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The effect of ligand basicity on the unconventional hydrogen-bond in $H(\mu\text{-}H)Os_3(CO)_{10}L$ ($L = $ amine) derivatives

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Abstract

The reaction of amine ligands with the unsaturated 46 e^- cluster $Os_3(\mu\text{-}H_2)(CO)_{10}$ yields a series of complexes of formula $Os_3H(\mu\text{-}H)(CO)_{10}$(amine). In these derivatives the presence of an unconventional hydrogen-bond M–H···H–N is detected by the evaluation of proton spin-lattice relaxation times. In order to elucidate the relationship between pK_b and H···H length, the M–H···H–N distances were quantified for amines of known pK_b. In practice, this was achieved by comparing the T_1 values of the terminal hydride resonances of the protonated isotopomer with the T_1 values of the corresponding derivative containing selectively deuterated amine. A nice correlation between the M–H···H–N distances and the pK_b of the amine ligands was found. DFT calculations were carried out for the cluster on $Os_3H(\mu\text{-}H)(CO)_{10}$(Benzylamine) to gain a fuller understanding of the possible coordination geometries of an amine ligand on the surface of a tri-osmium cluster. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since it was first reported [1], the occurrence of weak electrostatic interactions between metal hydrides and hydrogens bonded to an electronegative main group atom (N or O) have become widely acknowledged [2]. Weak H···H interactions may even be responsible for the stabilization of transient species, such as catalytic intermediates. Investigations of a number of metal complexes by IR spectroscopy [3] have established that the strength of these bonds is in the range 3–7 kcal mol^{-1}. Theoretical studies support the view that M–H···H–X interactions (where X = O or N) [4] involve polarization of the H···H interaction leading to a formally polarized $M\text{–}H^{\delta-}\cdots H^{\delta+}\text{–}X$ interaction. It has been suggested that there are three key factors that affect such an interaction: (a) a geometric arrangement which favors the close approach of the two interacting groups; (b) the polarizability of the $M^{\delta+}\text{–}H^{\delta-}$ upon the approaching $N^{\delta-}\text{–}H^{\delta+}$ moiety, as a greater polarizability strengthens the H···H interaction and (c) the influence of trans-substituents on the $\delta-$ charge of the hydride ligand [5]. The description view of the hydride as a soft and polarizable species would be corroborated by observation of a relationship between the experimentally determined H···H distance and the ligand basicity. $H(\mu\text{-}H)Os_3(CO)_{10}(X\text{–}H)$ adducts were chosen for this study as they are easily formed by the reaction of the cluster $(\mu\text{-}H_2)Os_3(CO)_{10}$ with X–H containing bases. Previously we have developed a methodology for evaluating the H···H distances by T_1 measurements, and have structurally characterized several imine [6] or amine [7] systems containing the M–H···H–N interactions. DFT calculations have now been performed on $Os_3H(\mu\text{-}H)(CO)_{10}$(Benzylamine) cluster (shown in Fig. 1 with the labeling scheme) to gain a fuller understanding of the possible coordination geometries of an amine ligand on the surface of a tri-Osmium cluster. Particular attention was paid to the possibility of the amine group to rotate around the Os2–Os1–N–C torsion angle.

Transition metal chemical shifts are a very sensitive indication of chemical environment [8]. With this in

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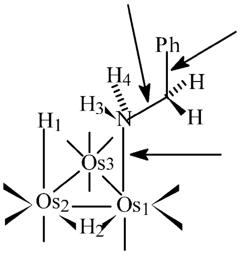

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Fig. 1. The model compound for the theoretical calculations with the adopted labeling scheme indicated, showing the degrees of freedom (black arrows), explored by the conformational search.

mind, we have also attempted, with only partial success, to relate changes in the amine basicity with the observed ^{187}Os chemical shifts.

2. Experimental

2.1. Materials

Routine NMR spectra were acquired on a JEOL EX400 spectrometer operating at 400 MHz ^{1}H, a JEOL GSX270 operating at 270 MHz ^{1}H, or a JEOL EX90 spectrometer operating at 90 MHz ^{1}H. Gradient selected spectra were acquired using a Bruker DMX600 equipped with an XYZ 10A gradients amplifier (z-gradient strength 0.05 T m^{-1}) and a 5 mm BBO probehead (inner coil X, outer coil ^{1}H) equipped with self-shielding z-gradients. $Os_3(CO)_{12}$ and $Os_3(\mu\text{-}H)_2(CO)_{10}$ were prepared as previously reported [9,10]. $Os_3(\mu\text{-}H)_2(CO)_{10}$ was recrystallized before use. ^{13}CO (99% ^{13}C) gas was used as supplied by Isotec, $Os_3(CO)_{12}$ was enriched as previously reported by gaseous exchange in octane solution at elevated temperature [11]. Benzylamine, 4-aminopyridine, p-anisidine, aniline, 4-chloroaniline, 3-fluoroaniline, 3-nitroaniline, 2,4-dichloroaniline, 4-nitroaniline were used as purchased from Aldrich. Selectively deuterated amines were prepared by the addition of 20 μl of D_2O to 4 mg of the ligand in a Younge's valve NMR tube. The mixture was shaken and allowed to stand for 1 min and then 0.7 cm^3 of CD_2Cl_2 was added.

2.2. The in situ synthesis of $H(\mu\text{-}H)Os_3(CO)_{10}(L)$

In a typical reaction, 10 mg of $Os_3(\mu\text{-}H)_2CO)_{10}$ (1.17×10^{-5} mol) was dissolved in 0.7 cm^3 of CD_2Cl_2 and transferred into a Younge's valve NMR tube. A 2 molar equiv. of base was then added. In the case of the more reactive bases (**1** and **2**) the solution immediately changed from purple to yellow, in the other cases there was little immediate observable color change.

2.3. NMR methods

Non selective inversion recovery was used to obtain ^{1}H T_1 values [12]. Samples for T_1 measurements were degassed using standard freeze–pump–thaw techniques. Spectra were acquired at 90, 270 and 400 MHz ^{1}H. Similarly, selectively deuterated samples were prepared and inversion recovery was used to obtain ^{1}H T_1 values. From the differences in the observed T_1 values, caused by deuteration, the effects of the H···H weak interaction were evaluated. Temperature calibrations were carried out with a standard methanol ^{1}H thermometer. Errors in the reported T_1 values were estimated to be in the ± 2% range.

2.4. ^{187}Os chemical shift determination

For the gradient selected HMQC and HMBC experiments, the gradient ratios were calculated according to the γ of the individual nuclei using the spectrometer software [13]. For ^{1}H–^{187}Os HMQC experiments, gradient ratios of 50:21:30 were used.

2.5. 2D Acquisition and processing strategy

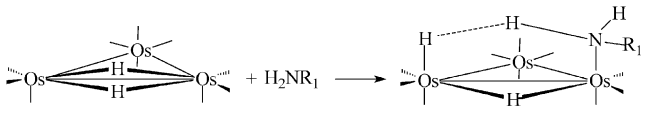
Initially, a spectrum was acquired with a spectral width of 100 kHz in the indirect dimension to ensure that the signal was not folded: ultimately this was reduced to 20 kHz and the number of increments increased to 512. The data were then transformed into a 2 by 4K data matrix with a SINE function. In all cases a magnitude calculation was performed in F1. Chemical shifts were referenced using the Ξ convention, with Ξ_{Os} taken as 2.303164 [13].

2.6. Theoretical calculations

DFT SCF-MO calculations [14] were performed on $Os_3H(\mu\text{-}H)(CO)_{10}(NPhH_2)$ (see Fig. 1), employing the BLYP [15] and B3-LYP [16] methods, as implemented in the GAUSSIAN 98 [17] program. The initial geometry of **1** was obtained by graphical manipulation (with the MOLDRAW [18] program) of the crystal structure of the related compound $H(\mu\text{-}H)Os_3(CO)_{10}(HN{=}CPh_2)$ [19], after which an exhaustive conformational search was performed, employing the MOLDRAW [17] and SPARTAN [20] programs. Geometrical optimizations were carried out at BLYP level [21], using Stuttgart RSC ECP pseudo-potentials and a related basis set [22] for the Os atoms and different basis sets, up to the 6-31G(d,p) [23], for the remaining atoms. Since full geometry optimizations gave unreasonably long Os–Os bonds, the Os–Os distances were constrained to the values observed in the crystal structure of the related compound $Os_3H(\mu\text{-}H)(CO)_{10}(HN{=}CPh_2)$ [19]. Single point energy calculations, using the BLYP/6-31G(d,p) optimized geometries, were carried out at the DFT level by adopting the hybrid B3-LYP [15] functional, employing the Stuttgart RSC ECP for the Os atoms and different basis sets, up to 6-311++G(2d,2p), for the remaining atoms. Only the results derived for the highest level of calculation [B3LYP/6-311++G(2d,2p)//BLYP/6-31G(d,p)] will be discussed here.

3. Results and discussion

The violet 46 e^-, formally unsaturated [24], cluster $Os_3(\mu\text{-}H)_2(CO)_{10}$ readily reacts, in CD_2Cl_2 solution at 273 K, with amine ligands (L) to form the corresponding $H(\mu\text{-}H)Os_3(CO)_{10}L$ derivative (L = benzylamine **1**, *p*-anisidine **2**, aniline **3**, 4-chloroaniline **4**, 3-fluoroaniline **5**) while 3-nitroaniline, 2,4-dichloroaniline and 4-nitroaniline do not react at all (Scheme 1).



Scheme 1. Reaction scheme leading to $Os_3H(\mu\text{-}H)(CO)_{10}NH_2R_1$.

The low temperature limiting ^1H spectrum (213 K, 400 MHz) of the adducts shows two major resonances at approximately −10.4 and −15.5 ppm, which are assigned to the terminal and bridging hydride ligands, respectively, the precise shift varies according to the ligand used (see Table 1).

Some of us have previously demonstrated that longitudinal relaxation time measurements (T_1) provide a viable method for the determination of the $H\cdots H$ distances in polyhydridic cluster systems [6,7,25]. As we wished to evaluate any correlation between the interaction strength and the ligand basicity, for a homologous series, we were constrained to use ligands of known basicity. Measurements of all the adducts formed (**1**–**5**) reveals that for any given adduct the terminal hydride had a shorter relaxation time than its bridging counterpart. The contribution from ^{189}Os ($I = 3/2$) cannot be responsible for this as the bridging hydride would be expected to relax faster (as it has 32% probability of being bound to ^{189}Os) than the terminal hydride (which had a 16% probability of being bound to ^{189}Os). Moreover, the T_1 measurements at three different magnetic field strengths allow us to rule out any preferential contribution, from the chemical shift anisotropy term, to the terminal hydride. One may, therefore, conclude that the difference in observed T_1's between bridging and terminal hydride comes mainly from the dipolar contribution of the amine proton.

The relaxation rates of the terminal and bridging hydrides, were then measured as function of the temperature in order to calculate the minimum T_1 values for each species. At the temperature of T_1 minimum, the actual τ_c value can easily be evaluated ($\tau_c = 0.62$ per ω_0). Thus the $H\cdots H$ distances may be calculated from the dipolar relaxation terms as previously reported [19].

However, there are possible errors in such a basic procedure as this would have neglected the differences in the Os–H dipolar interaction between the two hydrides and also the possibility that the N–H proton gives a dipolar contribution to the bridging hydride. Our proven methodology consists of determining the differences in the relaxation rates of the two isotopomers H,H and H,D which then allows us to quantify the dipolar contribution in the relaxation of a given hydride and then to evaluate the $H\cdots H$ distances.

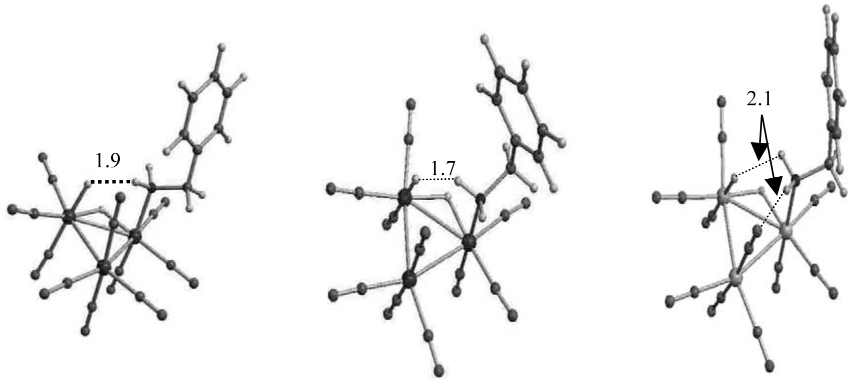
Whilst there is no great difference in the results obtained by the compensated and uncompensated methods, we believe that the selective deuteration method is likely to be more accurate. However, in most cases the difference is of a similar magnitude to the experimental error. The H–H distances evaluated by selective deuteration method are reported in Table 1. Whilst there was not 100% formation of the cluster ligand adduct, except in the case of **1**, we observed that the stronger the basicity of the ligand the higher the percentage of adduct formed. More interestingly the stronger the base the longer the interproton $Os\text{–}H\cdots H\text{–}N$ distance in the resulting adduct (see Table 1).

As all the nitrogen bases used in this work are primary amines, an open question is whether only one or both the hydrogen atoms of the NH_2 moiety interact with the terminal hydride. This has been tackled by an extended conformational search on compound **1** (see Fig. 1) using DFT to find its possible stable conformations. As carbonyl and hydride ligands have no conformational flexibility, they are therefore kept fixed in the conformational search. On the other hand, the degrees of freedom of the amine ligand were fully assessed by moving around the three torsion angles indicated by the arrows in Fig. 1. From this search process three conformers, c1, c2 and c3 shown in Fig. 2, were found. The relative stability and main geometrical features of these conformers are summarized in Table 2. These three conformers differ mainly in the value of the Os1–Os2–N–C torsion angle, which result in different *intra*-molecular contact patterns (shown as dotted lines in Fig. 2). Both c1 and c2 conformers form a single dihydrogen bond (DHB), involving H4 and H3, respectively. Whilst the geometry of conformer c1 was that expected from the crystal structure (see for example the related compound $H(\mu\text{-}H)Os_3(CO)_{10}(HN{=}CPh_2)$ [19], conformer c2 displays a quite different arrangement, in which the amine group points toward the axial carbonyl on Os3, but without showing particularly short contacts with this ligand (see Fig. 2(b)). Conformer c3 is characterized by the presence of a $N\text{–}H\cdots OC$ interac-

Table 1
NMR data for the $Os_3H(\mu\text{-}H)(CO)_{10}L$ adducts

Ligand	δ_{H1} (ppm)	δ_{H2} (ppm)	K_b^1	%	r_{H-H} 10^{-10} m	δ_{Os2} (ppm) δ ^{187}Os (N)	δ_{Os1} (ppm)	J_{Os2-H1} (Hz)	J_{Os2-H2} (Hz)	J_{Os1-H2} (Hz)
Benzylamine **1**	−10.47	−16.22	2.14×10^{-5}	100.0	1.99	−13288	−12291	37.4	33.5	38.0
p-anisidine **2**	−10.42	−15.54	2.19×10^{-9}	95.8	1.95	−13740	−12568	37.9	35.5	37.6
Aniline **3**	−10.38	−15.56	4.27×10^{-10}	89.7	1.93	−13430	−12267	38.7	34.6	36.1
4-chloroaniline **4**	−10.47	−15.53	1.41×10^{-10}	32.3	1.93	−13480	−12311	37.1	35.0	37.1
3-fluoroaniline **5**	−10.47	−15.52	3.16×10^{-11}	18.9	1.90	−13780	−12615	39.9	34.0	37.8
3-nitroaniline **6**			2.92×10^{-12}	0						
2,4-dichloroaniline **7**			1.12×10^{-12}	0						
4-nitroaniline **8**			1.00×10^{-13}	0						

For atoms labeling see Fig. 1. r_{H-H} were measured by selective deuteration T_1 methods: −70 °C in CD_2Cl_2 at 400 MHz. % refers to the percentage of the product with respect to the starting amount of $Os(\mu\text{-}H)_2(CO)_{10}$.



(a) – Conformer c1 **(b)** – Conformer c2 **(c)** – Conformer c3

Fig. 2. Stable energy minima for compound **1** (H· · ·H distance in Å).

Table 2
Geometrical parameters, energetic features and Mulliken charges of the conformations for compound **1** obtained after the conformational search (angles in °, distances in Å, relative stability in kcal mol^{-1})

	Conformer			NMR data
	c1	c2	c3	
Geometrical parameter				
Os2−Os1−N−C	162	239	204	
H1· · ·H3	1.93	3.10	2.48	1.99
H1· · ·H4	2.87	1.73	2.14	
ΔE [a]	0.34	0.0	+0.8	
Mulliken charges				
H1	−0.58	−0.59	−0.55	
H2	−0.41	−0.44	−0.39	
H3	0.20	0.24	0.15	
H4	0.22	0.23	0.25	

[a] Based on a B3LYP/6-311+ +G(2d,2p)//BLYP/6-31G(d,p) calculations (see supplementary material for further details).

tion, besides the Os−H· · ·H−N bond, as shown in Fig. 2(c).

DFT calculations indicate that the three conformers in Fig. 2 have similar stability [23]. Whilst the hypothetical 'bi-dentate' DHB conformation, in which both amine hydrogen atoms are involved in a DHB interaction (conformation c4 in Fig. 3) is not a minimum energy conformation on the BLYP/6-31G(d,p) potential surface. It is worth noting that geometrical optimization conformation c4 (unstable) leads to conformer c3 (stable), which is a minimum on the BLYP/6-31G(d,p) potential surface. Therefore, it could be suggested that H1· · ·OC contact in conformer c3 is more stabilizing (or less repulsive) than H1· · ·CO contact in conformation c4. However, a better steric arrangement of the ligands may equally well be the driving force for the stabilization of conformer c3 with respect to c4.

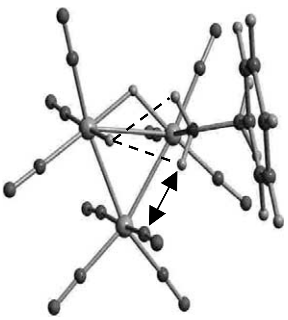


Fig. 3. The unstable c4 conformation, with the 'bi-dentate' DHB shown as dotted lines and the probably unfavorable contact as dashed arrow.

The H· · ·H distance of 1.99 Å found for **1** by NMR data in CD_2Cl_2 solution should be an average of the three conformers depicted in Fig. 2, with a rapid exchange between them. This dynamic exchange in solution is able to explain the differences between the observed NMR distance in solution, and that from theoretical calculations, as already demonstrated for the related $Os_3H(\mu\text{-}H)(CO)_{10}(HN{=}CPh_2)$ compound [19]. The other amine derivatives studied by NMR may probably be described by a similar dynamic model, since the small changes on the amine ligand should not be able to alter significantly the relative stability of conformations c1, c2 and c3. It is worth noting that the smaller benzylamine ligand in compound **1** may undergo larger molecular motions with respect to the bulkier benzophenoneimine in $Os_3H(\mu\text{-}H)(CO)_{10}(HN{=}CPh_2)$, where movements are limited to small vibration around the conformation observed in the X-ray structure.

3.1. ^{187}Os NMR spectroscopy

We were interested to see if trends in the ligand basicity were reflected in the metal chemical shifts. If we were able to measure the shifts of all the three metals it would, at least in principle, determine the actual effects of the steric and electronic parameters. Previously the chemical shifts of a series of related compounds $Os_3(\mu\text{-}H)_2(CO)_8\mu\text{-}L_2$ (L_2 = dppm, dppe, dppp and BINAP) and $Os_3(\mu\text{-}H)_2(CO)_{10}$ have been measured and found to be indicative of the metal-ligand ring size, as were the metal phosphine couplings and the hydride couplings [26].

In the $H(\mu\text{-}H)Os_3(CO)_{10}L$ derivatives there are of course three different osmium environments. Unfortunately the coupling from the bridging hydride to the remote osmium site proved to be too small to make such a measurement even by HMBC; for example, in the case of $Os_3(\mu\text{-}H)_2(CO)_{10}$ the coupling is only 1.4 Hz and, given that the hydride is likely forced further out of plane in $H(\mu\text{-}H)Os_3(CO)_{10}L$ derivatives, the coupling will be even smaller. For the osmium atom bearing the bridging and the terminal hydrides a reasonable correlation was found between the basicity and chemical shift for adducts **1**, **3**, **4** and **5**. We observed a high field shift of the osmium atom when the basicity of the amine ligand decreases. However, it is evident that other factors are involved in the case of **2**. Disappointingly no discernible trends have been found for the metal bearing the N donor and the bridging hydride.

4. Conclusions

In this study we were able to estimate by T_1 measurements the intramolecular hydrogen-bond distances between metal hydrides and N–H bonds present in a series of $H(\mu\text{-}H)Os_3(CO)_{10}(L)$ (L = amine) derivatives.

Moreover, we demonstrated that there is a clear relationship between the basicity of the ligand, the magnitude of the weak interaction and the interprotonic $H\cdots H$ distance.

The large freedom of motion of the mono-aromatic amines allows the presence of three possible conformers, with different hydrogen-bond patterns. However, experimentally a unique stable conformer was found for the related $H(\mu\text{-}H)Os_3(CO)_{10}(HN{=}CPh_2)$ compound [19], where the bulkier bi-aromatic $HN{=}CPh_2$ ligand causes greater rigidity. It has been shown for this compound that Mulliken charges of opposite sign are present in the hydride and the iminic proton, confirming an electrostatic contribution to the DHB [19]. The results obtained in this work qualitatively agree with this view. Thus a more electron depleted aminic hydrogen is expected when the basicity of the amine ligand decreases thus yielding a stronger DHB interaction. The correlation between the DHB distances and the amine basicity indicates that a simple polarizable model could explain the observed interaction between the hydride and the soft amine ligand.

5. Supplementary material

All the details about relative stability at the different level of theory are given in table S1, available as supplementary material.

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References

[1] (a) J.C. Lee, E. Peris, A.L. Rheingold, R.H. Crabtree, J. Am. Chem. Soc. 116 (1994) 11014;
(b) J.C. Lee, A.L. Rheingold, B. Muler, P.S. Pregosin, R.H. Crabtree, J. Chem. Soc., Chem. Commun. (1994) 1021;
(c) S. Park, R. Ramachandra, A.J. Lough, R.H. Morris, J. Chem. Soc., Chem. Commun. (1994) 2201.
[2] R.H. Crabtree, P.E.M. Siegbahn, O. Eisenstein, A.L. Rheingold, T.F. Koetzle, Acc. Chem. Res. 29 (1996) 348 (and references therein).
[3] L.M. Epstein, E.S. Shubina, J. Phys. Chem. 102 (1998) 359.
[4] D. Braga, F. Grepioni, E. Tedesco, M.J. Calhorda, E.M. Lopes, New J. Chem. (1999) 219.
[5] E. Peris, J.C. Lee, J.R. Rambo, O. Einsentein, R.H. Crabtree, J. Am. Chem. Soc. 117 (1995) 3485.
[6] (a) S. Aime, M. Ferriz, R. Gobetto, E. Valls, Organometallics 18 (1999) 2030;
(b) S. Aime, M. Ferriz, R. Gobetto, E. Valls, Organometallics 19 (2000) 707.
[7] S. Aime, R. Gobetto, E. Valls, Organometallics 16 (1997) 5140.
[8] W. Leitner, M. Buehl, R. Fornika, C. Six, W. Baumann, E. Dinjus, M. Kessler, C. Krueger, A. Rufinska, Organometallics 18 (1999) 1196.
[9] C.W. Bradford, R.S. Nyholm, Chem. Commun. (1967) 384.
[10] H. Kaesz, Chem. Brit. (1973) 344.
[11] See for example: (a) S. Aime, W. Dastru, R. Gobetto, J. Krause, L. Violano, Inorg. Chim. Acta 235 (1995) 357;
(b) S. Aime, W. Dastru, R. Gobetto, A.J. Arce, Organometallics 13 (1994) 3737;
(c) S. Aime, R. Bertoncello, V. Busetti, R. Gobetto, G. Granozzi, D. Osella, Inorg. Chem. 25 (1986) 4004.
[12] (a) A. Abragham, The Principles of Nuclear Magnetic Resonance, Oxford University Press, Oxford, 1961;
(b) A.E. Derome, Modern NMR Techniques for Chemistry Research, Pergamon, Oxford, 1987;
(c) T.D.W. Claridge, High-Resolution NMR Techniques in Organic Chemistry, Tetrahedron Organic Chemistry Series, vol. 19, Pergamon, Oxford, 1999.
[13] S. Berger, R. Braun, K.O. Kowinski, 150 and More NMR Experiments, Wiley VCH, Weinheim, 1999.
[14] Various platforms, among which the SGI O3K supercomputer of CINECA (www.cineca.it) were employed.

[15] Becke88 exchange functional: A.D. Becke, Phys. Rev. A 38 (1988) 3098 and LYP correlation functional: C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.

[16] A.D. Becke *J. Chem. Phys.* **98** (1993), p. 5648.

[17] Gaussian 98, Revision A.7, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople (1998) Gaussian, Inc., Pittsburgh, PA.

[18] P. Ugliengo, D. Viterbo, G. Chiari, Z. Kristallogr. 207 (1993) 9 (web site: http://www.ch.unito.it/ifm/fisica/moldraw/moldraw.html).

[19] S. Aime, E. Diana, R. Gobetto, M. Milanesio, E. Valls, D. Viterbo, Organometallics 21 (2002) 50.

[20] SPARTAN 5.0.2, Wavefunction Inc., 18401 Von Karman Ave., Ste. 370 Irvine, CA 92612 USA.

[21] BLYP, a pure DFT functional, was chosen to fully exploit the calculation speedup, obtainable using the fast multipole method (FMM algorithm, see J.M. Milliam, G.E. Scuseria, J. Chem. Phys. 106 (1997) 5569), as implemented in Gaussian 98.

[22] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, Theor. Chim. Acta 77 (1990) 123. STUTTGART ECPs can be retrieved in the following web site: http://www.theochem.uni-stuttgart.de/.

[23] W.J. Hehre, L. Radom, P.V. Schleyer, J. Pople, Ab Initio Molecular Orbital Theory, first ed. (Chapter 4), Wiley, New York, 1986.

[24] M.P. Brown, P.A. Dolby, M.M. Harding, A.J. Matthews, A.K. Smith, J. Chem. Soc., Dalton Trans. 11 (1993) 1671.

[25] S. Aime, M. Cisero, R. Gobetto, D. Osella, A.J. Arce, Inorg. Chem. 30 (1991) 1614.

[26] (a) A.E. Aliev, A.J. Deeming, M.J. Stchedroff, J.W. Steed, Organometallics, submitted for publication;
(b) M.J. Stchedroff, S. Aime, R. Gobetto, L. Salassa, E. Nordlander, Magnetic Reson. Chem. 40 (2002) 107.