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Persistent Phosphinyl Radicals Featuring a Bulky Amino Substituent and the 2,6-Bis(trifluoromethyl)phenyl Group

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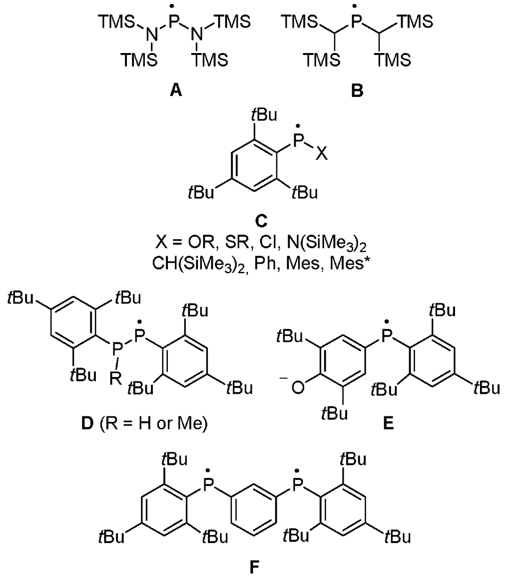
Persistent phosphinyl radicals featuring the 2,6-bis(trifluoromethyl)phenyl group were prepared and characterized. Their electronic structure was theoretically investigated, and their low-temperature dimerization into the corresponding diphosphines was found to be strongly inhibited when the sterically very demanding (*tert*-butyl)(trimethylsilyl)amino substituent was used.

Heavier main group elements (such as phosphorus) feature peculiar properties that have allowed for the stabilization of highly reactive species, including radicals, diradicals, and compounds featuring odd-electron bonds.[1,2] As far as phosphinyl radicals[3] are concerned, the first persistent derivatives **A** and **B** were reported by Lappert and co-workers in the late 1970s using $N(SiMe_3)_2$ and $CH(SiMe_3)_2$ substituents (Chart 1).[4]

Chart 1. Structure of the Persistent Phosphinyl Radicals and Diradical **A**−**F**



The variety of persistent phosphinyl radicals was then extended to aryl-substituted compounds **C**, the extremely bulky 2,4,6-tri(*tert*-butyl)phenyl ring (Mes*) having been combined with almost any other substituent (alkoxy, thioalkoxy, chlorine, amino, phosphino, alkyl, and aryl).[5] Recently, the number of persistent phosphinyl radicals further increased with the preparation of compounds **D**[6] and **E**,[7] a diphosphorus analogue of hydrazyls and a radical anion derived from a *p*-phosphaquinone, respectively. Notably, Janssen et al. also took advantage of the Mes* substituent to prepare a phosphinyl diradical **F**,[8] in which the two phosphorus-centered radicals are ferromagnetically coupled via a *m*-phenylene unit.

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(1) (a) Grützmacher, H.; Breher, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 4006. (b) Power, P. P. *Chem. Rev.* **2003**, *103*, 789.

(2) (a) Canac, Y.; Bourissou, D.; Baceiredo, A.; Gornitzka, H.; Schoeller, W. W.; Bertrand, G. *Science* **1998**, *279*, 2080. (b) Scheschkewitz, D.; Amii, H.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Science* **2002**, *295*, 1880.

(3) Tordo, P. In *The Chemistry of Organophosphorus Compounds*; Pataï, S., Hartley, F. R. Eds.; Wiley: New York, 1990; Vol. 1, p 137.

(4) (a) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1976**, 623. (b) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1980**, 2428.

(5) Cetinkaya, B.; Hudson, A.; Lappert, M. F.; Goldwhite, H. *J. Chem. Soc., Chem. Commun.* **1982**, 609.

(6) (a) Cattani-Lorente, M.; Geoffroy, M. *J. Chem. Phys.* **1989**, *91*, 1498. (b) Loss, S.; Magistrato, A.; Cataldo, L.; Hoffmann, S.; Geoffroy, M.; Röthlisberger, U.; Grützmacher H. *Angew. Chem., Int. Ed.* **2001**, *40*, 723.

(7) Sasaki, S.; Murakami, F.; Yoshifuji, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 340.

(8) Wienk, M. M.; Janssen, R. A. J. *Chem. Commun.* **1996**, 1919.

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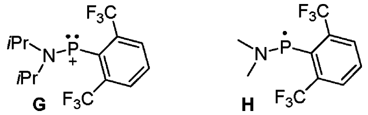
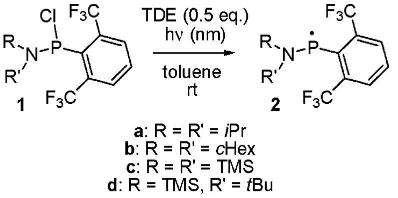
Chart 2. Structure of the Phosphenium Salt **G** and Phosphinyl Radicals **H** Featuring the 2,6-Bis(trifluoromethyl)phenyl Group Ar_F Substituent



Scheme 1. Synthesis of Radicals **2a**−**d**



Over the last 10 years, fluorinated aryl rings [such as the 2,6-bis(trifluoromethyl)phenyl group Ar_F] have attracted considerable attention due to their peculiar properties,[9] that are essentially their huge steric shielding and the higher inertness of C−F compared to C−H bonds. Representative examples of their powerful stabilizing effects are found in carbene chemistry, whatever the ground state spin multiplicity, triplet or singlet.[10−12] Despite its pronounced σ-withdrawing character, the Ar_F group also proved to be effective in the stabilization of group 15 carbenoids[13] such as the highly electrophilic phosphenium salt **G** (Chart 2). These results prompted us to investigate related radicals, and here we report the synthesis and EPR characterization of persistent amino−aryl−phosphinyl radicals **H** featuring the Ar_F group. Their electronic structure is discussed on the basis of ab initio calculations, and the influence of both the temperature and the steric demand of the amino substituent on their dimerization into diphosphines is studied.

The phosphinyl radicals **2a**,**b** were generated by UV irradiation (λ = 254 nm) of the corresponding chlorophosphines **1a**,**b** in degassed toluene at room temperature in the presence of tetrakis(dimethylamino)ethene (TDE) (Scheme 1).[4,5] The initially pale yellow solutions progressively turned deep red, with concomitant formation of white precipitates. After 24 h of irradiation, the solutions were filtered and analyzed.

The EPR spectra of **2a**,**b** at 293 K are nicely resolved (g_{iso} = 2.0060) and can be very satisfactorily simulated (Figure 1). Accordingly, the unpaired electron was found to be coupled with one ^{31}P (87.0 G), one ^{14}N (5.5 G), six ^{19}F (10.1 G), and two ^{1}H (1 G) nuclei. Notably, the a(P) coupling constant is in the typical range for phosphinyl radicals (70−110 G),[4,5] and it can thus be concluded that **2a**,**b** are π-radicals with the odd electron predominantly in a valence 3p(P) orbital.[3] Moreover, the EPR spectra remained unchanged in intensity over extended periods (>1 week) at room temperature, indicating the highly persistent character of these amino−aryl−phosphinyl radicals.

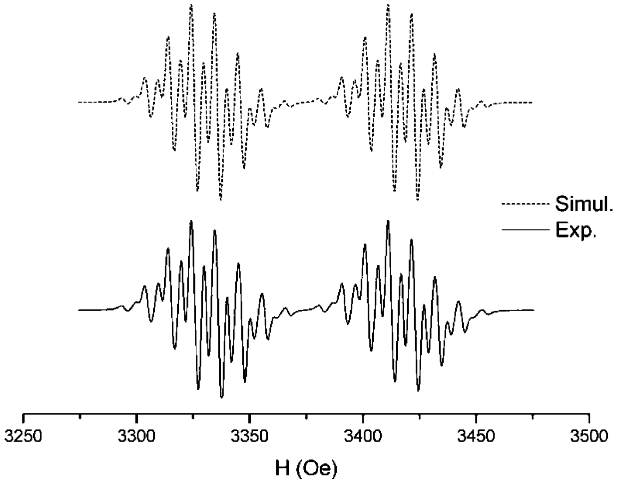


Figure 1. X-band EPR spectra of **2a**. Experimental spectrum in toluene at 293 K (approximate concentration, 0.02 M; microwave power, 20 mW; modulation amplitude, 0.965 G) and simulation using pure Gaussian functions of 2 G width.

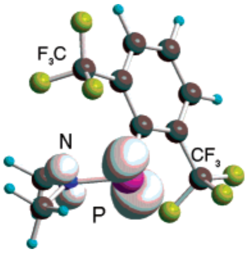


Figure 2. Graphical representation of the spin density distribution in the model radical **2***.

To gain more insight into the electronic structure of such amino−aryl−phosphinyl radicals, ab initio calculations at the UB3LYP/6-31g* level were performed on the model radical **2*** featuring the Ar_F group and a NMe_2 substituent at phosphorus (Figure 2). The optimized geometry suggests a stronger participation of the amino over the aryl substituent in the electronic delocalization. Indeed, the N−P bond length (1.713 Å) indicates some multiple bond character, whereas the long P−C bond distance (1.866 Å) is in the typical range for P−C single bonds; moreover, the orientation of the Ar_F ring (torsion angle: $NPC_{ipso}C_{ortho}$ 59.3°) prevents efficient $2p(C_{ipso})-3p(P)$ overlap. Accordingly, the spin density is predicted to be essentially confined to the phosphorus (72%) and nitrogen (19%) atoms, with only slight delocalization over the Ar_F ring.

The propensity of the amino−aryl−phosphinyl radicals **2a**,**b** to dimerize via σ-(P−P) coupling was then investigated by variable temperature EPR and ^{31}P NMR spectroscopy.[14] The EPR signal was found to be about 50 times less intense

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(9) Edelmann, F. T. *Comments Inorg. Chem.* **1992**, *12*, 259.

(10) (a) Hirai, K.; Tomioka, H. *J. Am. Chem. Soc.* **1999**, *121*, 10213. (b) Woodcock, H. L.; Moran, D.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **2001**, *123*, 4331.

(11) (a) Buron, C.; Gornitzka, H.; Romanenko, V.; Bertrand, G. *Science* **2000**, *288*, 834. (b) Despagnet-Ayoub, E.; Solé, S.; Gornitzka, H.; Rozhenko, A. B.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *J. Am. Chem. Soc.* **2003**, *125*, 124.

(12) Solé, S.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Science* **2001**, *292*, 1901.

(13) (a) Burford, N.; Macdonald, C. L. B.; LeBlanc, D. J.; Cameron, T. S. *Organometallics* **2000**, *19*, 152. (b) Dumitrescu, A.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Eur. J. Inorg. Chem.* **2002**, 1953.

(14) Since phosphinyl radicals **2** are only generated in modest yields by photolysis, no attempts were made to isolate the corresponding diphosphines.

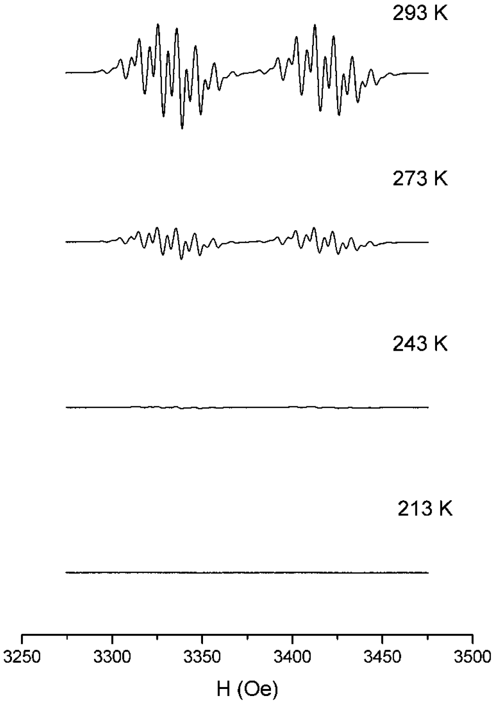

Figure 3. X-band EPR spectra of **2b** in toluene at various temperatures.

at 273 K compared to 293 K, and it almost completely vanished below 243 K (Figure 3). Simultaneously, an extremely broad signal centered at 70 ppm was observed in the ^{31}P NMR spectrum at 293 K. This signal, which is assigned to the corresponding diphosphines, became sharper and sharper upon cooling the solution. These results as a whole support the existence of an equilibrium between the radicals **2a**,**b** and the corresponding diphosphines. As expected, the enthalpic term associated with the P−P bond prevails at low temperature, whereas the entropic term predominates at room temperature.

Notably, a similar equilibrium has recently been pointed out for the related phosphinyl radicals $^{\bullet}P[CH(TMS)_2]$[15,16] and $^{\bullet}P(N\textit{i}Pr_2)[N(TMS)_2]$.[17] Due to the peculiar shape and flexibility of the [CH(TMS)$_2$] ligands, the corresponding diphosphines were demonstrated to behave as an energy storage reservoir, dissociation being observed upon melting, dissolution, or evaporation. We thus anticipated that the low temperature dimerization of the amino−aryl−phosphinyl radicals might be prevented by increasing the steric demand of the substituents. Following the same procedure, the related radicals **2c**,**d** were thus prepared. At 293 K, the EPR spectra consist of large doublets [$a(^{31}P) = 92$ G for **2c** and 75 G for **2d**]. Upon cooling, the intensity of the signal for **2c** remained almost unchanged down to 243 K but significantly decreased at 213 K. The equilibrium was found to be even more displaced with **2d** since the EPR signal remained practically identical up to 213 K (Figure 4).

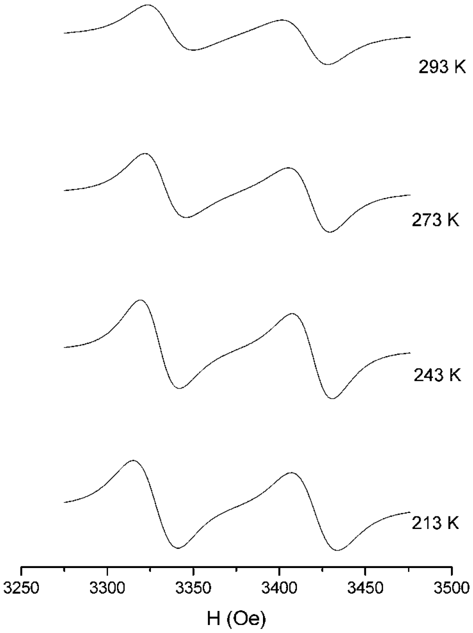

Figure 4. X-band EPR spectra of **2d** in toluene at various temperatures.

In conclusion, the Ar$_F$ substituent has been demonstrated to efficiently stabilize P-centered radicals. Combined with a sterically demanding amino group, this fluorinated aryl ring prevents the dimerization of phosphinyl radicals into the corresponding diphosphines, even at low temperature.

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Supporting Information Available: Experimental procedures, spectroscopic data, and computational details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) (a) Hinchley, S. L.; Morrison, C. A.; Rankin, D. W. H.; Macdonald, C. L. B.; Wiacek, R. J.; Cowley, A. H.; Lappert, M. F.; Gundersen, G.; Clyburne, J. A. C.; Power, P. P. *Chem. Commun.* **2000**, 2045. (b) Hinchley, S. L.; Morrison, C. A.; Rankin, D. W. H.; Macdonald, C. L. B.; Wiacek, R. J.; Voigt, A.; Cowley, A. H.; Lappert, M. F.; Gundersen, G.; Clyburne, J. A. C.; Power, P. P. *J. Am. Chem. Soc.* **2001**, *123*, 9045.

(16) Borisenko, K. B.; Rankin, D. W. H. *Inorg. Chem.* **2003**, *42*, 7129.

(17) (a) Bezombes, J. P.; Hitchcock, P. B.; Lappert, M. F.; Nycz, J. E. *Dalton Trans.* **2004**, 499. (b) Bezombes, J. P.; Borisenko, K. B.; Hitchcock, P. B.; Lappert, M. F.; Nycz, J. E.; Rankin, D. W. H.; Robertson, H. E. *Dalton Trans.* **2004**, 1980.