DALTON
FULL PAPER

Chemical bonding in methylidyne complexes: neutron diffraction study on a single crystal of BrW≡CH(dmpe-d$_{12}$)$_2$

Carole Ménoret,[a] Anne Spasojević-de Bire,*[a] Nguyen Quy Dao,[a] Alain Cousson,[b] Jean-Michel Kiat,[a,b] Joseph D. Manna[c] and Michael D. Hopkins[d]

[a] *Laboratoire Structures, Propriétés et Modélisation des Solides, UMR 8580 du C.N.R.S., Ecole Centrale Paris, F-92295 Châtenay-Malabry Cédex, France. E-mail: spaso@spms.ecp.fr*
[b] *Laboratoire Léon Brillouin, unité mixte CEA-CNRS, CE Saclay, F-91191 Gif sur Yvette Cédex, France*
[c] *Department of Chemistry and Materials Research Center, University of Pittsburg, PA 15260, USA*
[d] *Department of Chemistry, The University of Chicago, 5735 S. Ellis Avenue, Chicago, IL 60637, USA*

Received 7th May 2002, Accepted 15th July 2002
First published as an Advance Article on the web 3rd September 2002

Carbyne complexes have been extensively studied but only a few of them contain the M≡C–H moiety (M = transition metal). In order to contribute to the debate about the linearity of this fragment, two neutron diffraction experiments on single crystal have been performed at 100 and 293 K on the *trans*-W(CH)(dmpe)$_2$Br (dmpe = 1,2-bis(dimethylphosphino)ethane) (**1**). The results point, without ambiguity, to the linearity of the fragment. The specific behaviour of the dmpe ligand is modelled and interpreted.

Introduction

Our studies of metal–alkylidyne complexes are directed at developing a thorough understanding of the nature of the metal–carbon triple bond.[1] Elucidation of the molecular structure (Table 1) and bonding of complexes of the type *trans*-W(CH)(dmpe)$_2$X (dmpe = 1,2-bis(dimethylphosphino)ethane, X = halide or alkynyl, compounds **1** to **11**) or *trans*-W(CH)(PMe$_3$)$_4$X (X = halide or alkynyl, compounds **12** to **14**), especially of the geometry of the M≡C–H group, is particularly important. These are the simplest carbyne derivatives[2–8] known up to now, conjugation and hyperconjugation effects[1b,9] 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 groups. 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 **12** was inconclusive due to disorder within the crystal. The tungsten atom lies on a crystallographic C_2 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 **1**, the X-ray structure of which has been determined.[3a] Interestingly, the molecules are so arranged that the W≡C–H $\cdots$ H–C≡W moieties are in a parallel configuration, a peculiarity which has been observed for all the methylidyne compounds (complexes **1**

Table 1 Crystallographic structures[2–8] of W (≡C–H)(dmpe-d$_{12}$)$_2$L and W (≡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 have been performed. Comments on the possible disorder do not concern the *cis* ligand. N = neutron source, Sync. = synchrotron source, X-Ray = classical X-Ray source

	Complexes	Source, temperature	Comment	Bond angles M≡C–H/°	References
1-d	W(≡C–H)(dmpe-d$_{12}$)$_2$Br	N, 100 K		this work	this work
1-d	W(≡C–H)(dmpe-d$_{12}$)$_2$Br	N, 293 K		this work	this work
1	W(≡C–H)(dmpe)$_2$Br	Sync., 123K		178.01(12)	2
1	W(≡C–H)(dmpe)$_2$Br	X-Ray, 213 K		164(6)	3
2	W(≡C–H)(dmpe)$_2$F	X-Ray, 296 K	disorder (F, C)	—	3
3	W(≡C–H)(dmpe)$_2$Cl	X-Ray, 296 K	2 molecules	—	3
3	W(≡C–H)(dmpe)$_2$Cl	X-Ray, 296 K	2 molecules	158(8)	4
4	W(≡C–H)(dmpe)$_2$I	X-Ray, 218 K		176(8)	3
5	W(≡C–H)(dmpe)$_2$(n-Bu)	X-Ray, 224 K		162(4)	3, 5
6	W(≡C–H)(dmpe)$_2$(OTf)	X-Ray, 227 K		177(4)	3
7	W(≡C–H)(dmpe)$_2$(CN)	X-Ray, 212 K		177(2)	3
8	W(≡C–H)(dmpe)$_2$(CCH)	X-Ray, 213 K		169(5)	3
9	W(≡C–H)(dmpe)$_2$(CCSiMe$_3$)	X-Ray, 209 K		164(5)	3
9	W(≡C–H)(dmpe)$_2$(CCSiMe$_3$)	X-Ray, 225 K		174(3)	6
10	W(≡C–H)(dmpe)$_2$(CCPh)	X-Ray, 218 K		174(3)	3
11	W(≡C–H)(dmpe)$_2$(CCp–C$_6$H$_4$CCPr)	X-Ray, 227 K		—	3
11	W(≡C–H)(dmpe)$_2$(CCp–C$_6$H$_4$CCPr))	X-Ray, 218 K		—	3
12	W(≡C–H)(PMe$_3$)$_4$Cl	X-Ray, 296 K	disorder (Cl, C), 2 molecules	—	7, 8
13	W(≡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
14	W(≡C–H)(PMe$_3$)$_3$OTf·THF	X-Ray, 208 K		173(3)	3

DOI: 10.1039/b204383a

to **14** in Table 1). The W≡C–H bond angle of the former series varies apparently from 158(8)° for **3** [4] to 173(3)° for **14** [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 or Schrock-type carbyne complexes (Fig. 1) shows that a small number of compounds present a bent conformation. This bending is explained by sterical considerations as reported by the authors[12j,v–x,z] or by an unusually long metal–carbyne bond[10a–b,d] (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 for establishing the methylidyne–hydrogen position.

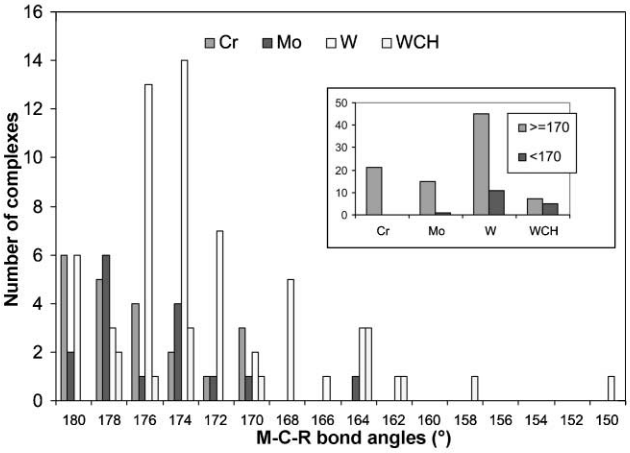

Fig. 1 Distribution of the M≡C–R bond angles for the carbyne complexes of Cr,[10] Mo[11] and W.[3–8,10a,b,10d,11f,12] The polymetallic complexes have been excluded of the comparison but the bis-carbyne has been included. R is any substituent. Insert : distribution of the "bent" M≡C–R bond angles (<170°) *versus* the linear moiety (≥170°).

This study reports the results obtained by neutron diffraction of an isotopomer of **1**: to avoid excessive background and reducing beam attenuation due to the presence of hydrogen atoms in the structure, $P(CD_3)_2$ groups were preferred to the $P(CH_3)_2$ for the neutron diffraction study, since the crystal structures of the isotopomers are known to be identical. For that reason, $W(CH)((CD_3)_2PCH_2CH_2P(CD_3)_2)_2Br$, **1-d** was synthesised for this study. We performed two neutron experiments: one at low temperature (100 K) to minimize the thermal parameters, and an other at room temperature in order to avoid the technical constraints due to the cryostat sheath and to answer to the eventual question of a phase transition, the first X-ray crystal structure of **1** having been performed at 213 K.

Experimental

Synthesis of W(CH)(dmpe-d$_{12}$)$_2$Br (1-d)

All manipulations were performed under an inert atmosphere using a standard glove box and Schlenk techniques. The ligands dmpe and $(CD_3)_2PCH_2CH_2P(CD_3)_2$ (dmpe-d$_{12}$) were prepared by treating $Cl_2PCH_2CH_2PCl_2$ with $Li(CH)_3$ and $Li(CD_3)$, 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 by ^{1}HNMR after 2 days, at which point the solvent was removed *in vacuo* and the remaining yellow solid was extracted into a solution of 3 : 1 pentane/toluene (60 mL) and filtered. The pentane was then removed under vacuum, and the yellow product 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 and 293 K

The single crystal of **1-d** used for the neutron diffraction experiment at low temperature is cylindrical (diameter of 5 mm, height of 1.2 mm) and was glued with an araldite glue inside an aluminium cylindrical box filled with helium due to the high sensitivity of the compound. The crystal was kept at 100(1) K with a closed-cycle cryo-refrigerator.[13] A second single crystal was used at room temperature for the neutron diffraction experiment, it is roughly hexagonal (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 λ_{100K} = 1.51 Å and λ_{293K} = 1.54 Å 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 experiments[3] at 213 K. The neutron parameters are at 100 K: a = 8.98(3) Å, b = 18.23(8) Å, c = 12.57(7) Å and β = 100.548(6)°, V = 2022(15) 10^9 Å^3 and at 293 K: a = 9.12(3) Å, b = 18.42(6) Å, c = 12.77(3) Å and β = 101.228(5)°, V = 2104(12) 10^9 Å^3 compared to the X-ray values[3] (213 K) a = 9.138(2) Å, b = 18.468(4) Å, c = 12.793(3) Å and β = 101.07(3)°, V = 2119(1) 10^9 Å^3.

At low temperature, the intensity data were collected for one complete quadrant of the reciprocal sphere up to 0.57 Å^{-1} and equivalent reflections were measured for some low order Bragg peaks. Intensities of the two reflections (0 4 0) and (2 4 0), monitored every 100 reflections, have a variation of less than 3%. The ω-step, ω/θ, and $\omega/2\theta$-step-scan methods were used for the intensity recording, depending on the θ values. The intensities were calculated using the Lehman and Larsen algorithm,[14] 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. 1053 of those were such as $I = 2\sigma$ with an internal reliability factor† $R_{int}(F^2) = 0.029$.

At room temperature, the intensity data were collected for all the reciprocal sphere up to 0.35 Å^{-1} and for one complete quadrant of the reciprocal sphere between 0.35 and 0.57 Å^{-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 on the θ values and leading to 4179 recorded reflections. A first rough integration was done using the Lehman and Larsen algorithm[14] 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. 868 of the latter show an intensity higher than 2σ with an internal reliability factor $R_{int}(F^2) = 0.060$.

CCDC reference numbers 185256 and 185257.

See http://www.rsc.org/suppdata/dt/b2/b204383a/ for crystallographic data in CIF or other electronic format.

Results and description of the structure

Full matrix least-square refinements were performed using the CRYSTAL program[15] and the SHELXL97 program[16] package. Coherent scattering lengths were taken from Sears.[17] For the low temperature experiment, a first refinement converged to $R_1(F) = 0.102$ and G.O.F. = 1.03 for 1053 reflections with $I \geq 2\sigma$ and 209 parameters (consisting in scale factor,

---

† $R_{int}(I) = \sum_{K=1}^{M}[\sum_{J=1}^{N}(I_M - I_J)^2]_K / \sum_K \sum_J (I_J{}^2)_K$ with J = sum over a symmetric equivalent group and K = sum over a symmetric independent reflection.

Table 2 Interatomic distances (Å) for **1-d** at 100 and 213 K [3a]

Distances	100 K (N)	213 K (X-ray)
W–Br	2.76(2)	2.760(1)
W–C1	1.750(12)	1.786(8)
⟨W–P⟩	2.424(5)	2.442(1)
⟨P–C(Me)⟩	1.822(3)	1.133(3)
P3–C10	1.844(8)	1.854(11) 1.908(44)
P4–C11	1.845(9)	1.875(12) 1.788(24)
C4–C5	1.510(7)	1.499(9)
C10–C11	1.506(7)	1.563(15) 1.475(57)
C1–H1	1.155(13)	0.792(81)

nuclear position, isotropic thermal parameters). Then a very meticulous anisotropic refinement, using constraints on 51 bond distances. These constraints were suppressed for the last cycle ($R_1(F)$ = 0.054 and G.O.F. = 1.17 for 1053 reflections with $I \geq 2\sigma$ and 470 parameters). At room temperature the isotropic refinement converged to $R_1(F)$ = 0.1702 and G.O.F. = 1.01 for 868 reflections with $I \geq 2\sigma$ and 209 parameters. 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 was the elimination of the contaminated reflection by the aluminium diffraction peaks coming from the sample holder and the cryostat. Despite, the low number of used reflections, the model fits a stable and reliable solution. Indeed the interatomic distances and bond angles remain stable within the errors, whatever the level of refinement. The greater variation between the isotropic/anisotropic refinement at 100 K lies on the W≡C1–H1 distance which is (1.77(1) Å, 1.13(1) Å) for the isotropic and (1.75(1) Å, 1.15(1) Å) for the anisotropic refinement, the variation of which is still within three σ. Therefore, the anisotropic results are used in the rest of the paper in order to be able to discuss (*vide supra*) the anomalous behaviour of some atoms. A special attention was paid on the methylidyne hydrogen atom determination which was easily located on the difference maps.

Fig. 2 shows the molecular structure of the complex at low temperature. The results obtained at room temperature are similar but less precise, therefore only the main interatomic distances and bond angles at low temperature are given in Tables 2 and 3. In a general manner, the results obtained by neutron diffraction confirm, more precisely, the preliminary structure determined previously by X-ray diffraction.[3] Indeed, all the hydrogen or deuterium atoms are localised and the averaged distances C–H or C–D are very satisfying (⟨$d_{\text{C–H}}$ = 1.113(4) Å⟩, ⟨$d_{\text{C–H}}$ = 1.10(2) Å⟩ and ⟨$d_{\text{C–D}}$ = 1.072(1) Å⟩, ⟨$d_{\text{C–D}}$ = 1.05(1) Å⟩ respectively at 100 and 293 K).

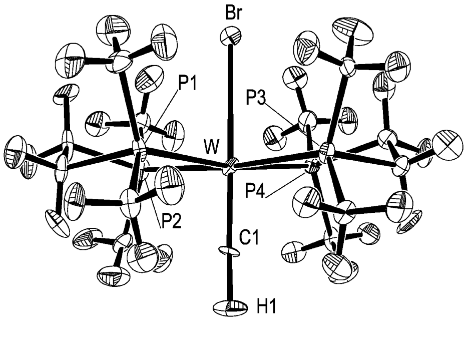

Fig. 2 (a) Molecular structure of **1-d** as determined by neutron diffraction at 100 K.

The general features of the structure can be briefly described as following: (i) The metal lies in a pseudooctahedral environment. (ii) The W≡C bond distance is one of the shortest distance reported ‡ (1.75(1) Å at 100 K and 1.77(1) Å at 293 K). (iii) The four phosphorus atoms are globally situated on the equatorial plane. The P–W–P intra-angles (⟨P–W–P = 81.1(2)°⟩ at 100 K, ⟨P–W–P = 80.9(4)°⟩ at 293 K) differ significantly from the P–W–P inter-angle (⟨P–W–P = 98.5(2)°⟩ at 100 K, ⟨P–W–P = 98.7(4)°⟩ at 293 K) as observed for other similar complexes §. In a first approximation these dmpe ligands are bent toward the bromine atom (⟨C1–W–P = 93.3(1)°⟩ at 100 K, ⟨C1–W–P = 93.2(3)°⟩ at 293 K). A deeper analysis of the behaviour of the dmpes in *trans*-W(≡CH)(dmpe)$_2$X will be discussed later. (iv) The most significant result of the present work is the precise determination of the W≡C–H bond angle (178.0(7)° at 100 K, 177.8(18)° at 293 K).

Table 3 Interatomic bond angles (°) for **1-d** at 100 and 213 K [3a]

Angles	100 K (N)	213 K (X-ray)
W–C1–H1	178.0(7)	164(6)
Br–W–C1	179.2(3)	177.8(2)
⟨Br–W–P⟩	86.7(2)	86.2(1)
⟨C1–W–P⟩	93.3(1)	93.0(2)
⟨P–W–P intra⟩	81.1(2)	80.6(1)
⟨P–W–P inter⟩	98.5(2)	99.1(1)
⟨P–W–P *trans*⟩	177.3(3)	173.9(1)
⟨W–P–C(Et)⟩	109.1(2)	109.1(1)
⟨W–P–C(Me)⟩	120.3(1)	120.0(1)
⟨C(Me)–P–C(Me)⟩	101.5(2)	101.1(2)
⟨C(Me)–P–C(Et)⟩	101.2(1)	101.6(3)
⟨P–C–C⟩	110.5(2)	113.4(6)
⟨H–C–P⟩	108.5(2)	
⟨H–C–C⟩	111.0(2)	
⟨H–C–H⟩	106.9(4)	
⟨D–C–P⟩	105.2(1)	
⟨D–C–D⟩	104.5(1)	

Discussion

Temperature effect

A fine observation of the distances for the three experiments (neutron at 100 K, X-ray at 213 K, neutron at 293 K) leads to the following conclusion: (i) Despite the small number of used reflections, the neutron experiment at low temperature is of the same quality level as the X-ray experiment, except obviously for the hydrogen and deuterium atom for which this work gives an accurate determination. (ii) As expected, the accuracy decreases 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 temperature range from 100 K to 300 K.

Specific behaviour of the dmpe ligand

Kostic and Fenske[19] have demonstrated that the *cis* carbonyl ligands are oriented towards the groups with the weakest π-acceptor, *i.e.* that carbyne ligands are among the best π-acid ligands. These theoretical results have been already observed experimentally for octahedral chromium carbyne complexes.[9,20] In order to extend this trend to the phosphine ligand, the behaviour of some octahedral tungsten carbyne complexes containing phosphine and carbonyl *cis* ligands has been studied (complexes presenting sterical effects have been excluded). One can find than for four complexes[12c,s,w,z,ae] the ⟨C≡W–P⟩ angle =

---

‡ The average interatomic distance W≡C is ⟨1.82 Å⟩ deduced from 49 structures (ref. 3–8, 10*a–b*, 10*d*, 11*e*, 12). Only two complexes exhibit shorter values: 1.728(7) Å (ref. 12*z*) and 1.746(9) Å (ref. 12*x*).

§ The average P–W–P intra-angles reported in complexes containing a dmpe ligand is ⟨80.2°⟩ (ref. 3–6, 18).

Table 4 Steric parameter (SP) of some methylidyne complexes. Model : structure calculated after a 180° rotation of the dmpe ligand which presents the shorter C1–W–P angles. C1 is the carbynic atom. SP = Σ (3.9 − $d_{C\cdots C}$) for intermolecular contacts shorter than 3.9 Å. The C1 ··· C1 distance is excluded of the summation

Complex	$d_{C1\cdots C1}$/Å	$d_{C\cdots C\ min}$/Å	SP (real)	Number of distances < 3.9 (real)	SP (model)	Number of distances < 3.9 Å (model)	SP model − SP real
1a	3.453	3.746	0.406	6	1.737	7	1.331
1b	3.531	3.849	0.079	2	0.808	5	0.729
2a	3.484	3.788	0.141	3	1.231	5	1.136
2b	3.596	3.833	0.067	1	2.331	9	2.264
5	3.458	3.933	0	0	0.710	4	0.710
6	3.577	3.887	0.013	1	0.782	4	0.769
7	3.772	3.639	0.598	4	0.513	6	−0.085
8	3.479	3.874	0.026	1	1.280	8	1.254
9	3.760	3.665	0.655	6	1.651	8	0.996
10a	3.507	3.575	0.825	4	0.968	4	0.143

95.8° while ⟨C≡W–C(CO)⟩ = 89.9°, 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 complexes,[12f,g,x] one obtains ⟨C≡W–P⟩ = 93.2° over 60 bond angles.

The behaviour of the dmpe ligand presents some specific characteristics that have to be emphasised. (i) The C1–W–P angles are not equal. Three of them give an average value of ⟨92.3(2)°⟩ at 100 K and ⟨92.4(3)°⟩ at 293 K compared to the fourth value (96.4(3)° at 100 K and 95.6(6)° at 293 K). (ii) Disorder in one of the two dmpes has been modelled in this work by abnormally large isotropic displacement parameters (U_{eq}); 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).¶ (iii) The disordered dmpe ligand is the one without the phosphorus atom which is most bent toward the bromine ligand.

For all the complexes except **10**, one phosphorus atom presents the specific behaviour (point i) described above. One of the two dmpes is disordered in all the complexes for which the structure can be simply determined, *i.e.* except for **2** and **3**. This disorder (point ii) is described by two branches (case of **1** (X-ray at 213 K), **7**, **8**, **9** (X-ray at 209 K) and **11** (X-ray at 227 K)) or by using abnormally large U_{eq} values (case of **1-d** (neutron at 123 K and 293 K), **1** (Sync. at 123 K), **4**, **5** and **6**). (The ratio of the averaged U_{eq} value of the carbon atoms of each dmpe is 1.33 for **1** (Sync. at 123 K), 1.76 for **4** and 1.32 for **5** and **6**).

An accurate examination of the packing arrangement explains the special position of one phosphorus atom. We have eliminated two compounds (**10** and **11**) for which the *trans* ligand presents a great steric bulk and two complexes for which the determination of the dmpe ligands was uncertain (**2** and **3**). Therefore we have worked with 10 structures (7 compounds). A modelled 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 4) compared to the C1 ··· C1 intermolecular distance (C1 is the carbynic atom). In order to model a steric effect, we have arbitrarily fixed a value (3.9 Å) above which the intermolecular distance has no more influence on the steric bulk. We have simply estimated the relative influence of each intermolecular distance inferior to 3.9 by the quantity defined as the summation of (3.9 − $d_{C\cdots C}$) over all the C ··· C distances shorter than 3.9.

This parameter (SP)|| can give an estimation of the constraints in the molecule. The greater this parameter is, the bigger the steric constraints are. One can observe (Table 4) that except for **6** where SP is similar in the real and in the modelled structure, all the steric effects are minimised in the real molecule. In other words, that means that one phosphorus atom kicked out from the equatorial plane (C1–W–P ≈ 96°) gives less steric effects than all four phosphorus atoms presenting a similar C1–W–P value (≈92°).

In order to explain the disorder of only one dmpe for the compounds (**1** (X-ray at 213 K), **7** and **9** (X-ray at 209 K)) where the disorder is modelled in the refinement by two dmpes (named A and B branch) with 50% occupation each, we have calculated two modelled structures containing two A or two B dmpes.** As previously done a steric parameter has been calculated in the real molecule and in the two modelled conformations. The calculations also show that steric constraints are responsible for the disorder of one dmpe ligand.

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

Nature of the W≡C–H bond angle

Now we want to focus on the question of the different W≡C–H bond angle values in methylidyne complexes. As observed in Table 1, half of the previous W≡C–H bond angle values reported from classical X-ray diffraction experiments are between 158(8) and 169(5)°, leading to a bent carbyne (**1** (X-ray at 213 K), **5**, **8** and **13**) whereas the other half presents W≡C–H bond angle values between 173(3) and 177(4)°, leading to a linear carbyne (**3**, **6**, **7**, **9** (X-ray at 209 K), **10** and **14**).

In order to obtain a tentative explanation of these different behaviours, it is important to recall the following parameters which influence the M≡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≡C bond distance (*i.e.* longer for a soft ligand[21] or a conjugated R); (iii) The nature of the *cis* ligand. For example, substituting four PMe_3 by two dmpes changes the conformation and leads 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

---

¶ For **1** (X-ray at 213 K) the disorder has been modelled 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.

|| All the C ··· C intermolecular distances inferior to 3.9 Å have been included in the calculation. For **1-d** (neutron at 100 K) 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.

** For the three structures presenting two disordered dmpe ligands the calculations have been performed in a lower space group with two independent molecules in the asymetric unit. For the modelled structure two different rotations have been done for each molecule.

orbitals. The interatomic distance M–L$_{cis}$ is also important, as shown by *ab initio* calculations[9a,22] and experimental works based on Raman spectroscopy[23] or density deformation study[9a,9c] of a methylmethylidyne complex; (iv) The intermolecular bonding. All these parameters can induce an asymmetry in the π-orbital of the carbyne bond, and a relative contribution of the M≡C resonant form.

Some common explanations for the bending of the 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 feature. Manna *et al.*[5] have made the hypothesis that a short $C_{carbyne} \cdots C_{carbyne}$ distance between two adjacent molecules may be responsible for the bent linkage. Moreover, Jorgensen[24] has studied the influence of a ligand *trans* to the M≡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 the precise examination of the behaviour of complexes from Table 1 as a function of those two hypotheses, one has to remember that X-ray data concerning the geometry of the carbyne groups are to be considered with care when H-atom positions are concerned. It could be noticed, for example, that two experiments were performed with classical X-ray diffraction for **9** at 209 K[3] and at 225 K.[6] The results of these experiments are not in agreement concerning the determination of the W≡C–H bond angle: at 209 K the axis W≡C–H is bent whereas at 225 K the axis is linear. Therefore, as expected, the geometry of the W≡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 $C_{carbyne} \cdots C_{carbyne}$ 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 **1**, **1-d** the $C_{carbyne} \cdots C_{carbyne}$ bond is measured as significantly shorter for the neutron experiments and nevertheless the W≡C–H axis remains linear. So the linear geometry is not a consequence of the packing effect.

The hypothesis of Jorgensen[24] which states that soft ligands *trans* to the carbyne carbon create more bending than hard ligands is valid for our results (**1-d**, **1** (Sync. at 123 K): that compound possesses a *trans* hard ligand (Br) and experimental observations indicate a linear linkage. The behaviour of the complexes **4**, **6** and **7** (hard ligand) and **5**, **8** and **9** (X-ray at 209 K) (soft ligand) seems consistent with this interpretation while **1** (X-ray at 213 K), **3 9** (X-ray at 225 K) and **10** do not verify this hypothesis. However, we have previously demonstrated for **1** (X-ray at 213 K) and **9** (X-ray at 225 K) that the ambiguity was due to the accuracy expected with a classical X-ray measurement. Therefore, it is not possible to validate Jorgensen's hypothesis even for the compounds (**4**, **5**, **6**, **7**, **8** and **9** (X-ray at 209 K)) for which it seems consistent. The only solution to validate or confirm Jorgensen's hypothesis is to perform a neutron diffraction experiment or a precise synchrotron experiment[2] on a simple carbyne complex with a soft ligand.

The situation of **13** seems to be different because it presents a short intramolecular $C_{carbyne} \cdots Al$ bond distance which can induce a bending.

In the previous works,[9] we have experimentally studied the bonding of $Cl(CO)_4Cr{\equiv}C{-}C_6H_5$ (**16**) and $Cl(CO)_4Cr{\equiv}C{-}CH_3$ (**17**) methylidyne complexes. A conjugation effect has been clearly demonstrated for **16** from the electron deformation density maps. The same trend has not been established for the methyl compound **17**. Thus, the strong influence of the R group for the contribution of the M≡C–R resonant form was shown. Concerning the M≡C–H moiety, simple chemical considerations should lead to a total sp character, and therefore to a linear behaviour, with a shorter M≡C bond distance. These trends are effectively observed for **1-d**.

Conclusion

The structure of a methylidyne compound possessing a hard ligand has been studied by neutron diffraction at low and room temperature. Despite the low number of used reflections in the refinements the two structures have been solved and gave consistent results. The main characteristics of the complex 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 phosphorus 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 for this behaviour. The linearity of simple methylidyne has been prooved without ambiguity, which was expected for a total sp character of the M≡C. The bent linkage observed previously for some compounds seems an artefact of the classical X-ray measurements. Nevertheless, it will be interesting to 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 metal carbyne moiety behaviour.

References

1 (*a*) E. O. Fischer, *Angew. Chem.*, 1974, **86**, 651–682; (*b*) U. Schubert, in *Carbyne Complexes*, ed. H. Fischer, P. Hofmann, F. R. Kreiβl, R. R. Schrock, U. Schubert and K. Weiss, VCH Publishers, Weinheim, 1988, pp. 39–58; (*c*) J. S. Murdzeck and R. S. Schrock, in *Carbyne Complexes*, ed. H. Fischer, P. Hofmann, F. R. Kreiβl, R. R. Schrock, U. Schubert and K. Weiss, VCH Publishers, Weinheim, 1988, pp. 147–203; (*d*) H. P. Kim and R. J. Angelici, *Adv. Organomet. Chem.*, 1987, **27**, 51–111; (*e*) A. Mayr and H. Hoffmeister, *Adv. Organomet. Chem*, 1991, **32**, 227–324.

2 C. Ménoret, A. Spasojević-de Biré, G. Baldinozzi and M. D. Hopkins, *ESRF experimental report no. CH487*, ESRF, Grenoble, 1999.

3 (*a*) J. Manna, PhD Thesis, University of Pittsburg, PA, USA, 1995; (*b*) J. Manna, R. F. Dallinger, V. M. Miskowski and M. D. Hopkins, *J. Phys. Chem. B*, 2000, **104**, 10928–10939.

4 J. Manna, L. A. Mlinar, R. J. Kuk, R. F. Dallinger, S. J. Geib and M. D. Hopkins, in *Transition Metal Carbyne Complexes*, ed. F. R. Kreiβl, Kluwer Academic Publishers, Dordrecht, 1993, vol. 392, pp. 75–77.

5 J. Manna, S. J. Geib and M. D. Hopkins, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 858–861.

6 J. Manna, S. J. Geib and M. D. Hopkins, *J. Am. Chem. Soc.*, 1992, **114**, 9199–9200.

7 M. R. Churchill, A. L. Rheingold and H. J. Wasserman, *Inorg. Chem.*, 1981, **20**, 3392–3399.

8 P. R. Sharp, S. T. Holmes, R. R. Schrock, M. R. Churchill and H. J. Wasserman, *J. Am. Chem. Soc.*, 1981, **103**, 965–966.

9 (*a*) A. Spasojević-de Biré, Nguyen Quy Dao, C. Thieffry, A. Strich and M. Bénard, *Inorg. Chem.*, 1990, **29**, 4908–4915; (*b*) A. Spasojević-de Biré, Nguyen Quy Dao, E. O. Fischer and N. K. Hansen, *Inorg. Chem.*, 1993, **32**, 5354–5361; (*c*) A. Spasojević-de Biré, Nguyen Quy Dao, P. J. Becker, M. Benard, A. Strich, C. Thieffry, N. K. Hansen and C. Lecomte, in *Application of Charge Density Research to Chemistry and Drug Design*, ed. G. A. Jeffrey and J. F. Piniella, Plenum Publisher, Nato ASI Series, New York and London, 1991, pp. 385–399.

10 (*a*) G. Huttner, H. Lorenz and W. Gartzke, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 609–611; (*b*) E. O. Fischer and U. Schubert, *J. Organomet. Chem.*, 1975, **100**, 59–81; (*c*) E. O. Fischer, G. Huttner, W. Kleine and A. Franck, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 760; (*d*) G. Huttner, A. Franck and E. O. Fischer, *Isr. J. Chem.*, 1976/77, **15**, 133–142; (*e*) E. O. Fischer, A. Schwanzer, H. Fischer, D. Neugebauer and G. Huttner, *Chem. Ber.*, 1977, **110**, 53–66; (*f*) A. Franck, U. Schubert and G. Huttner, *Chem. Ber.*, 1977, **110**, 3020–3025; (*g*) A. Franck, E. O. Fischer and G. Huttner, *J. Organomet. Chem.*, 1978, **161**, C27–C30; (*h*) S. Fontana, O. Orama, E. O. Fischer, U. Schubert and F. R. Kreiβl, *J. Organomet. Chem.*, 1978, **149**, C57–C62; (*i*) E. O. Fischer, W. R. Wagner, F. R. Kreissl and D. Neugebauer, *Chem. Ber.*, 1979, **112**, 1320; (*j*) C. Krüger, R. Goddard and K. H. Claus, *Z. Naturforsch.*, 1983, **38b**, 1431–1440; (*k*) N. A. Ustynyuk,

V. N. Vinogradova, V. G. Andrianov and Y. T. Struchkov, *J. Organomet. Chem.*, 1984, **268**, 73–78; (*l*) A. C. Filippou, B. Lungwitz, K. M. Wanninger and A. E. Herdtweck, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 924–927; (*m*) A. C. Filippou, D. Wossner, G. Kociok-Kohn and I. Hinz, *J. Organomet. Chem.*, 1997, **541**, 333–343.

11 (*a*) M. Green, A. G. Orpen and I. D. Williams, *J. Chem. Soc., Chem. Commun.*, 1982, 493–495; (*b*) T. Desmond, F. J. Lalor, G. Ferguson and M. Marvez, *J. Chem. Soc., Chem. Commun.*, 1984, 75–77; (*c*) A. Mayr, A. M. Dorries, G. A. Mc Dermott and D. van Engen, *Organometallics*, 1986, **5**, 1504; (*d*) S. R. Allen, R. G. Beevor, M. Green, A. G. Orpen, K. E. Paddick and I. D. Williams, *J. Chem. Soc., Dalton Trans.*, 1987, **3**, 591–594; (*e*) M. Bottrill, M. Green, A. G. Orpen, D. R. Saunders and I. D. Williams, *J. Chem. Soc., Chem. Commun.*, 1989, **3**, 511–18; (*f*) M. Bottrill, M. Green, A. G. Orpen, D. R. Saunders and I. D. Williams, *J. Chem. Soc., Dalton Trans.*, 1989, 511; (*g*) P. Dahlke, J. C. Jeffery, M. D. Mortimer and F. G. A. Stone, *Polyhedron*, 1992, **11**, 1587; (*h*) M. D. Mortimer, J. D. Carter, K. B. Kingsbury, K. A. Abboud and L. Mc Elwee-White, *J. Am. Chem. Soc.*, 1994, **116**, 8629; (*i*) H. Adams, N. A. Bailey, G. W. Bentley, J. E. Muir and M. J. Winter, *J. Chem. Soc., Chem. Commun.*, 1995, 515; (*j*) W. M. Vaughan, K. A. Abboud and J. M. Boncella, *Organometallics*, 1995, **14**, 1567; (*k*) G. M. Jamison, R. S. Saunders, D. R. Wheeler, T. M. Alam, M. D. Mc Clain, D. A. Loy and J. W. Ziller, *Organometallics*, 1996, **15**, 3244; (*l*) G. Nakamura, Y. Harada, Y. Mizobe and M. Hidai, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 3305–3315; (*m*) F.-W. Lee, M. C.-W. Chan, K.-K. Cheung and C.-M. Che, *J. Organomet. Chem.*, 1998, **552**, 255–263; (*n*) H. Wadepohl, U. Arnold, H. Pritzkow, M. J. Calhorda and L. F. Veiros, *J. Organomet. Chem.*, 1999, **587**, 233.

12 (*a*) E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrich, F. R. Kreissl and J. O. Besenhard, *Chem. Ber.*, 1977, **110**, 3397; (*b*) D. Neugebauer, E. O. Fischer, Nguyen Quy Dao and U. Schubert, *J. Organomet. Chem.*, 1978, **153**, C41–C44; (*c*) W. W. Greaves, R. J. Angelici, B. J. Helland, R. Klima and R. A. Jacobson, *J. Am. Chem. Soc.*, 1979, **101**, 7618–7620; (*d*) A. Mayr, A. M. Dorries, G. Mc Dermott, S. Geib and A. L. Rheingold, *J. Am. Chem. Soc.*, 1979, **107**, 7775–7776; (*e*) M. R. Churchill and W. J. Youngs, *Inorg. Chem.*, 1979, **18**, 2454–2458; (*f*) M. R. Churchill and J. J. Waserman, *Inorg. Chem.*, 1981, **20**, 4119–4123; (*g*) S. M. Rocklage, R. R. Schrock, M. R. Churchill and H. J. Waserman, *Organometallics*, 1982, **1**, 1332–1338; (*h*) M. H. Chisholm, J. C. Huffman and N. S. Marchant, *J. Am. Chem. Soc.*, 1983, **105**, 6162–6163; (*i*) F. A. Cotton and W. Schwotzer, *Inorg. Chem.*, 1983, **22**, 387–390; (*j*) F. A. Cotton and W. Schwotzer, *Inorg. Chem.*, 1983, **22**, 387; (*k*) F. A. Cotton, W. Schwotzer and E. S. Shamshoum, *Organometallics*, 1984, **3**, 1770; (*l*) F. A. Cotton, W. Schwotzer and E. S. Shamshoum, *J. Organomet. Chem.*, 1985, **296**, 55; (*m*) M. R. Churchill and Y.-J. Li, *J. Organomet. Chem.*, 1985, **282**, 239–246; (*n*) M. Green, J. A. K. Howard, A. P. James, C. M. Nunn and G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1986, 187–197; (*o*) O. Johnson, J. A. K. Howard, M. Kapan and G. M. Reisner, *J. Chem. Soc., Dalton Trans.*, 1988, 2903–2904; (*p*) S. J. Crennell, D. D. Devore, S. J. B. Henderson, J. A. K. Howard and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1989, **7**, 1363–74; (*q*) G. A. Carriedo, V. Riera, G. J. M. Rubio and G. Sanchez, *Acta Crystallogr.*, 1990, **C46**, 581–584; (*r*) R. A. Doyle and R. J. Angelici, *J. Am. Chem. Soc.*, 1990, **112**, 194–198; (*s*) G. A. Carriedo, G. Sanchez, V. Riera, C. Bois, Y. Jeannin and D. Miguel, *J. Chem. Soc., Dalton Trans.*, 1990, 3355–3362; (*t*) A. Mayr, A. M. Dorries, A. L. Rheingold and S. J. Geib, *Organometallics*, 1990, **9**, 964; (*u*) M. H. Chisholm, J. C. Huffman and J. A. Klang, *Polyhedron*, 1990, **9**, 1271; (*v*) A. C. Filippou, C. Volkl, W. Grunleitner and P. Kiprof, *Z. Naturforsch., B*, 1990, **45**, 351; (*w*) J. D. Carter, K. B. Kingsbury, A. Wilde, T. K. Schoch, C. J. Leep, E. K. Pham and L. McElwee-White, *J. Am. Chem. Soc.*, 1991, **113**, 2947–54; (*x*) L. M. Atagi, S. C. Critchlow and J. M. Mayer, *J. Am. Chem. Soc.*, 1992, **114**, 1483–1484; (*y*) C. M. Bastos, N. Daubenspeck and A. Mayr, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 743–745; (*z*) A. Mayr, R. T. Chang, T.-Y. Lee, O. K. Cheung, M. A. Kjelsberg, G. A. McDermott and D. Van Engen, *J. Organomet. Chem.*, 1994, **479**, 47–53; (*aa*) C. J. Jeffery, J. A. Mc Cleverty, M. D. Mortimer and M. D. Ward, *Polyhedron*, 1994, **13**, 353; (*ab*) A. Mayr and Tsung-Yi Lee, *Inorg. Chim. Acta*, 1996, **252**, 131; (*ac*) Lei Zhang, M. P. Gamasa, J. Gimeno, R. J. Carbajo, F. Lopez-Ortiz, M. Lanfranchi and A. Tiripicchio, *Organometallics*, 1996, **15**, 4274; (*ad*) G. A. Cairns, N. Carr, M. Green and M. F. Mahon, *J. Chem. Soc., Dalton Trans.*, 1996, **21**, 2431–2432; (*ae*) J. C. Jeffery and A. S. Weller, *J. Organomet. Chem.*, 1997, **548**, 195–203; (*af*) Lei Zhang, M. P. Gamasa, J. Gimeno, A. Galindo, C. Mealli, M. Lanfranchi and A. Tiripicchio, *Organometallics*, 1997, **16**, 4099; (*ag*) M. Pui Yin Yu, A. Mayr and Kung-Kai Cheung, *J. Chem. Soc., Dalton Trans.*, 1998, 475; (*ah*) P. J. Dyson, A. F. Hill, A. G. Hulkes, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1998, **37**, 1430; (*ai*) C. M. Bastos, K. S. Lee, M. A. Kjelsberg, A. Mayr, D. Van Engen, S. A. Koch, J. D. Franolic, W. T. Klooster and T. F. Koetzle, *Inorg. Chim. Acta*, 1998, **279**, 7; (*aj*) M. P. Y. Yu, K.-K. Cheung and A. Mayr, *J. Chem. Soc., Dalton Trans.*, 1998, **14**, 2373–2378; (*ak*) F.-W. Lee, M. C.-W. Chan, K.-K. Cheung and C.-M. Che, *J. Organomet. Chem.*, 1998, **563**, 191–200; (*al*) T. H. Warren, R. R. Schrock and W. M. Davis, *J. Organomet. Chem.*, 1998, **569**, 125–137; (*am*) F.-W. Lee, M. C.-W. Chan, K.-K. Cheung and C.-M. Che, *J. Organomet. Chem.*, 1998, **552**, 255–263; (*an*) L. Giannini, E. Solari, S. Dovesi, C. Floriani, N. Re, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1999, **121**, 2784–2796; (*ao*) H. Wadepohl, U. Arnold, H. Pritzkow, M. J. Calhorda and L. F. Veiros, *J. Organomet. Chem.*, 1999, **587**, 233; (*ap*) L. Zhang, M. P. Gamasa, J. Gimeno, M. F. C. G. da Silva, A. J. L. Pombeiro, C. Graiff, M. Lanfranchi and A. Tiripicchio, *Eur. J. Inorg. Chem.*, 2000, 1707.

13 Laboratoire Léon Brillouin prototype derived from an Oxford Instruments device.

14 M. S. Lehman and F. K. Larsen, *Acta Crystallogr.*, 1974, **A30**, 580.

15 D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Betteridge, *Crystals, Chemical Crystallography Laboratory*, University of Oxford, Oxford, 1996, 10.

16 G. M. Sheldrick, SHELXL97, Program for the refinement of crystal structures, University of Göttingen, Germany, 1997.

17 V. F. Sears, *Neutron News*, 1992, **3**, 26–37.

18 (*a*) A. Gourdon and K. Prout, *Acta Crystallogr.*, 1983, **C39**, 865–868; (*b*) M. H. Chisholm, K. Folting, K. S. Kramer and W. E. Streib, *J. Am. Chem. Soc.*, 1997, **119**, 5528–5539.

19 (*a*) N. M. Kostic and R. F. Fenske, *J. Am. Chem. Soc.*, 1981, **103**, 4677–4685; (*b*) N. M. Kostic and R. F. Fenske, *Organometallics*, 1982, **1**, 489–496; (*c*) N. M. Kostic and R. F. Fenske, *J. Am. Chem. Soc.*, 1982, **104**, 3879–3884.

20 Nguyen Quy Dao, D. Neugebauer, H. Février, E. O. Fischer, P. J. Becker and J. Pannetier, *Nouv. J. Chim.*, 1982, **6**, 359.

21 (*a*) R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533; (*b*) R. G. Pearson, *Chem. Brit.*, 1967, **3**, 103; (*c*) R. G. Pearson, *Inorg. Chem.*, 1988, **27**, 734.

22 (*a*) J. M. Poblet, A. Strich, R. Wiest and M. Bénard, *Chem. Phys. Lett.*, 1986, **126**, 169–175; (*b*) A. A. Low and M. B. Hall, *Organometallics*, 1990, **9**, 701–708.

23 Nguyen Quy Dao, G. P. Foulet-Fonseca, M. Jouan, E. O. Fischer, H. Fischer and J. Schmid, *C. R. Acad. Sci., Ser. II (Paris)*, 1988, **307 II**, 245.

24 K. A. Jorgensen, *J. Organomet. Chem.*, 1994, **478**, 9.