PERKIN 2 COMMUNICATION

The EPR identification of bis(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphaallyl radical

Angelo Alberti,*[a] Massimo Benaglia,[a] Maurizio Guerra,*[a] Andrew Hudson[b] and Dante Macciantelli[a]

[a] *I.Co.C.E.A. CNR, Area della Ricerca, Via P. Gobetti 101, I-40129 Bologna, Italy*
[b] *School of Chemistry, Physics and Environmental Sciences, University of Sussex, Brighton, UK BN1 9QJ*

Received (in Cambridge) 17th May 1999, Accepted 10th June 1999

The paramagnetic species detected by EPR spectroscopy upon electrochemical reduction of bis(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphaallene in THF solution has been unambiguously identified as the title radical, the identification being supported by DFT calculations.

The radicals and radical ions from bis(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphaallene (**1**) have recently been the subject of a number of investigations with results that were, in some cases, controversial.[1–4] This was particularly the case for the electrochemical reduction of this compound in THF solution that leads to the detection of a rather peculiar EPR spectrum apparently consisting of a 7.64 mT triplet (coupling of the unpaired electron with two equivalent, or nearly so, phosphorus atoms) and a g-factor ≈ 2.009 which was initially attributed to the diheterocumulene radical anion **2**.[3] The unusual intensity pattern would reflect dipolar broadening of the lines associated with the triplet state of the two equivalent phosphorus nuclei. In a subsequent investigation we showed that the EPR spectrum is in fact much more complex than previously perceived, and that its high resolution hyperfine pattern, clearly exhibiting an additional 0.328 mT doublet splitting, is not consistent with the proposed diphosphaallene radical anion.[4] In addition, the results of DFT calculations on the radical anion of an acceptably simplified model compound, *i.e.* the unsubstituted diphenyl-1,3-diphosphaallene, were incompatible with the observed spectrum. Although the correct spectrum could instead be observed upon chemical reduction of ArP=C=PAr at low temperature,[4] no hypothesis was then put forth as to the nature of the radical responsible for the misassigned spectrum.

In a recent EPR and computational study on the electrochemical reduction of monophosphaallenes of general structure $ArP{=}C{=}CAr_2$ that appeared after the submission of our paper,[5] it was suggested that the observed spectra were due to allyl radicals of general structure $ArP^{\bullet}{-}C(H){=}CAr_2$ rather than to the radical anions $[ArP{=}C{=}CAr_2]^{\bullet -}$. Although convincing, this assignment was based mainly on the results of calculations, while unambiguous experimental evidence could not be derived from the recorded spectra. In this light, it occurred to us that the EPR spectrum observed upon electrochemical reduction of **1** and as yet unassigned could in fact be due to the diaryl-substituted 1,3-diphosphaallyl radical **3**. The results of experiments carried out in deuterated solvents showed that this is indeed the case.

The room temperature electrochemical reduction of an argon purged THF solution of **1** containing some tetrabutylammonium perchlorate as supporting electrolyte led to the detection of the already known spectra shown in Fig. 1a and b. As previously observed, when using a ^{13}C-labelled diphosphaallene the spectra exhibited an additional 1.09 mT doublet;[4] and the signal, whose intensity initially increased after disconnecting the cell from the power source, could be observed for a long time.[4] An identical spectrum was observed when replacing THF with THF-d_8. On the other hand, if a drop of D_2O was added to the solution (THF or THf-d_8) prior to electrolysis, the spectra that could be observed after the reduction exhibited a similarly unusually shaped 7.68 mT triplet with additional hyperfine structure, but lacked the 0.328 mT doublet (see Fig. 1c and d). The spectra could be simulated by admitting that the unpaired electron, besides interacting with the two phosphorus atoms, is coupled with the 36 equivalent hydrogen (0.047 mT) of the four *o*-*tert*-butyl groups and with a deuterium atom (0.054 mT).

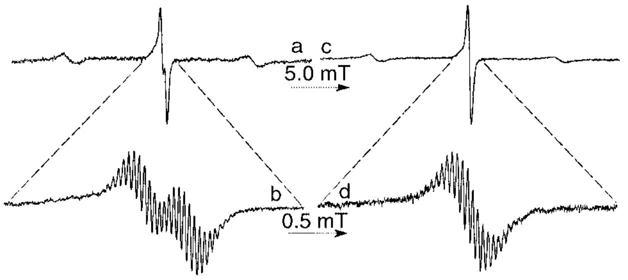
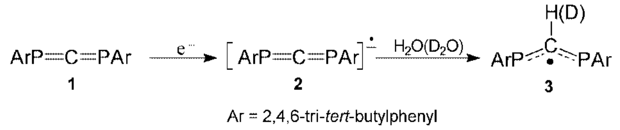


Fig. 1 Room temperature EPR spectra of radical **3** observed after electrolytic reduction of diphosphaallene **1** in THF-d_8 at high (**a**; m.a. = 0.1 mT) and low (**b**; m.a. = 0.01 mT) magnetic field modulation and in THF-d_8 with D_2O at high (**c**; m.a. = 0.1 mT) and low (**d**; m.a. = 0.01 mT) magnetic field modulation.

Based on these results we believe that the spectra detected upon electrochemical reduction of **1** in THF are actually due to the diphosphaallyl radical **3**, which would originate through protonation of the radical anion immediately after its formation (Scheme 1).



Scheme 1

The fact that the deuterium splitting is about one sixth of the 0.328 mT doublet is in agreement with expectations, as is the rather high value of the g-factor, the unpaired electron in radical **3** being mainly located on the phosphorus atoms. The experiments in THF-d_8 and in the presence of D_2O clearly indicate that protonation must be brought about by the traces of water remaining in the anhydrous THF.

DFT calculations (UB3LYP/VTZP) performed on the unsubstituted diphenyl-1,3-diphosphaallyl radical,[6] employing the same geometry constraints previously adopted in studying the corresponding radical anion, further substantiate the identification of **3**. The DFT-optimized valence triple-ζ basis set (VTZP)[7] has been used instead of the split valence 6-311G** basis set (UB3LYP/6-311G**)[4] since it was recently shown that it describes spin density better at phosphorous.[8] At the UB3LYP/VTZP level of theory the structure about the central carbon atom is computed to be planar and the proton hfs constant ($a_{^1\mathrm{H}} = 0.37$ mT) is in excellent accord with experiment (0.328 mT). Also the hfs constant at the central carbon atom of the ^{13}C labelled derivative (1.09 mT) is reproduced well by DFT calculations ($a_{^{13}\mathrm{C}} = -1.23$ mT) whereas that at phosphorus (7.68 mT) is underestimated ($a_{^{31}\mathrm{P}} = 5.90$ mT) as previously found for the radical anion ($a_{\mathrm{exp}} = 6.2$ mT, $a_{^{31}\mathrm{P}} = 5.0$ mT at the UB3LYP/VTZP level). The addition of a tight *s*-function to the core orbitals of the heavy atoms[9] improves only slightly the agreement with experiment both for the neutral and anion radicals ($a_{^{31}\mathrm{P}} = 6.06$ and 5.23 mT, respectively, at the UB3LYP/VTZP level).[4] In any case, the decrease of the ^{31}P hfs constant on going from the neutral to the anion radical is well reproduced as well as the increase of the ^{13}C hfs constant ($a_{\mathrm{exp}} = 1.09$ and 1.45 mT, respectively; $a_{^{13}\mathrm{C}} = -1.23$ and 1.65 mT at the UB3LYP/VTZP level).

References

1 A. Alberti, M. Benaglia, M.-A. Della Bona, M. Guerra, A. Hudson and D. Macciantelli, *Res. Chem. Intermed.*, 1996, **22**, 381.

2 M. Chentit, H. Sidorenkova, A. Jouaiti, G. Terron, M. Geoffroy and Y. Ellinger, *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, 921.

3 H. Sidorenkova, M. Chentit, A. Jouaiti, G. Terron, M. Geoffroy and Y. Ellinger, *J. Chem. Soc.*, *Perkin Trans. 2*, 1998, 71.

4 A. Alberti, M. Benaglia, M. D'Angelantonio, S. S. Emmi, M. Guerra, A. Hudson, D. Macciantelli, F. Paolucci and S. Roffia, *J. Chem. Soc.*, *Perkin Trans. 2*, 1999, 309.

5 M. Chentit, H. Sidorenkova, M. Geoffroy and Y. Ellinger, *J. Phys. Chem. A*, 1998, **102**, 10469.

6 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, 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 and J. A. Pople, GAUSSIAN98, Revision A.5, Gaussian, Inc., Pittsburgh PA, 1998.

7 N. Godbout, D. R. Salahub, J. Andzelm and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560.

8 M. T. Nguyen, S. Creve, L. A. Eriksson and L. G. Vanquickenborn, *Mol. Phys.*, 1997, **91**, 537.

9 M. T. Nguyen, S. Creve and L. G. Vanquickenborn, *J. Phys. Chem. A*, 1997, **101**, 3174.

Communication 9/03893K