

Isolation and X-ray Crystal Structures of Triarylphosphine Radical Cations

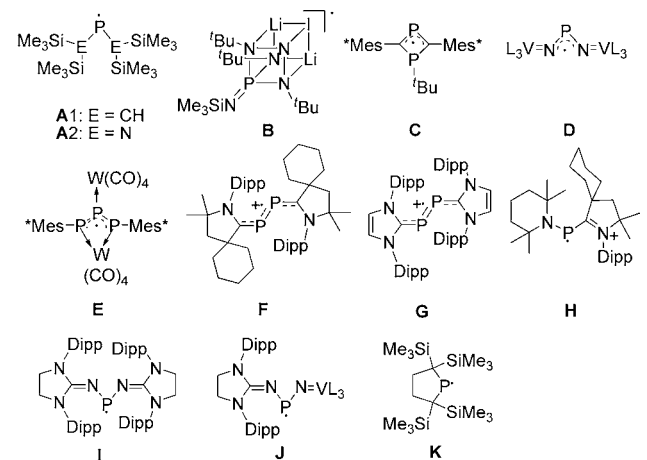
Xiaobo Pan, Xiaoyu Chen, Tao Li, Yizhi Li, and Xinping Wang*

State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

S Supporting Information

ABSTRACT: Salts containing triarylphosphine radical cations $1^{\bullet+}$ and $2^{\bullet+}$ have been isolated and characterized by electron paramagnetic resonance (EPR) and UV–vis absorption spectroscopy as well as single-crystal X-ray diffraction. Radical $1^{\bullet+}$ exhibits a relaxed pyramidal geometry, while radical $2^{\bullet+}$ becomes fully planar. EPR studies and theoretical calculations showed that the introduction of bulky aryl groups leads to enhanced p character of the singly occupied molecular orbital, and the radicals become less pyramidalized or fully flattened.

The isolation and characterization of stable radicals of heavier main-group elements is an area of high current interest.¹ A number of phosphorus radicals in solution have been observed by electron paramagnetic resonance (EPR) spectroscopy,² but only a few species have been structurally characterized in the gas phase (Figure 1A)³ or the solid state



Mes*: 2,4,6-*t*Bu₃C₆H₂; L: (3,5-Me₂C₆H₃)(Np)N, Np = neopentyl; Dipp: 2,6-*i*Pr₂C₆H₃

Figure 1. Structurally characterized phosphorus radicals.

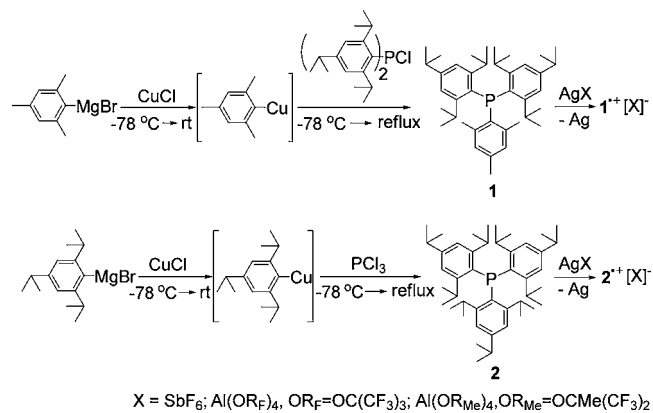
(Figure 1B–K).⁴ On the other hand, triarylphosphines (Ar₃P) not only have a wide variety of catalytic applications^{5,6} but are potential candidates for redox centers in functional materials.⁷ Although the structures of hundreds of Ar₃P species are known, no X-ray structural data have appeared on the corresponding oxidized radical species Ar₃P^{•+}. In fact, triarylphosphine radical cations have been the subject of numerous solution EPR studies and were shown to adopt a pyramidal geometry,⁸ in contrast to

the planar geometry for the nitrogen analogues (Ar₃N^{•+}).⁹ Although extremely crowded aryl ligands cause significant flattening,⁸ whether Ar₃P^{•+} radicals have a planar geometry remains ambiguous. Conspicuously lacking is an X-ray diffraction structure.

By using weakly coordinating anions,¹⁰ we recently succeeded in stabilizing aniline, benzidine, and anthracene radical cations.¹¹ In this paper, we report the isolation, characterization, and structures of two triarylphosphine radical cations, one of which displays a perfectly planar geometry.

Phosphine **1** was synthesized by the reaction of MesCu(I) (Mes = 2,4,6-trimethylphenyl) with Trip₂PCl (Trip = 2,4,6-triisopropylphenyl) (Scheme 1). Previously reported phosphine

Scheme 1



2 was synthesized by the reaction of TripCu(I) with phosphorus trichloride.^{8d} Upon one-electron oxidation with AgX (X = SbF₆⁻; [Al(OR_F)₄]⁻; OR_F = OC(CF₃)₃; [Al(OR_{Me})₄]⁻; OR_{Me} = OC(CF₃)₂Me) in CH₂Cl₂,^{10,12} **1** and **2** were converted to deep-red radical cations $1^{\bullet+}$ and $2^{\bullet+}$, respectively, in high yields.¹³ Their absorption spectra (Figure 2; for those of $2^{\bullet+}$ with other anions, see Figure S2 in the Supporting Information)¹³ are similar to those of previously reported crowded triarylphosphine radical cations in solution.⁸ The solution EPR spectra of $1^{\bullet+}$ [Al(OR_F)₄]⁻ and $2^{\bullet+}$ SbF₆⁻ (Figure 3)¹⁴ at 273 and 77 K show typical signals of triarylphosphine radical cations.⁸ The EPR signals of $2^{\bullet+}$ [Al(OR_F)₄]⁻ and $2^{\bullet+}$ [Al(OR_{Me})₄]⁻ show high-resolution anisotropic hyper-

Received: February 3, 2013

Published: February 20, 2013

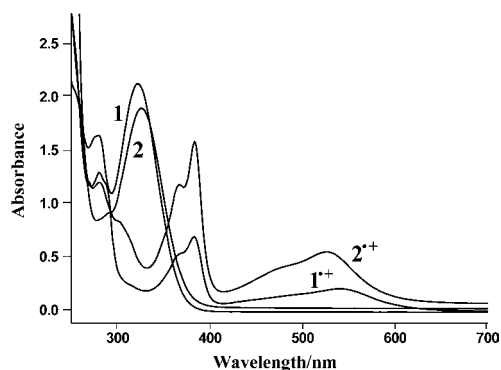


Figure 2. Absorption spectra of 1×10^{-4} M **1**, **2**, $1^{+\bullet}[\text{Al}(\text{OR}_F)_4]^-$, and $2^{+\bullet}\text{SbF}_6^-$ in dichloromethane at 25 °C.

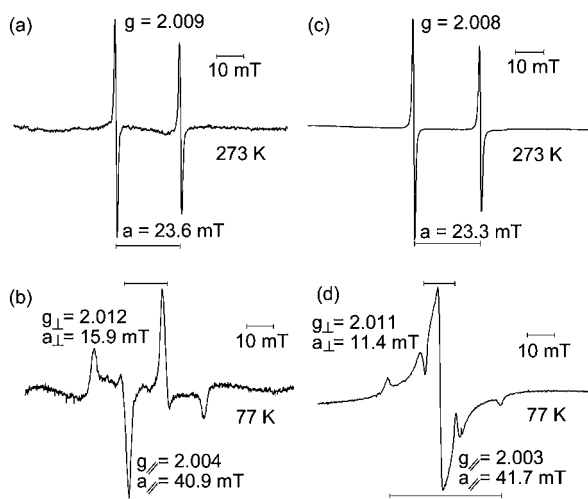


Figure 3. EPR spectra of 1×10^{-3} M solutions of (a, b) $1^{+\bullet}[\text{Al}(\text{OR}_F)_4]^-$ in CH_2Cl_2 at (a) 273 and (b) 77 K and (c, d) $2^{+\bullet}\text{SbF}_6^-$ in (c) CH_2Cl_2 at 273 K and (d) frozen CH_3CN at 77 K.¹⁴

couplings in the frozen solutions at 160 K but become broad at 77 K (Figures S4 and S5). The ratios of isotropic and anisotropic hyperfine constants between the radicals and phosphorus atoms suggest that ~ 64 and $\sim 5\%$ of the unpaired electron are localized on the P 3p and P 3s orbitals, respectively, in $1^{+\bullet}[\text{Al}(\text{OR}_F)_4]^-$ (~ 77 and $\sim 4\%$, respectively, in $2^{+\bullet}\text{SbF}_6^-$).^{8,15} The sums of C–P–C angles in solution (349° in $1^{+\bullet}[\text{Al}(\text{OR}_F)_4]^-$ and 352° in $2^{+\bullet}\text{SbF}_6^-$) were consequently estimated from Coulson's equation.¹⁵

Crystals suitable for X-ray crystallographic studies were obtained by cooling solutions of $1^{+\bullet}[\text{Al}(\text{OR}_F)_4]^-$ and $2^{+\bullet}\text{X}^-$ ($\text{X} = \text{SbF}_6, [\text{Al}(\text{OR}_F)_4], [\text{Al}(\text{OR}_{\text{Me}})_4]$) in various solvents.^{13,16} The structures of $1^{+\bullet}$ (in $1^{+\bullet}[\text{Al}(\text{OR}_F)_4]^-$) and $2^{+\bullet}$ (in $2^{+\bullet}\text{SbF}_6^-$) are shown in Figure 4, and their important structural parameters, as well as those of the parent molecules **1** and **2**, are given in Table 1. The structural parameters of radical cation $2^{+\bullet}$ with the three different anions are similar, except that the C–P bonds in $2^{+\bullet}[\text{Al}(\text{OR}_F)_4]^-$ and $2^{+\bullet}[\text{Al}(\text{OR}_{\text{Me}})_4]^-$ are slightly shorter than those in $2^{+\bullet}\text{SbF}_6^-$, which is probably associated with the weaker coordinating property of larger anions. In the structures of $1^{+\bullet}$ and $2^{+\bullet}$, the Mes and Trip ligands are aligned in a propeller shape. The C–P bond lengths are shorter and the C–P–C angles are larger than those in the corresponding neutral phosphines **1** and **2**. It is worth noting that radical $1^{+\bullet}$ becomes less pyramidalized and that radical $2^{+\bullet}$

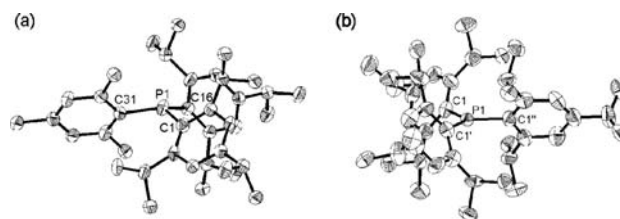


Figure 4. Thermal ellipsoid (50%) drawings of (a) $1^{+\bullet}$ (in $1^{+\bullet}[\text{Al}(\text{OR}_F)_4]^-$) and (b) $2^{+\bullet}$ (in $2^{+\bullet}\text{SbF}_6^-$). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) in $1^{+\bullet}$: C31–P1, 1.798(3); P1–C16, 1.820(3); P1–C1, 1.820(3); C1–P1–C16, 111.76(3); C16–P1–C31, 119.16(4); C1–P1–C31, 118.23(4). In $2^{+\bullet}$: C1–P1, 1.817(4); C1–P1–C1', 119.997(4); C1–P1–C1'', 119.995(4); C1'–P1–C1'', 120.001(4).

is fully flattened with a plane through the central triangle of the three ipso carbon atoms of the Trip rings.

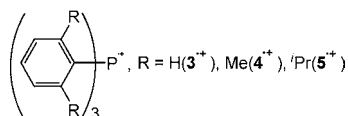
The above data show that the removal of one electron from triarylphosphines have considerable effects on their ground-state structures. To rationalize the experimental results, we carried out some calculations for the model radical species $\text{Ph}_3\text{P}^{+\bullet}$ ($3^{+\bullet}$), $\text{Dmp}_3\text{P}^{+\bullet}$ ($4^{+\bullet}$; Dmp = 2,6-dimethylphenyl), and $\text{Dipp}_3\text{P}^{+\bullet}$ ($5^{+\bullet}$; Dipp = 2,6-diisopropylphenyl). Full geometry optimizations were performed at the UB3LYP/6-31G(d) level, and the obtained stationary points were characterized by frequency calculations.¹⁷ As shown in Table 2, consistent with the experimental data, the addition of bulky substituents causes significant flattening of triarylphosphine radical cations that is induced by the steric crowding and electron donation of the alkyl groups.^{8f} The flattening is accompanied by an increase in the Mulliken spin density on the phosphorus atom. The spin density of 0.89 on the phosphorus atom of $5^{+\bullet}$ calculated at the UM05-2X/def2-SVP level is consistent with the considerably high spin localization on the phosphorus atom observed by EPR spectroscopy.¹⁸ This value is close to that of dialkylphosphinyl radical **K** (0.90)⁴ⁱ and significantly higher than that of carbene-stabilized phosphoniumyl radical **H** (0.67).^{4g}

The singly occupied molecular orbital (SOMO) of $5^{+\bullet}$ calculated at the UB3LYP/6-31G(d) level has almost pure P 3p character with small contributions from carbon atoms (Figure 5). In contrast, a mixing of P 3s and P 3p orbitals for the SOMO of $3^{+\bullet}$ is observed, and that of $4^{+\bullet}$ is in the middle. In the hybridization term, the mixing of P 3s and P 3p character affords pyramidalization at phosphorus (Figure S6).^{8f} The introduction of bulky aryl group leads to enhanced P 3p character of the SOMO, and the radical becomes less pyramidalized.^{8f} In $5^{+\bullet}$ (and hence experimental $2^{+\bullet}$), the repulsive interactions between the Dipp/Trip groups are so strong that the mixing of the P 3s and P 3p orbitals is effectively resisted, and the radicals become fully planar, leading to an ideal trigonal planar sp^2 hybridization with one P 3p orbital (the SOMO) perpendicular to the plane.

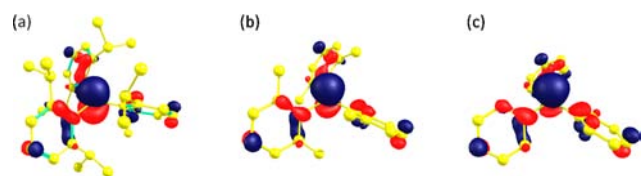
We herein have described the stabilization and structural characterization of the triarylphosphine radical cations $1^{+\bullet}$ and $2^{+\bullet}$. The former shows a relaxed pyramidal geometry while the latter has a perfectly planar structure. These radical species are thermally stable under anaerobic conditions at room temperature. Preliminary investigations of the reactivities of $1^{+\bullet}$ and $2^{+\bullet}$ showed that both species readily react with O_2 . With excess $n\text{Bu}_3\text{SnH}$ in CH_2Cl_2 , the $1^{+\bullet}[\text{Al}(\text{OR}_F)_4]^-$ solution rapidly turns pale yellow, but the deep-red solutions of $2^{+\bullet}\text{X}^-$ ($\text{X} = \text{SbF}_6,$

Table 1. X-Ray Structural Parameters for 1, 1^{•+}, 2, and 2^{•+}

	1	1 ^{•+} [Al(OR _F) ₄] ⁻	2 ^a	2 ^{•+} SbF ₆ ⁻	2 ^{•+} [Al(OR _F) ₄] ⁻	2 ^{•+} [Al(OR _{Me}) ₄] ⁻
C–P (Å)	1.835(2)	1.798(3)	1.843(2)	1.817(4)	1.783(4)	1.789(3)
	1.841(2)	1.820(3)	1.839(2)	1.817(4)	1.806(5)	1.786(3)
	1.854(2)	1.820(3)	1.851(2)	1.817(4)	1.772(4)	1.783(3)
∠C–P–C (deg)	111.35(10)	118.23(4)	111.61(3)	119.997(4)	119.5(2)	118.82(4)
	110.28(10)	119.16(4)	110.88(1)	120.001(4)	119.0(2)	119.82(5)
	110.78(10)	111.76(3)	111.93(3)	119.995(4)	121.3(2)	121.00(4)
∑(∠C–P–C) (deg)	332.41	349.15	334.42	359.993	359.8	359.64

^aData taken from ref 8d.Table 2. Calculated Bond Lengths (Å), Bond Angles (deg), and Spin Densities on P in 3^{•+}, 4^{•+}, and 5^{•+}

	3 ^{•+} (C ₃)	4 ^{•+} (C ₃)	5 ^{•+} (C ₂)
C–P ^a	1.790	1.798	1.814
	1.790	1.798	1.815
	1.790	1.798	1.815
∠C–P–C ^a	114.1	118.4	120.0
	114.1	118.4	120.0
	114.1	118.4	120.0
∑(∠C–P–C) ^a	342.3	355.2	360.0
spin density on P ^b	0.66	0.79	0.89

^aCalculated at the UB3LYP/6-31G(d) level. ^bCalculated at the UM05-2X/def2-SVP level.Figure 5. SOMOs of (a) 5^{•+}, (b) 4^{•+}, and (c) 3^{•+} calculated at the UB3LYP/6-31G(d) level.

[Al(OR_F)₄], [Al(OR_{Me})₄] remain unchanged. The higher stability of 2^{•+} radicals is very possibly due to their higher degree of steric crowding. Further studies of oxidized triarylphosphines with various ligands and their chemical reactivities are underway.

■ ASSOCIATED CONTENT

Supporting Information

Experimental section, crystallographic data (CIF), EPR and UV–vis spectra, results of DFT calculations, and complete ref 17a. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

xpwang@nju.edu.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (Grants 91122019 and 21171087) and the Natural Science

Foundation of Jiangsu Province (Grant BK2011549) for financial support.

■ REFERENCES

- (1) (a) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, *2*, 389. (b) Konu, J.; Chivers, T. In *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds*; Hicks, R. G., Ed.; Wiley: Chichester, U.K., 2010; p 395. (c) Armstrong, A.; Chivers, T.; Boere, R. T. *ACS Symp. Ser.* **2006**, *917*, 66. (d) Marque, S.; Tordo, P. *Top. Curr. Chem.* **2005**, *250*, 43. (e) Power, P. P. *Chem. Rev.* **2003**, *103*, 789. (f) Geoffroy, M. *Recent Res. Dev. Phys. Chem.* **1998**, *2*, 311.
- (2) Selected examples: (a) Giffin, N. A.; Hendsbee, A. D.; Roemmele, T. L.; Lumsden, M. D.; Pye, C. C.; Masuda, J. D. *Inorg. Chem.* **2012**, *51*, 11837. (b) Förster, D.; Dilger, H.; Ehret, F.; Nieger, M.; Gudat, D. *Eur. J. Inorg. Chem.* **2012**, 3989. (c) Edge, R.; Less, R. J.; McInnes, E. J. L.; Mütter, K.; Naseri, V.; Rawson, J. M.; Wright, D. S. *Chem. Commun.* **2009**, 1691. (d) Ndiaye, B.; Bhat, S.; Jouaiti, A.; Berclaz, T.; Bernardinelli, G.; Geoffroy, M. *J. Phys. Chem. A* **2006**, *110*, 9736. (e) Sasamori, T.; Mieda, E.; Nagahora, N.; Sato, K.; Shiomi, D.; Takui, Y.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 12582. (f) Cataldo, L.; Dutan, C.; Misra, S. K.; Loss, S.; Grützmacher, H.; Geoffroy, M. *Chem.—Eur. J.* **2005**, *11*, 3463. (g) Dutan, C.; Shah, S.; Smith, R. C.; Choua, S.; Berclaz, T.; Geoffroy, M.; Protasiewicz, J. D. *Inorg. Chem.* **2003**, *42*, 6241. (h) Rosa, P.; Gouverd, C.; Bernardinelli, G.; Berclaz, T.; Geoffroy, M. *J. Phys. Chem. A* **2003**, *107*, 4883. (i) Loss, S.; Magistrato, A.; Cataldo, L.; Hoffmann, S.; Geoffroy, M.; Röthlisberger, U.; Grützmacher, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 723. (j) Sasaki, S.; Murakami, F.; Yoshifujii, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 340.
- (3) (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. (c) 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.
- (4) (a) Armstrong, A.; Chivers, T.; Parvez, M.; Boere, R. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 502. (b) Biaso, F.; Cantat, T.; Mezailles, N.; Ricard, L.; Le Floch, P.; Geoffroy, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7036. (c) Ito, S.; Kikuchi, M.; Yoshifujii, M.; Arduengo, A. J., III; Konovalova, T. A.; Kispert, L. D. *Angew. Chem., Int. Ed.* **2006**, *45*, 4341. (d) Agarwal, P.; Piro, N. A.; Meyer, K.; Muller, P.; Cummins, C. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 3111. (e) Scheer, M.; Kuntz, C.; Stubenhofer, M.; Linseis, M.; Winter, R. F.; Sierka, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 2600. (f) Back, O.; Donnadiou, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. *Nat. Chem.* **2010**, *2*, 369. (g) Back, O.; Celik, M. A.; Frenking, G.; Melaimi, M.; Donnadiou, B.; Bertrand, G. *J. Am. Chem. Soc.* **2010**, *132*, 10262. (h) Back, O.; Donnadiou, B.; von Hopffgarten, M.; Klein, S.; Tonner, R.; Frenking, G.; Bertrand, G. *Chem. Sci.* **2011**, *2*, 858. (i) Ishida, S.; Hirakawa, F.; Iwamoto, T. *J. Am. Chem. Soc.* **2011**, *133*, 12968.
- (5) Tolman, C. *Chem. Rev.* **1977**, *77*, 313.

(6) For recent examples, see: (a) Kawamoto, S.; Miyazaki, T.; Iwai, T.; Ohmiya, H.; Sawamura, M. *J. Am. Chem. Soc.* **2012**, *134*, 12924. (b) Hatakeyama, T.; Hashimoto, T.; Kondo, Y.; Fujiwara, Y.; Seike, H.; Takaya, H.; Tamada, Y.; Ono, T.; Nakamura, M. *J. Am. Chem. Soc.* **2010**, *132*, 10674. (c) Tschan, M. J.-L.; García-Suárez, E. J.; Freixa, Z.; Launay, H.; Hagen, H.; Benet-Buchholz, J.; van Leeuwen, P. W. N. M. *J. Am. Chem. Soc.* **2010**, *132*, 6463.

(7) Baumgartner, T.; Réau, R. *Chem. Rev.* **2006**, *106*, 4681.

(8) (a) Boéré, R. T.; Bond, A. M.; Cronin, S.; Duffy, N. W.; Hazendonk, P.; Masuda, J. D.; Pollard, K.; Roemmele, T. L.; Tran, P.; Zhang, Y. *New J. Chem.* **2008**, *32*, 214. (b) Sasaki, S.; Yoshifuji, M. *Curr. Org. Chem.* **2007**, *11*, 17. (c) Sasaki, S.; Chowdhury, R.; Yoshifuji, M. *Tetrahedron Lett.* **2004**, *45*, 9193. (d) Sasaki, S.; Sutoh, K.; Murakami, F.; Yoshifuji, M. *J. Am. Chem. Soc.* **2002**, *124*, 14830. (e) Chaliier, F.; Berchadsky, Y.; Finet, J.; Gronchi, G.; Marque, S.; Tordo, P. *J. Phys. Chem.* **1996**, *100*, 4323. (f) Palau, C.; Berchadsky, Y.; Chaliier, F.; Finet, J.; Gronchi, G.; Tordo, P. *J. Phys. Chem.* **1995**, *99*, 158. (g) Culcasi, M.; Berchadsky, Y.; Gronchi, G.; Tordo, P. *J. Org. Chem.* **1991**, *56*, 3537.

(9) Brown, G. M.; Freeman, G. R.; Walter, R. I. *J. Am. Chem. Soc.* **1977**, *99*, 6910.

(10) (a) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. (b) Reed, C. *Acc. Chem. Res.* **1998**, *31*, 133. (c) Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066.

(11) (a) Chen, X.; Wang, X.; Zhou, Z.; Li, Y.; Sui, Y.; Ma, J.; Wang, X.; Power, P. P. *Angew. Chem., Int. Ed.* **2013**, *52*, 589. (b) Chen, X.; Wang, X.; Sui, Y.; Li, Y.; Ma, J.; Zuo, J.; Wang, X. *Angew. Chem., Int. Ed.* **2012**, *51*, 11878. (c) Chen, X.; Ma, B.; Wang, X.; Yao, S.; Ni, L.; Zhou, Z.; Li, Y.; Huang, W.; Ma, J.; Zuo, J.; Wang, X. *Chem.—Eur. J.* **2012**, *18*, 11828.

(12) Krossing, I. *Chem.—Eur. J.* **2001**, *7*, 490.

(13) $1^{*+}SbF_6^-$ is unstable in solution. $1^{*+}[Al(OR_{Me})_4]^-$ did not afford crystals suitable for X-ray crystallography, and no detailed structure was obtained.

(14) The EPR spectrum of $2^{*+}SbF_6^-$ has a sharp peak in the frozen CH_2Cl_2 solution at 77 K, and no hyperfine coupling was observed (Figure S3).

(15) (a) Coulson, C. A. In *Contributions à l'Etude de la Structure Moléculaire: Volume Commémoratif Victor Henri*; Maison Desoer: Liège, Belgium, 1948; p 15. (b) Coulson's equation is rough approximation and not sensitive to subtle differences in the structure close to $\angle C-P-C = 120^\circ$.^{8b} Whether the radical cations have a planar geometry in solution remains elusive.

(16) X-ray data for $1^{*+}[Al(OR_F)_4]^-$, $2^{*+}X^-$, and neutral **1** are listed in Table S1 in the SI. CCDC 921459–921463 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(17) (a) All of the calculations were performed using the Gaussian 09 program suite: Frisch, M. J.; et al. *Gaussian 09*, revision B.01; Gaussian, Inc.: Wallingford, CT, 2010. See the SI for geometries and coordinates. (b) A highly relaxed pyramidal geometry for 5^{*+} [$\angle C-P-C = 118.9^\circ$, $\sum(\angle C-P-C) = 356.7^\circ$] was obtained upon optimization at the UHF/6-31G(d) level by Boéré and co-workers.^{8a}

(18) Calculated spin densities are usually overestimated in comparison to those generated from experimental EPR spectra.^{4f-i}