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Photoelectron spectroscopy and electronic structure of the hexaphosphatitanocene $[Ti(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ †

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Density functional calculations on $[Ti(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ gave estimates of structural parameters in excellent agreement with experiment and predicted a diamagnetic ground state as has been found. Back donation from the metal to the π LUMO of the ring forming a δ bond accounts for the inter-ring angle and the diamagnetism. The He I photoelectron spectrum of $[Ti(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ is assigned. Agreement between calculated and experimental ionization energies lends support to the detailed orbital analysis that is presented.

Introduction

Of the first row transition metals only Sc and Ti fail to form simple metallocenes of stoichiometry $M(\eta^5\text{-}C_5H_5)_2$. Permethylation of the rings enabled $[Ti(\eta^5\text{-}C_5Me_5)_2]$ to be characterized; in solution it is in equilibrium with a C–H activated species.[1] More recently use of the very bulky ligands $C_5Me_4(SiMe_2Bu^t)$ and $C_5Me_4(SiMe_3)$ enabled the isolation and structural characterization of the paramagnetic titanocenes.[2,3] Phosphorus substituted carbocyclic rings have been shown to be particularly effective at stabilizing low oxidation states of the early transition metals.[4] The 1,2,4-triphosphacyclopentadienyl analogue $P_3C_2Bu^t_2$ has been used to prepare diamagnetic $[Ti(\eta^5\text{-}P_3C_2Bu^t_2)_2]$, **1a**.[5] The rings are approximately planar with the *tert*-butyl groups staggered so as to minimize inter-ring interactions. The angle between the ring planes is 16.05°.

As part of a continuing investigation of the electronic structure of transition metal complexes of polyphospholyl ligands,[6,7] we have carried out a photoelectron spectroscopic and density functional study of $[Ti(\eta^5\text{-}P_3C_2Bu^t_2)_2]$.

Experimental

Photoelectron spectroscopy

The HeI photoelectron spectrum was measured using a PES laboratories 0078 spectrometer interfaced with an Atari microprocessor. The spectrum was calibrated with He, Xe and N_2. Low counting rates prevented acquisition of a He II spectrum.

Theoretical methods

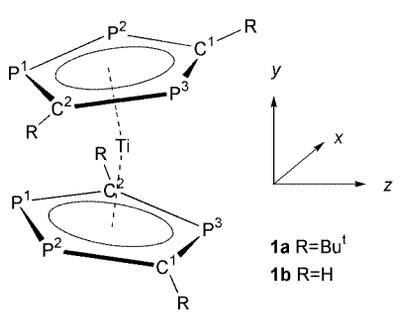
All calculations were performed using density functional methods of the Amsterdam Density Functional package (Version 2.3 or 1999). The basis set used triple-ζ accuracy sets of Slater type orbitals, with a single polarization functional added to the main group atoms. The cores of the atoms were frozen [C (1s), P (2p), Cr (2p), Mo (3d), W (5p)] and treated relativistically using the Dirac utility. The GGA (non-local) method was used, using Vosko, Wilk and Nusair's local exchange correlation[8] with non-local-exchange corrections by Becke[9] and non-local correlation corrections by Perdew.[10] The non-local correction terms were not utilized in calculating gradients during geometry optimizations. The valence calculations were quasi-relativistic using the Pauli formalism. Vertical ionization energies were estimated, using the optimized structure, from the difference between the total energy for the molecule and that for the molecular ion in the appropriate state. Convergence was most readily achieved for the ion states when the input basis function for the SCF calculation was the MOs of the molecular calculation. This also enabled a ready check on how precisely the "hole" in the ion could be described as a single MO in the molecule. A fragment analysis was carried out on $[Ti(\eta^5\text{-}P_3C_2H_2)_2]$ in order to ascertain the contribution to the MO of the various metal and ring basis orbitals.

† Electronic supplementary information (ESI) available: colour version of Fig. 2. See http://www.rsc.org/suppdata/dt/b0/b005657j/

Results and discussion

Structural studies

The structure of compound **1a** has C_2 symmetry and shows the rings to be slightly tilted with the two P(1) atoms being the closest point of approach. The *tert*-butyl groups are staggered in this conformation.



1a R=Bu^t
1b R=H

Geometry optimization of compound **1a** gave structural parameters in excellent agreement with the experimental values (Table 1). In order to investigate the extent to which the conformation is controlled by the bulky substituents, the structure of **1b**, where the *tert*-butyl groups are replaced with hydrogens, was also optimized. The same conformation and inter-ring angle were predicted, the only difference being marginally

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Table 1 Calculated and experimental structural parameters (distances in Å, angles in °) for $[Ti(\eta^5\text{-}P_3C_2R_2)_2]$

	Calc. R = H	Calc. R = Bu^t	Exp. R = Bu^t
Ti–C(1)	2.30	2.32	2.354(2)
Ti–C(2)	2.41	2.44	2.470(2)
Ti–P(1)	2.45	2.46	2.477(1)
Ti–P(2)	2.49	2.50	2.535(1)
Ti–P(3)	2.64	2.63	2.637(1)
C(1)–P(1)	1.77	1.81	1.790(2)
C(1)–P(3)	1.77	1.77	1.764(2)
C(2)–P(2)	1.77	1.80	1.784(2)
C(2)–P(3)	1.77	1.75	1.739(2)
P(1)–P(2)	2.17	2.21	2.167(1)
Inter-ring angles	16	15	16.05(07)
M–Ti–M′	175	175	173.9(1)

M and M′ are the two ring centroids.

Table 2 Orbital energies (eV) and calculated and experimental IE (eV) for $[Ti(\eta^5\text{-}P_3C_2Bu^t_2)_2]$

Orbital	Energy	IE calc.	IE exp.	Orbital type[a]
40b (LUMO)	−4.03			d + π_5
40a (HOMO)	−4.66	6.50	6.45 A	d + π_4
39b	−5.28	7.13	7.56 B_1	Pσ_3 + π_3
39a	−5.62	7.43	7.87 B_2	Pσ_3 + π_3
38b	−6.13	7.91	8.27 C_1	π_3 + π_2 + Pσ_3
38a	−6.35	8.17		π_3 + Pσ_3
37b	−6.45	8.27	8.65 C_2	π_2 + Pσ_2 + d
37a	−6.51	8.31		Pσ_3 + π_2 + Pσ_2 + d
36b	−6.98	8.72	9.51 D	Pσ_1
35b	−7.10	8.86		Pσ_2
36a	−7.12	8.87		Pσ_1
35a	−7.32	9.07		Pσ_2 + Pσ_1

[a] The basis orbitals are listed in decreasing order of contribution to the MO.

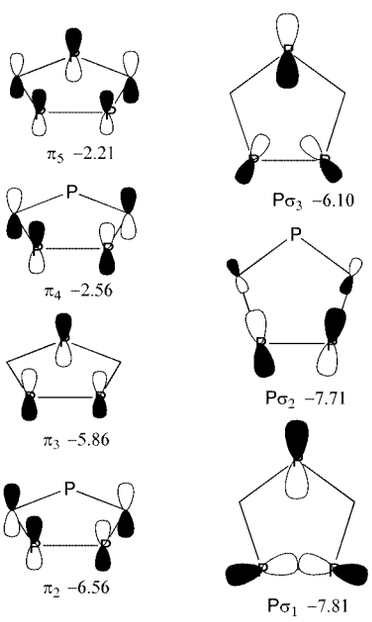

Fig. 1 Representations of the frontier orbitals of $P_3C_2H_2$; energies of the orbitals are given in eV.

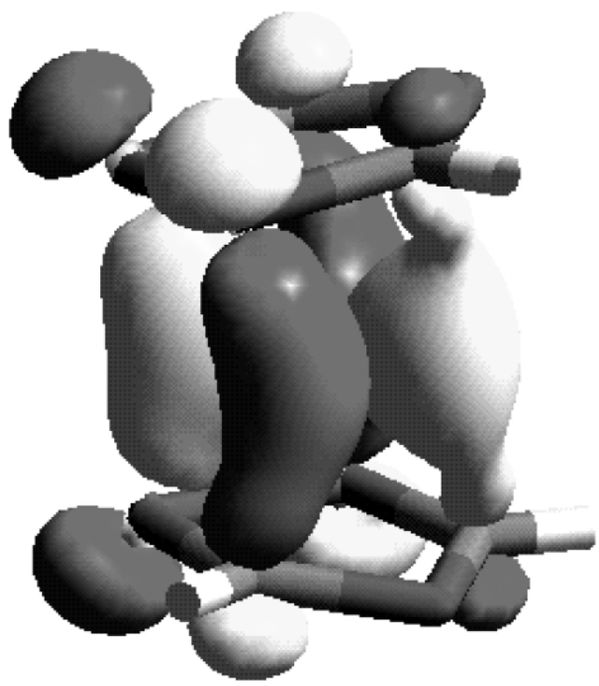

Fig. 2 Isosurface for the HOMO of compound **1b**. A colour version of this figure is available as ESI.†

shorter bond lengths (Table 1). This strongly suggests that both the ring conformations and the tilt angle are partly electronic in origin rather than just steric.

Compound **1a** was also optimized in a triplet state. The energy was found to lie 0.05 eV higher than the singlet in accord with the diamagnetism of the compound. NMR evidence suggests that the triplet state is not thermally accessible in the range 185–385 K[5] so the calculation appears to under estimate the singlet–triplet energy gap. The inter-ring angle was predicted to be 9°; this was also the case when the molecule was optimized in the triplet state with H atoms replacing *tert*-butyl groups.

Electronic structure

The frontier orbitals of a $P_3C_2H_2$ ring are represented in Fig. 1. The form of the π orbitals resembles that of C_5H_5, however there are two significant differences. First the smaller pπ overlap of the P atoms compared to C atoms leads to a closer spacing of the π levels. Whereas π_2 and π_3 are of similar energy to that of the e_1 cyclopentadienyl π orbitals, π_4 and π_5 are significantly more stable than the e_2 levels. Secondly, lowering of symmetry removes the degeneracies found for C_5H_5. Notably π_4, which has a node at P(3), is more stable than π_5. In addition there are three σ orbitals largely localized on P atoms. One, Pσ_3, is of comparable energy to π_2 and π_3, the other two, Pσ_1 and Pσ_2, are more stable but lie above π_1 in energy.

Owing to the similarity of the ring π orbitals the bonding in compound **1a** is analogous to that in a metallocene. However, where other titanocenes are paramagnetic,[1,2] **1a** is diamagnetic.[5] Table 2 gives the orbital energies and a description of their fragment constituents. The calculation shows a HOMO–LUMO gap of 0.63 eV. The HOMO (shown in Fig. 2) is principally titanium 3d in character but involves back donation into the ring π_4 orbitals; it constitutes a δ bond between the metal and the rings. The relatively low energy of the π_4 orbital encourages greater mixing than found for the corresponding carbocyclic ring. The delocalized nature of the ensuing orbital will also reduce the spin-pairing energy involved in the formation of the diamagnetic state. As noted above π_4 has a node at P(3). Two consequences of double occupation of this HOMO are relatively long Ti–P(3) distances and tilting of the rings.

The lower lying orbitals are mainly ligand in character and are in descending order of energy mainly Pσ_3 > π > Pσ_2 > Pσ_1 (Table 2). There is, however, significant σ–π mixing in the complex, which presumably enhances overlap with the metal d orbitals, though their contribution to 37a and 37b is only around 10%. The gross population of the fragment orbitals is

Table 3 Gross populations of ligand orbitals for $[Ti(\eta^5\text{-}P_3C_2H_2)_2]$ and $[Ti(\eta^5\text{-}C_5H_5)_2]$

Compound	π_1	π_2	π_3	π_4	π_5	$P\sigma_1$	$P\sigma_2$	$P\sigma_3$
1b	1.88	1.65	1.64	0.41	0.01	1.95	1.99	1.90
$TiCp_2$	1.79	1.69	1.62	0.11	0.11	na	na	na

na = Not applicable.

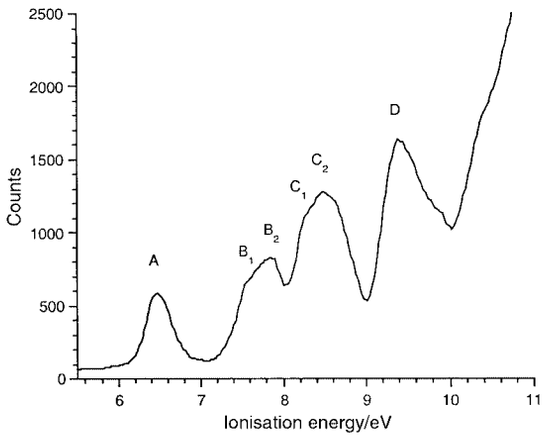

Fig. 3 He I PE spectrum of compound **1a**.

shown in Table 3, where comparable values for $[Ti(\eta^5\text{-}C_5H_5)_2]$ ($S = 1$) are also given. The π_4, π_5 populations show the $P_3C_2H_2$ ring to be a better acceptor than C_5H_5, whereas the π_1, π_2, π_3 populations show that they are comparable donors.

Photoelectron spectrum

The He I PE spectrum of compound **1a** is shown in Fig. 3. Vertical ionization energies (IE) are tabulated (Table 2). The first band, A, is assigned to ionization of 40a HOMO. The intensity pattern of bands B–E suggests assignment of B_1 and B_2 to $P\sigma_3$ ionizations, C_1 and C_2 to π ionizations and D to the four remaining $P\sigma$ orbitals. Such an assignment is consistent with the band positions found for $In(\eta^5\text{-}P_3C_2Bu^t_2)$. Calculated IEs are in reasonable agreement with the experimental values. The pattern of bands is well reproduced as is the first IE. Subsequent IEs tend to be overestimated by on average 0.5 eV.

The vertical first IE of 6.45 eV may be compared with those of other d bands of titanium sandwich compounds involved in δ bonding. These are 5.4 eV for $[Ti(\eta^6\text{-}C_6H_5Me)_2]$,[11] 6.83 eV for $[Ti(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)]$ and 7.62 eV for $[Ti(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_8)]$.[12] On this criterion $P_3C_2Bu^t_2$ is most comparable to C_7H_7 in its acceptor ability.

Conclusion

The P_3C_2 ring has low lying acceptor π orbitals that enable it to form δ bonds to transition metals. This δ interaction is of particular importance in stabilizing low oxidation states of early transition metal complexes such as $[Ti(\eta^5\text{-}P_3C_2Bu^t_2)_2]$.

Acknowledgements

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