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Metal vapour synthesis and conformational analysis of bis(2-trimethylsilyl-3-methyl-phosphobenzene)†

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Reaction between chromium and 2-trimethylsilyl-3-methylphosphobenzene {$C_5PH_3[Si(CH_3)_3](CH_3)$} vapours using metal vapour synthesis techniques produces an extremely air-sensitive yellow oil at room temperature; after sublimation and characterization by mass spectrometry and ^1H and ^{31}P NMR spectroscopy this oil proves to be a mixture of two isomers, which various techniques failed to separate. With the impossibility of obtaining crystal structures, we have used evidence from the NMR data that one of the isomers shows a long-distance P–P interaction, and extended Hückel calculations, to access the conformations of the two isomers. The calculations show that absolute minima occur for stereochemical reasons when both trimethylsilyl groups are pointing in opposite directions. Copyright © 2000 John Wiley & Sons, Ltd.

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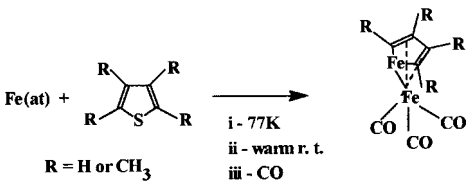
INTRODUCTION

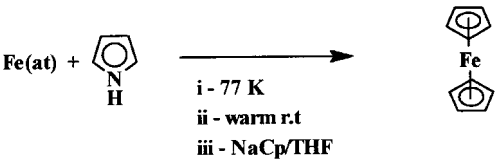
Early attempts of reactions between metal vapours and heterocyclic compounds demonstrated difficulties posed by the heteroatom for the synthesis of organometallic complexes: Timms[1] found that the reaction between iron and thiophene gave only one isolable product, the metallocyclopentadiene compound as a tricarbonyl adduct, by allowing the reaction mixture to warm up in a carbon monoxide (CO) atmosphere (Eqn [1]); in the absence of added CO or in the presence of other possible ligands, such as dienes or phosphines, no compounds were isolated.



[1]

When Cloke tried the reaction of metal atoms (Cr and Mo) with benzothiophene[2] he found that complexes in which the benzothiophene was η^6 coordinated by the benzene ring were formed. Again in the Mo-atom reactions there was evidence for desulfurization of the benzothiophene molecule.

Metal atom reactions with pyrrole gave no simple adducts but the iron–pyrrole reaction (Eqn [2]) formed a kind of 'slurry' that produced complexes when it reacted with other ligands.[3]



[2]

Six-membered heterocycles have been considerably more successful in reactions with metal vapours, except in the case of pyridine, where only bulky substituted pyridines gave isolable complexes.[4] Being a poorer base than pyridine, so reducing the possibility of η^1 As–M interactions, arsobenzene was used to obtain the bis-arsobenzene chromium (Eqn [3]).[5] Phosphobenzene, a π-donor as good as benzene, when reacted with vanadium

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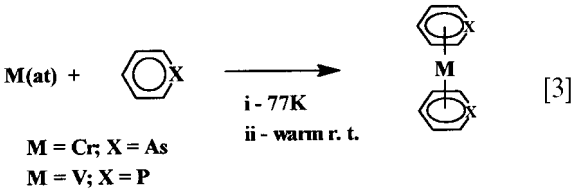
vapour, gave the bis-phosphobenzene vanadium $[V(\eta^6\text{-}C_5H_5P)_2]$.[6,7]



[3]

With the aim of investigating the relative contributions of stereochemical and electronic interactions to the stability of possible conformations, we chose to use as a ligand 2-trimethylsilyl-3-methylphosphobenzene.

Table 1 ^{1}H NMR assignments for bis(2-trimethylsilyl-3-methylphosphobenzene)

Proton	Chemical shift (ppm)	Couplings (Hz)
Ortho **A**	4.156	$3J_{ortho-meta}$**A** = 7.8 $2J_{ortho-P}$**A** = 36.7
Ortho **B**	3.888	$3J_{ortho-meta}$**B** = 7.9 $2J_{ortho-P}$**B** = 36.1
Meta **A**	4.875	$3J_{ortho-meta}$**A** = 7.8 $2J_{ortho-P}$**A** = 36.7
Meta **B**	4.626	$3J_{ortho-meta}$**B** = 7.9 $2J_{ortho-P}$**B** = 36.1
Para **A**	4.912	$3J_{meta-para}$**A** = 6.2
Para **B**	4.750	$3J_{meta-para}$**B** = 6.1
(CH_3) **A**	2.099	
(CH_3) **B**	1.865	
$[Si(CH_3)_3]$ **A**	0.377	
$[Si(CH_3)_3]$ **B**	0.415	

RESULTS AND DISCUSSION

A solution of 5 ml of freshly distilled 2-trimethylsilyl-3-methylphosphobenzene in 20 ml of hexane was placed in the ligand inlet system of a metal vapour synthesis (MVS) reactor.[8,9]

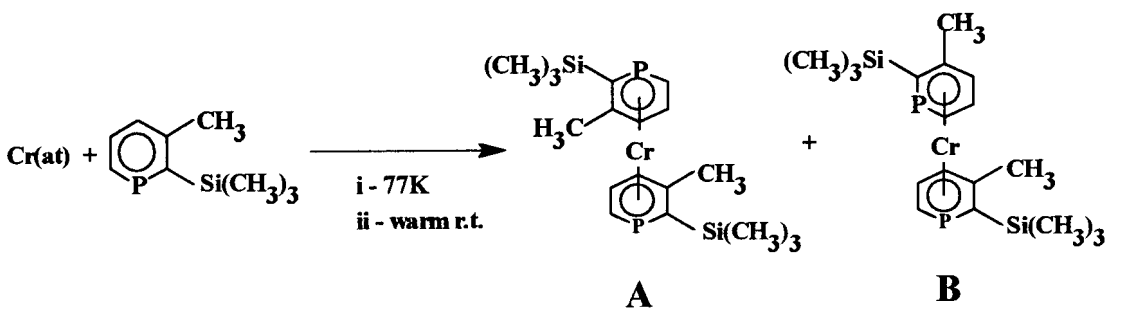
Chromium atoms, generated from an electron gun furnace (*ca* 3.05 g, using a power of 420 W), and the phosphobenzene solution were co-condensed during 90 min onto the glass reaction vessel walls cooled by liquid nitrogen. The product matrix was allowed to warm up to room temperature and the products were extracted with petroleum ether (30–40 °C). Products were treated and characterized by normal techniques for air-sensitive compounds. The excess of chromium metal was removed by filtration through a Celite bed and the solvent was pumped off the filtrate. Excess of ligand was removed by evaporation in vacuum (10^{-2} mbar) at 50 °C to a cold-finger. The initial product was a brown solid from which a bright yellow oil was finally isolated by sublimation in vacuum (10^{-7} mbar) at 100 °C.

This oil was extremely air-sensitive and all the attempts to recrystallize it or to purify it by chromatography were unsuccessful.

The reaction product was studied by ^{1}H and ^{31}P NMR spectroscopy, using a Bruker AMX 500 spectrometer. The analysis of the ^{1}H NMR spectra (Table 1), and integration of the aromatic protons, showed the yellow oil to be a mixture of two isomers of bis(2-trimethylsilyl-3-methylphosphobenzene), composed of 40% of isomer **A** and 60% of isomer **B** (Eqn. 4).

The 'shoulders' on each side of the doublets assigned to the *ortho* protons of isomer **B** (Fig. 1, indicated by an *) were assigned, after a ^{1}H NMR coupling computer simulation,[10] to a long-range interaction between the two phosphorus atoms, with a P–P coupling constant of 15 Hz. This P–P interaction could only be detected in isomer **B**, in which the two phosphorus atoms are closer than in isomer **A** (see Fig. 2).

The ^{31}P NMR spectrum shows two doublets, one at −17.39 ppm, corresponding to isomer **A**, and one at −25.30 ppm, due to isomer **B**; the coupling



[4]

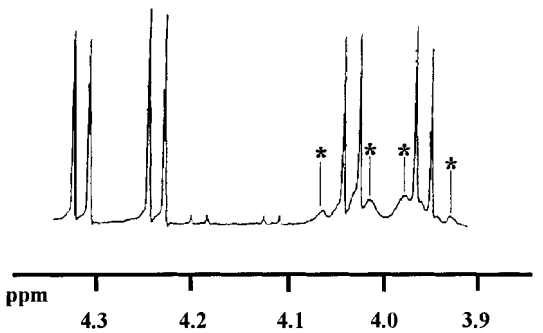


Figure 1 ^{1}H NMR spectra (H atoms *ortho*) of bis(2-trimethylsilyl-3-methylphosphobenzene).

constants between *ortho* protons and P are identical to the ones previously detected in the ^{1}H spectra.

The compound was also characterized by mass spectrometry, using a Kratos MS-25 GC–MS, and shows a parent molecular ion peak at $m/z = 416$. The fragmentation pattern was complex and indicates not only the loss of ligand but also fragmentation (Table 2).

EXTENDED HÜCKEL MO CALCULATIONS

In order to investigate the conformational preferences of isomers **A** and **B**, Extended Hückel MO (EHMO) calculations were carried out on a sandwich-type model complex with the parameters d(Cr–centroid) = 1.61 Å, d(P–centroid) = 1.82 Å, d(C–centroid) = 1.40 Å, d(C–Me) = 1.50 Å, d(C–Si) = 1.90 Å, d(Si–Me) = 1.87 Å and d(C–H) = 1.08 Å. When one of the six-member rings is allowed to rotate around the Cr–centroid bond, absolute minima are found when the trimethylsilyl groups are pointing in opposite directions with a 180 ° (**A**) or 60 ° (**B**) P-centroid-centroid-P dihedral angle (Fig. 2).

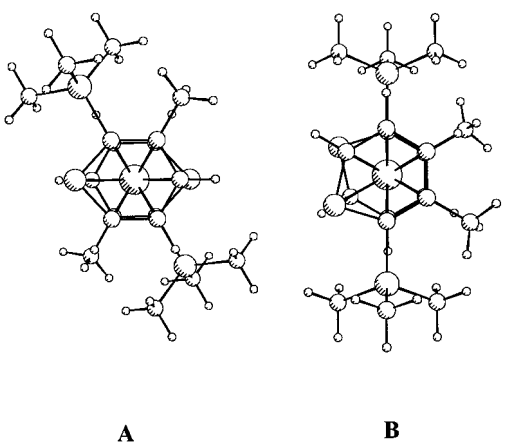


Figure 2 EHMO-optimized structures of conformers **A** and **B**.

Table 2 Mass spectra fragment identification for bis(2-trimethylsilyl-3-methylphosphobenzene)

m/z	Fragment
52	$\{Cr\}^+$
73	$\{Si\}^+$
167	$\{C_5H_3P(Si(CH_3)_3)\}^+$
182	$\{C_5H_3P(CH_3)(Si(CH_3)_3)\}^+$
234	$\{Cr[C_5H_3P(CH_3)(Si(CH_3)_3)]\}^+$
386	$\{Cr[C_5H_3P(Si(CH_3)_3)]_2\}^+$
416	$\{Cr[C_5H_3P(CH_3)(Si(CH_3)_3)]_2\}^+$

The two isomers **A** and **B** were found to differ in energies by only 0.09 eV (Fig. 3), which accounts for the occurrence of both in the products.

The stability of **A** and **B** was attributed to stereochemical reasons rather than to electronic interactions. Calculations carried out on a model complex in which there were only hydrogen substituents on the six-membered ring depicted a sharp descent in energy until a twist of 60 ° (P-centroid-centroid-P) was achieved; there was flattening after this value to an absolute minimum at 120 ° (*meta*).

The P–P interaction observed in the ^{1}H NMR of **B** is also supported by the calculated overlap population of 0.013 electrons for conformer **B** against −0.001 electrons for **A**.

We conclude that the interaction of the bulky

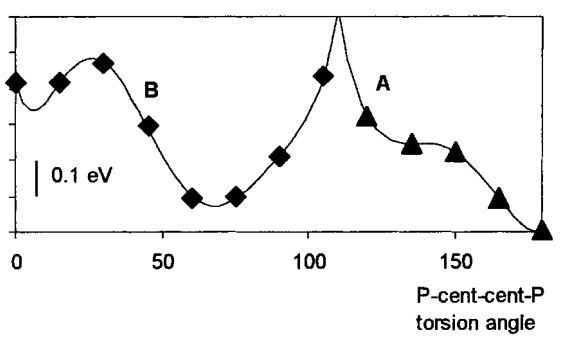


Figure 3 Energy plots for the optimization of conformers **A** and **B**.

trimethylsily groups stops the 'free' rotation of the rings and give rise to freezing of the conformers at the two absolute minima.

Extended Hückel[11,12]-type calculations were carried out with modified H_{ij}.[13] The basis set for the metal atoms consisted of *ns*, *np* and $(n-1)d$ orbitals. The *s* and *p* orbitals were described by single Slater-type wavefunctions, and *d* orbitals were taken as contracted linear combinations of two Slater-type wavefunctions. Standard parameters were used for all atoms. The EHMO calculations were made using *CACAO*.[14]

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