11} , Mo^{12} and $W^{3-8,13}$. The polymetallic complexes has been excluded of the comparison but the bis carbyne has been included.

FIGURE 2a

Molecular structure of **1a** as determined by neutron diffraction at 100 K.

FIGURE 2b

Molecular structure of **1b** as determined by neutron diffraction at 298 K.

FIGURE 3

Molecular packing of two adjacent molecules of **1a**.

TABLES CAPTIONS

TABLE 1

Crystallographic structures²⁻⁸ of $W (\equiv C - H) (dmpe-d_{12})_2 L$ and $W (\equiv C - H) (PMe_3)_n L'$ complexes where L and L' are various ligands and n = 3 or 4. A letter follows the number used to define a complex when two different experiments has been performed. Comments on the possible disorder doesn't concern the *cis* ligand. N = neutron source, Sync. = synchrotron source, X-Ray = classical X-ray source.

TABLE 2

Atomic coordinates for the **1a** experiment.

TABLE 3

Atomic coordinates for the **1b** experiment.

TABLE 4

Interatomic distances (Å) for **1a**, **1b** and **2b**³. For similar chemical groups, the minimum and the maximum interatomic distance has been reported (the concerned atoms is mentioned in the second column) and the averaged value (<>) is indicated in italic (the number of averaged distances is precised).

TABLE 5

Interatomic distances (°) for **1a**, **1b** and **2b**³. Same convention as in Table 4.

TABLE 6

Steric parameter (SP) of some methyldiyne complexes. C1 is the carbynic atom.

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16 Formula of $R_{int}(I)$

$$R_{int}(I) = \frac{\sum_{K=1}^M \left[\sum_{J=1}^N (I_M - I_J)^2 \right]_K}{\sum_{K=1}^M \sum_{J=1}^N (I_J^2)_K}$$

with J = sum over a symmetric equivalent group and K = sum over symmetric independent reflections.

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- 25 For **2b** the disorder has been modelised by two different positions (A and B) of one dmpe. That leads to a larger dispersion of the interatomic distances or bond angles involving that branch.
- 26 All the C...C intermolecular distances inferior to 3.9 \AA has been included in the calculation. For **1a** we have also checked that for the shorter C...C intermolecular distances in the model the corresponding H...H or D...D are also shorter.
- 27 For the three structures presenting two disordered dmpe ligands the calculations has been performed in a lower space group with two independant molecules in the assymetric unit. For the modelised structure two different rotations has been done for each molecules.

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Table 1.

	complexes	source, temperature	comment	bond angles M≡C-H (°)	references
1a	W (≡ C - H) (dmpe-d ₁₂) ₂ Br	N, 100 K		this work	this work
1b	W (≡ C - H) (dmpe-d ₁₂) ₂ Br	N, 293 K		this work	this work
2a	W (≡ C - H) (dmpe) ₂ Br	Sync., 123K		178.01(12)	2 (unpub)
2b	W (≡ C - H) (dmpe) ₂ Br	X-Ray, 213 K		164(6)	3 (thèse)
3	W (≡ C - H) (dmpe) ₂ F	X-Ray, 296 K	disorder (F, C)	-	3 (thèse)
4a	W (≡ C - H) (dmpe) ₂ Cl	X-Ray, 296 K	2 molecules	-	3 (thèse)
4b	W (≡ C - H) (dmpe) ₂ Cl	X-Ray, 296 K	2 molecules	158(8)	4 (W102)
5	W (≡ C - H) (dmpe) ₂ I	X-Ray, 218 K		176(8)	3 (thèse)
6	W (≡ C - H) (dmpe) ₂ (n-Bu)	X-Ray, 224 K		162(4)	3 (thèse), 5 (W101)
7	W (≡ C - H) (dmpe) ₂ (OTf)	X-Ray, 227 K		177(4)	3 (thèse)
8	W (≡ C - H) (dmpe) ₂ (CN)	X-Ray, 212 K		177(2)	3 (thèse)

9	W (\equiv C - H) (dmpe) ₂ (CCH)	X-Ray, 213 K		169(5)	3 (thèse)
10a	W (\equiv C - H) (dmpe) ₂ (CCSiMe ₃)	X-Ray, 209 K		164(5)	3 (thèse)
10b	W (\equiv C - H) (dmpe) ₂ (CCSiMe ₃)	X-Ray, 225 K		174(3)	6 (W100)
11	W (\equiv C - H) (dmpe) ₂ (CCPh)	X-Ray, 218 K		174(3)	3 (thèse)
12a	W (\equiv C - H) (dmpe) ₂ (CCp-C ₆ H ₄ CCPr)	X-Ray, 227 K		-	3 (thèse)
12b	W (\equiv C - H) (dmpe) ₂ (CCp- C ₆ H ₄ CCPr)	X-Ray, 218 K		-	3 (thèse)
13	W (\equiv C - H) (PMe ₃) ₄ Cl	X-Ray, 296 K	disorder (Cl, C), 2 molecules	-	7 (W105)
14	W (\equiv C - H) (PMe ₃) ₃ Cl . Al Cl _{1+x} Me _{2-x}	X-Ray, 296 K	disorder, x = 0.16, 2 molecules	164(4)	7 (W105)
15	W (\equiv C - H) (PMe ₃) ₃ OTf . THF	X-Ray, 208 K		173(3)	3 (thèse)
16	W (\equiv C - H) (PMe ₃) ₃ (C ₂ H ₄)	?		?	8 (organomet 84)

Table 2

atoms	x	y	z	Ueq
W	0.0192(5)	0.1060(3)	0.2996(5)	0.0180(14)
Br	0.0215(4)	0.1461(2)	0.0885(3)	0.0275(11)
P1	-0.1997(5)	0.0340(2)	0.2201(4)	0.0195(12)
P2	0.1489(6)	-0.0063(2)	0.2675(4)	0.0256(14)
P3	-0.1041(5)	0.2222(2)	0.3170(4)	0.0206(14)
P4	0.2421(5)	0.1826(2)	0.3525(4)	0.0242(14)
C1	0.0173(4)	0.0818(2)	0.4341(3)	0.0190(11)
C2	-0.3468(5)	0.0660(2)	0.1117(4)	0.0373(13)
C3	-0.3114(4)	-0.0039(2)	0.3146(4)	0.0284(12)
C4	-0.1356(5)	-0.0491(2)	0.1584(4)	0.0306(12)
C5	0.0052(4)	-0.0794(2)	0.2289(4)	0.0273(11)
C6	0.2764(4)	-0.0502(2)	0.3759(3)	0.0227(11)
C7	0.2512(5)	-0.0125(2)	0.1556(4)	0.0266(12)
C8	-0.2466(5)	0.2609(2)	0.2103(4)	0.0372(14)
C9	-0.1928(6)	0.2340(2)	0.4347(4)	0.0402(14)
C10	0.0363(5)	0.2971(2)	0.3334(5)	0.0434(15)
C11	0.1821(4)	0.2712(2)	0.4018(4)	0.0312(13)
C12	0.3907(5)	0.1550(2)	0.4624(4)	0.0326(13)
C13	0.3536(5)	0.2130(3)	0.2531(4)	0.0408(14)
Hy1	0.0163(12)	0.0637(6)	0.5221(8)	0.060(3)
Hy01	-0.0117(9)	0.3466(4)	0.3692(9)	0.052(3)
Hy02	0.0549(11)	0.3126(5)	0.2558(8)	0.049(3)
Hy11	0.1645(10)	0.2611(5)	0.4845(8)	0.047(3)
Hy12	0.2719(10)	0.3112(5)	0.4100(9)	0.050(3)
Hy41	-0.2327(10)	-0.0908(4)	0.1440(7)	0.044(3)
Hy42	-0.1068(10)	-0.0315(5)	0.0794(9)	0.051(3)

Table 2 (continue)

atoms	x	y	z	Ueq
Hy51	-0.0234(13)	-0.1028(4)	0.3076(9)	0.058(3)
Hy52	0.0522(8)	-0.1253(5)	0.1896(8)	0.047(3)
D21	-0.4194(5)	0.0226(3)	0.0760(4)	0.0489(15)
D22	-0.4114(6)	0.1072(3)	0.1416(4)	0.051(2)
D23	-0.2942(5)	0.0909(3)	0.0521(4)	0.0427(15)
D31	-0.3992(5)	-0.0410(3)	0.2728(4)	0.0467(15)
D32	-0.2384(5)	-0.0326(3)	0.3783(4)	0.050(2)
D33	-0.3680(5)	0.0417(3)	0.3448(4)	0.0455(15)
D61	0.3120(6)	-0.1040(2)	0.3554(4)	0.0485(15)
D62	0.3772(5)	-0.0175(3)	0.3945(4)	0.0440(14)
D63	0.2227(5)	-0.0532(3)	0.4469(4)	0.0444(15)
D71	0.3022(6)	-0.0661(3)	0.1523(4)	0.0496(15)
D72	0.1764(6)	-0.0019(4)	0.0797(4)	0.069(2)
D73	0.3371(6)	0.0268(3)	0.1649(5)	0.060(2)
D81	-0.2686(6)	0.3185(3)	0.2248(5)	0.052(2)
D82	-0.2024(6)	0.2591(3)	0.1372(6)	0.062(2)
D83	-0.3467(6)	0.2295(3)	0.1975(5)	0.060(2)
D91	-0.2410(7)	0.2859(3)	0.4367(5)	0.059(2)
D92	-0.2789(6)	0.1932(3)	0.4306(5)	0.064(2)
D93	-0.1086(7)	0.2218(4)	0.5059(5)	0.066(2)
D121	0.4623(5)	0.2005(2)	0.4921(5)	0.0471(15)
D122	0.3387(6)	0.1342(3)	0.5260(5)	0.054(2)
D123	0.4556(6)	0.1120(3)	0.4345(5)	0.060(2)
D131	0.4442(5)	0.2490(3)	0.2903(5)	0.057(2)
D132	0.4005(6)	0.1651(3)	0.2205(6)	0.078(2)
D133	0.2797(7)	0.2412(4)	0.1899(5)	0.069(2)

Table 3

atoms	x	y	z	Ueq
W	0.0192(11)	0.1061(5)	0.2977(7)	0.040(3)
Br	0.0129(9)	0.1447(4)	0.0888(6)	0.063(3)
P1	-0.2022(11)	0.0335(5)	0.2218(7)	0.051(3)
P2	0.1386(11)	-0.0071(5)	0.2606(8)	0.056(3)
P3	-0.1044(11)	0.2208(6)	0.3179(8)	0.056(3)
P4	0.2396(10)	0.1801(5)	0.3463(8)	0.053(3)
C1	0.0217(9)	0.0816(4)	0.4319(5)	0.054(3)
C2	-0.3487(12)	0.0665(6)	0.1138(6)	0.073(4)
C3	-0.3089(12)	-0.0003(6)	0.3120(8)	0.078(4)
C4	-0.1402(11)	-0.0477(5)	0.1620(8)	0.076(4)
C5	-0.0008(11)	-0.0798(5)	0.2289(7)	0.072(3)
C6	0.2664(13)	-0.0489(5)	0.3719(7)	0.075(5)
C7	0.2379(11)	-0.0121(6)	0.1513(7)	0.070(4)
C8	-0.2368(18)	0.2632(7)	0.2083(11)	0.116(8)
C9	-0.2000(15)	0.2283(7)	0.4247(8)	0.106(7)
C10	0.0315(13)	0.2960(6)	0.3305(15)	0.141(9)
C11	0.1847(13)	0.2693(5)	0.3882(11)	0.099(5)
C12	0.3820(11)	0.1568(6)	0.4585(9)	0.081(4)
C13	0.3456(14)	0.2018(8)	0.2427(12)	0.118(7)
Hy1	0.0241(25)	0.0640(14)	0.5152(17)	0.129(10)
Hy01	-0.0064(27)	0.3418(12)	0.3658(28)	0.162(15)
Hy02	0.0424(29)	0.3097(9)	0.2555(17)	0.114(15)
Hy11	0.1650(32)	0.2627(13)	0.4794(19)	0.153(16)
Hy12	0.2728(25)	0.3070(13)	0.3974(22)	0.133(11)
Hy41	-0.2384(22)	-0.0904(12)	0.1455(18)	0.119(9)
Hy42	-0.1238(20)	-0.0348(10)	0.0822(15)	0.090(8)

Table 3 (continue)

atoms	x	y	z	Ueq
Hy51	-0.0267(21)	-0.1044(10)	0.3014(18)	0.099(8)
Hy52	0.0393(23)	-0.1266(12)	0.1893(15)	0.104(8)
D21	-0.4177(14)	0.0226(7)	0.0812(10)	0.123(6)
D22	-0.4118(14)	0.1082(7)	0.1421(10)	0.120(6)
D23	-0.3034(14)	0.0907(7)	0.0511(8)	0.117(6)
D31	-0.3983(15)	-0.0350(7)	0.2760(10)	0.119(6)
D32	-0.2409(14)	-0.0281(8)	0.3745(9)	0.122(7)
D33	-0.3612(15)	0.0414(8)	0.3466(10)	0.124(7)
D61	0.2993(14)	-0.0989(6)	0.3494(9)	0.108(5)
D62	0.3687(16)	-0.0163(8)	0.3878(11)	0.131(7)
D63	0.2233(14)	-0.0527(8)	0.4406(8)	0.120(7)
D71	0.2840(17)	-0.0651(7)	0.1479(11)	0.136(7)
D72	0.1666(15)	-0.0056(10)	0.0817(9)	0.152(9)
D73	0.3257(16)	0.0215(8)	0.1626(12)	0.148(9)
D81	-0.2631(18)	0.3143(8)	0.2285(11)	0.150(8)
D82	-0.2039(20)	0.2561(10)	0.1392(12)	0.168(10)
D83	-0.3318(20)	0.2299(9)	0.2039(13)	0.153(9)
D91	-0.2433(17)	0.2821(8)	0.4350(11)	0.142(8)
D92	-0.2744(24)	0.1921(9)	0.4269(20)	0.220(22)
D93	-0.1116(21)	0.2207(10)	0.4950(11)	0.165(9)
D121	0.4581(12)	0.1980(7)	0.4867(10)	0.124(7)
D122	0.3299(15)	0.1357(8)	0.5207(10)	0.127(7)
D123	0.4434(15)	0.1126(8)	0.4353(11)	0.131(7)
D131	0.4287(18)	0.2432(8)	0.2798(12)	0.149(8)
D132	0.4089(23)	0.1572(12)	0.2329(17)	0.196(13)

D133	0.2769(20)	0.2299(12)	0.1822(13)	0.184(11)
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Table 4bis Interatomic distances for the 1a, 1b and 2b experiments

distances	1a	100 K (N)	1b	293 K (N)	2b	213 K (RX)
W-Br		2.76(2)		2.751(14)		2.760(1)
W-C1		1.750(12)		1.769(15)		1.786(8)
W-P min	W-P3	2.419(11)	W-P4	2.41(2)	W-P4	2.435(2)
W-P max	W-P4	2.432(9)	W-P1	2.46(2)	W-P1	2.450(2)
W-P $\langle \rangle$	4 dist.	2.424(5)	4 dist.	2.43(1)	4 dist.	2.442(1)
P-C min	P2-C6	1.800(8)	P1-C3, P3-C9	1.76(2)	P4-C12	1.812(7)
P-C max	P2-C5	1.858(8)	P2-C5	1.84(2)	P2-C5	1.856(7)
P-C $\langle \rangle$	10 dist.	1.822(3)	10 dist.	1.81(1)	10 dist.	1.833(3)
P3-C10		1.844(8)		1.85(2)		1.854(11) 1.908(44)
P4-C11		1.845(9)		1.83(2)		1.875(12) 1.788(24)
C4-C5		1.510(7)		1.51(2)		1.499(9)
C10-C11		1.506(7)		1.53(3)		1.563(15) 1.475(57)
C1-H1		1.155(13)		1.11(3)		0.792(81)
C-H min	C10-Hy02	1.058(14)	C10-Hy02	1.01(5)		
C-H max	C5-Hy51	1.148(13)	C11-Hy11	1.22(6)		
C-H $\langle \rangle$	8 dist	1.108(4)	8 dist	1.10(2)		
C-D min	C9-D91	1.042(8)	C9-D92	0.96(3)		
C-D max	C3-D31	1.097(6)	C6-D62	1.09(2)		
C-D $\langle \rangle$	24 dist.	1.059(7)	24 dist.	1.07(2)		

Table 5 Bond angles for the 1a, 1b and 2b experiments

Angles about Tungsten

	100 K	293 K	213 K (RX)
Br-W-C1	179.2(3)	179.5(7)	177.8(2)
Br-W-P1	84.0(3)	84.1(5)	84.1(1)
Br-W-P2	88.6(3)	87.6(5)	88.65(1)
Br-W-P3	86.5(3)	87.5(5)	87.3(1)
Br-W-P4	87.7(3)	87.9(5)	87.9(1)
C1-W-P1	96.4(3)	95.6(6)	96.9(2)
C1-W-P2	92.2(3)	92.8(6)	93.5(2)
C1-W-P3	92.7(3)	92.1(6)	90.6(2)
C1-W-P4	91.9(3)	92.4(6)	91.05(2)
P1-W-P2	81.5(3)	79.8(6)	80.6(1)
P3-W-P4	80.8(3)	82.0(6)	80.6(1)
P1-W-P3	99.3(3)	98.7(6)	99.4(1)
P2-W-P4	97.7(4)	98.8(6)	98.9(1)
P1-W-P4	171.7(3)	171.9(6)	172.0(1)
P2-W-P3	174.9(3)	175.0(6)	175.9(1)

Angle about C1

	100 K	293 K	213 K (RX)
W-C1-H1	178.0(7)	177.8(18)	164(6)

Table 5 (continue)

Angles about Phosphorus

	1a	100 K	1b	293 K	2b	213 K (RX)
W-P-C(Et) min	W-P2-C5, W-P4-C11	108.5(4)	W-P1-C4	108.3(8)	W-P3-C10	105.5(13)
W-P-C(Et) max	W-P3-C10	110.1(4)	W-P2-C5	110.5(8)	W-P4-C11	112.4(7)
W-P-C(Et) $\langle \rangle$	4 dist.	<i>109.1(2)</i>	4 dist.	<i>109.4(4)</i>	6 dist.	<i>109.1(1)</i>
W-P-C(Me) min	W-P3-C9	117.0(3)	W-P2-C6	116.8(8)	W-P1-C3	116.7(2)
W-P-C(Me) max	W-P1-C2	124.2(4)	W-P1-C2	122.7(8)	W-P1-C2	123.5(3)
W-P-C(Me) $\langle \rangle$	8 dist.	<i>120.3(1)</i>	8 dist.	<i>119.4(3)</i>	8 dist.	<i>120.0(1)</i>
C(Me)-P-C(Me) min	C12-P4-C13	100.8(5)	C2-P1-C3	101.3(11)	C8-P3-C9	101.5(4)
C(Me)-P-C(Me) max	C6-P2-C7	102.4(5)	C6-P2-C7	103.9(11)	C6-P2-C7	100.6(4)
C(Me)-P-C(Me) $\langle \rangle$	4 dist.	<i>101.5(2)</i>	4 dist.	<i>102.5(6)</i>	4 dist.	<i>101.1(2)</i>
C(Me)-P-C(Et) min	C8-P3-C10	99.8(4)	C8-P3-C10	94.5(14)	C9-P3-C10	85.1(19)
C(Me)-P-C(Et) max	C9-P3-C10	102.4(4)	C9-P3-C10	107.4(14)	C8-P3-C10	119.5(15)
C(Me)-P-C(Et) $\langle \rangle$	8 dist.	<i>101.2(1)</i>	8 dist.	<i>101.7(4)</i>	12 dist.	<i>101.6(3)</i>

Table 5 (continue)

Angles about the carbon of the dmpe ligand

	1a	100 K	1b	293 K	2b	213 K (RX)
P-C-C min	P3-C10-C11	109.7(4)	P2-C5-C4	108.1(10)	P3-C10-C11	106.9(7)
P-C-C max	P4-C11-C10	111.1(4)	P4-C11-C10	115.2(14)	P4-C11-C10	119.4(24)
P-C-C \diamond	4 dist.	<i>110.5(2)</i>	4 dist.	<i>111.3(6)</i>	10 dist.	<i>113.4(6)</i>
H-C-P min	Hy11-C11- P4	105.9(6)	Hy11-C11- P4	106.9(17)		
H-C-P max	Hy12-C11- P4	111.4(6)	Hy52-C5-P2	113.3(17)		
H-C-P \diamond	8 dist.	<i>108.5(2)</i>	8 dist.	<i>110.2(6)</i>		
H-C-C min	Hy42-C4-C5	108.7(6)	Hy11-C11- C10	101.6(22)		
H-C-C max	Hy12-C11- C10	113.5(6)	Hy12-C11- C10	116.6(22)		
H-C-C \diamond	8 dist.	<i>111.0(2)</i>	8 dist.	<i>110.4(7)</i>		
H-C-H min	Hy11-C11- Hy12	105.0(8)	Hy51-C5- Hy52	102.1(21)		
H-C-H max	Hy41-C4- Hy42	110.1(8)	Hy01-C10- Hy02	107.9(30)		
H-C-H \diamond	4 dist.	<i>106.9(4)</i>	4 dist.	<i>103.6(12)</i>		
D-C-P min	D33-C3-P1	106.6(5)	D83-C8-P3	101.8(24)		
D-C-P max	D61-C6-P2	113.6(5)	D121-C12- P4	115.5(16)		
D-C-P \diamond	24 dist.	<i>105.2(1)</i>	24 dist.	<i>105.3(4)</i>		
D-C-D min	D92-C9-D93	106.3(6)	D91-C9- D93	104.1(29)		
D-C-D max	D91-C9-D93	113.4(7)	D132-C13- D133	125.7(48)		

D-C-D ◇	24 dist.	<i>104.5(1)</i>	24 dist.	<i>104.2(5)</i>
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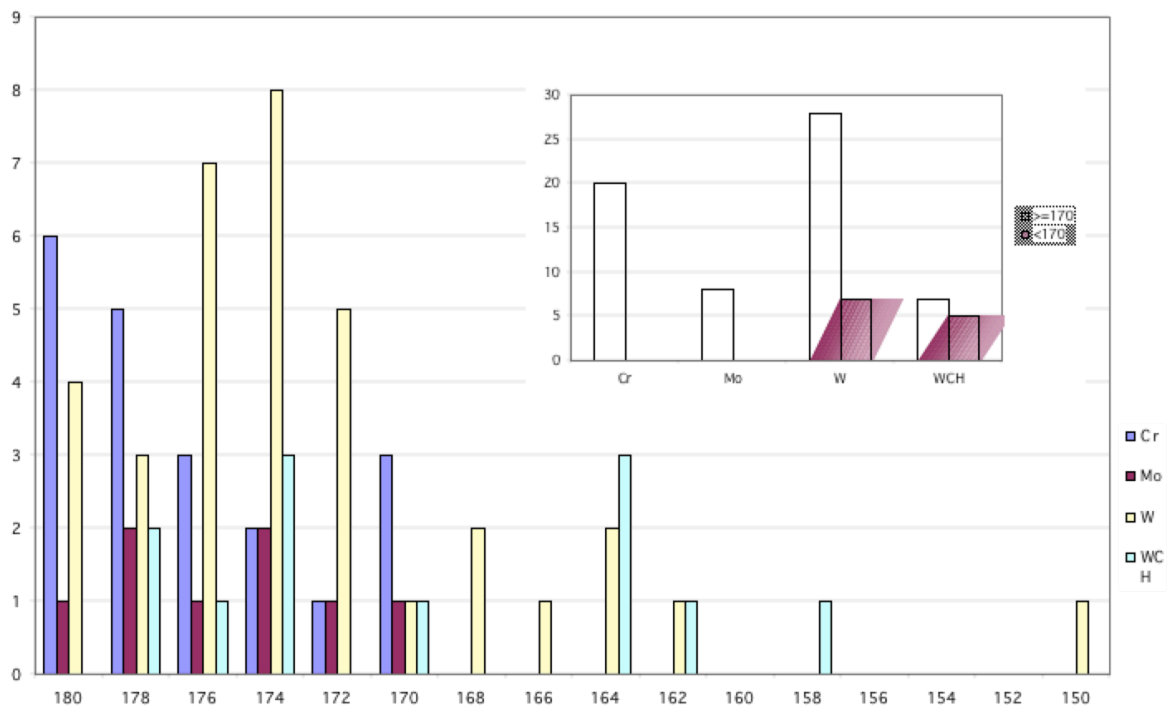


Figure 2a

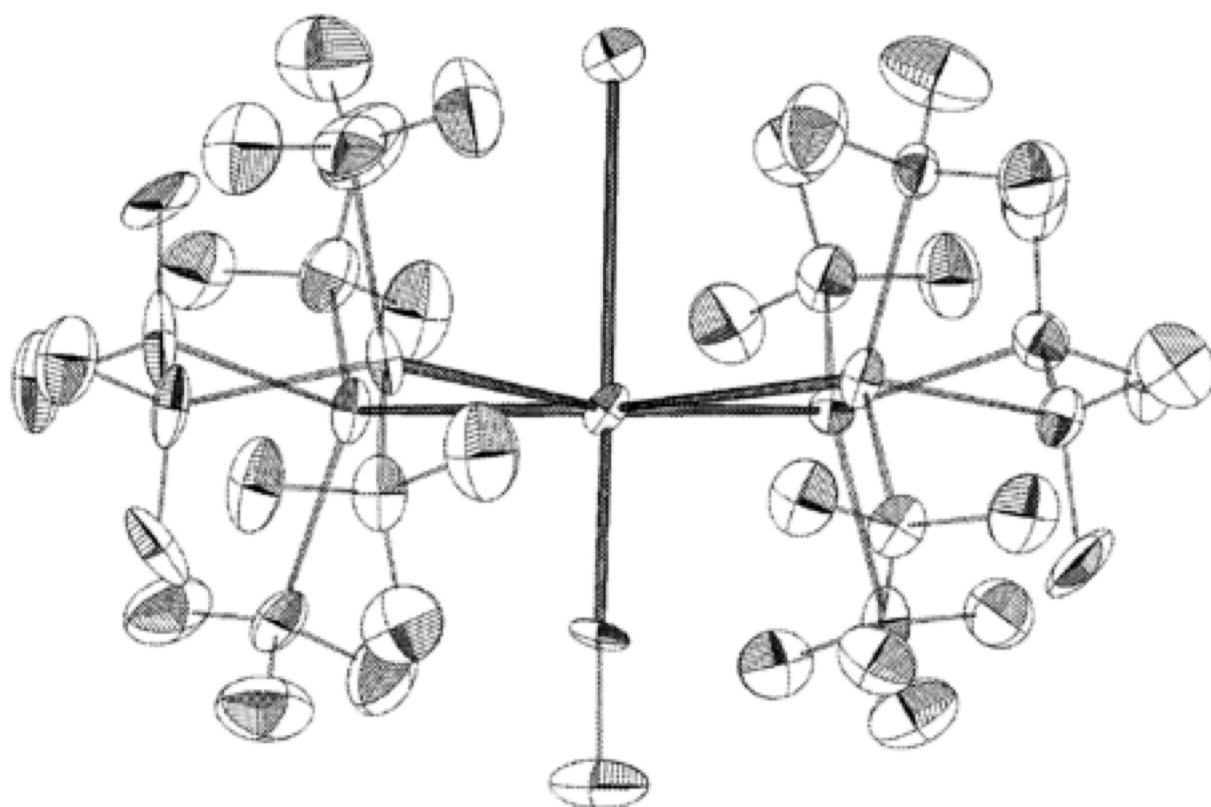


Figure 2b

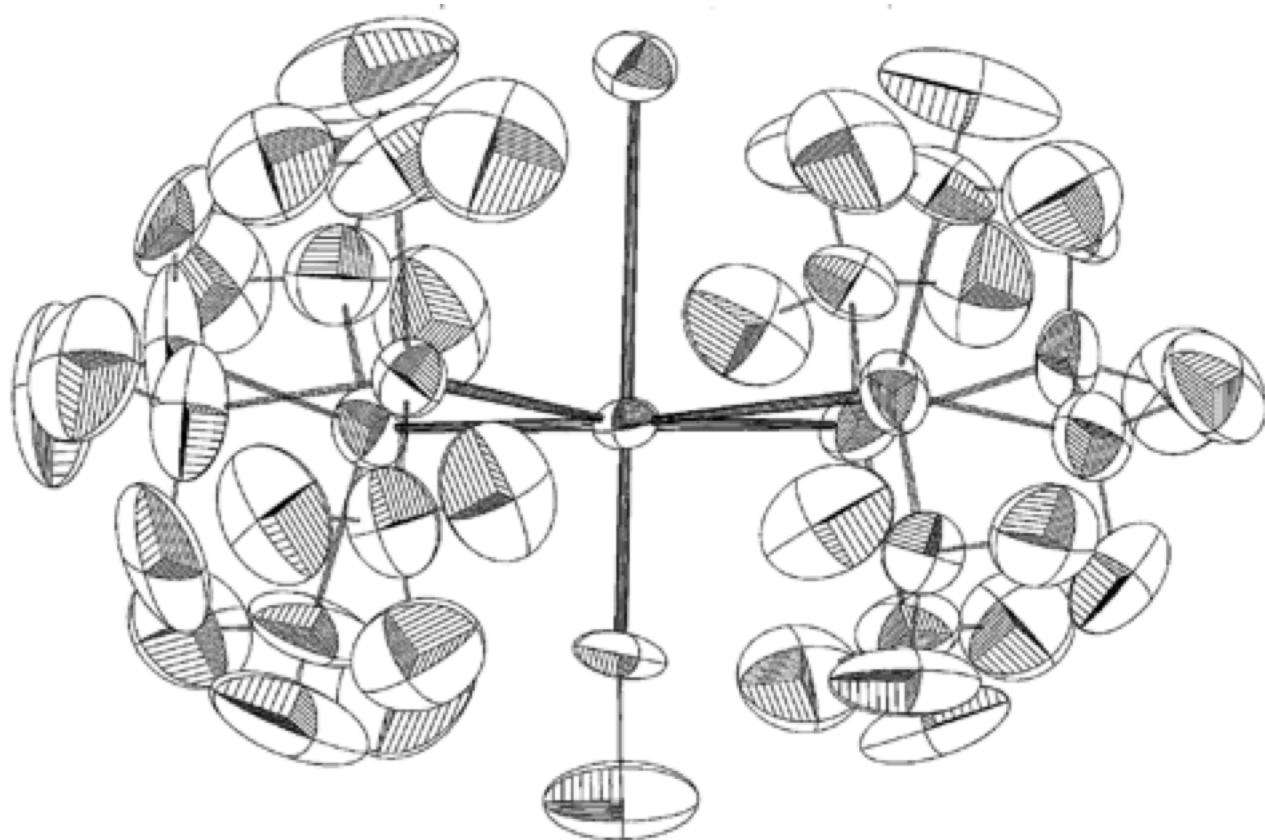


Figure 3

