Reviewers' Comments:

Reviewer #1: This is a terrific paper and well suited for publication in CHEM. eta-5
Cp* phosphorus dication is very novel and adds to greater body of main group arene complexes. The transfer reactions illustrate the strong Lewis acidity of 3. I have only one main comment-concern.

The P***C distances involving the coordinated toluene in the structure of 3 appear to be ALL shorter than reported for other coordinated olefins to P cations, see for example
E.Niecke, M.Nieger, F.Reichert, Angew.Chem.,Int.Ed. 1988, 27, 1715.
N.Burford, J.A.C.Clyburne, P.K.Bakshi, T.S.Cameron, J.Am.Chem.Soc. 1993, 115, 8829.
N.Burford, J.A.C.Clyburne, P.K.Bakshi, T.S.Cameron, Organometallics 1995, 14, 1578.
D.Gudat, A.Haghverdi, H.Hupfer, M.Nieger, Chem.-Eur.J. 2000, 6, 3414.
[J.Price, M.Lui, N.D.Jones, P.J.Ragogna, Inorg.Chem. 2011, 50, 12810.
T.Scherpf, R.Wirth, S.Molitor, K.-S.Feichtner, V.H.Gessner, Angew.Chem.,Int.Ed. 2015, 54, 8542.

I would thus urge the authors to contemplate if the toluene should be considered eta-5 as well! I would argue so. If so, maybe this is more of a bent sandwich? If not, please add text and more description.

Reviewer #2: Comments enter in this field will be shared with the author; your identity will remain anonymous.
In the manuscript "The η5-Pentamethylcyclopentadienyl Phosphorus Dication [(η5-Cp*)P]2+:
A Phosphorus Lewis Super Acid" the authors describe the synthesis of [(η5-Cp*)P]2+ (3) by defluorination of Cp*PF2 with two equivalents of [Et3Si][B(C6F5)4]. They characterized compound 3 by NMR and X-ray analysis. Further they did some DFT calculations, which suggested that the phosphorus atom should exhibit significant Lewis acidity. To prove this Lewis acidity, compound 3 was reacted with [NBu4][SbF6] or SiEt3Cl resulting in the formation of compound 2 and in the case of Et3SiCl in a mixture of compound 1 and [Et3Si][B(C6F5)4], which are in an equilibrium with the starting materials. The authors further reacted 3 with 2,2'-bipyridine and Et3SiH resulting in the compounds 4 and 5, respectively. The formation of both compounds was additionally investigated by DFT calculations. The paper is nicely written and the topic is surely of interest for chemist of many different research areas. The reported reactions for sure are challenging, nevertheless the experiments were performed and reported expertly. Therefore, I recommend publication in Chem, but only after major alterations, because there are many X-ray problems!
1) Summary: "Treatment of (Cp*PF2) with 2 equivalents of [Et3Si][B(C6F5)4] gave [(η2-Cp*)P][B(C6F5)4]2 (3) representing…" it should be [(η5-Cp*)P][B(C6F5)4]2 (3).
2) Page 2: "… as well as their applicationin frustrated Lewis pair chemistry…" "… application in …"
3) Page 3: 1,2-difluorobenzene.
4) Figure S14: There is a signal in the 19F{1H} NMR at -139.2 ppm, which should not originate from 1,2-difluorobenzene since the other signals arising from the F atoms in ortho-, metha- and para-position are present. Is there an interaction with 3 or is there another explanation for this signal.
5) Page 5: "… consistent with η5-coordination of the Cp* ligand to P." should be ""… consistent with η5-coordination of the Cp* ligand to P"
6) Figure 2 and 4: It should be considered to show the atoms of the molecular structures with ellipsoids (ortep-style) instead of spheres.
7) Ref [26]: the title is not correct
8) Experimental part: NMR studies and a X-ray analysis is not enough for a comprehensive characterization of a new compound. Therefore a mass spectrum and an elemental analysis should be done for each compound.

9) X-ray analysis: It is confusing that CIF2 corresponds to compound 3 and CIF3 corresponds to compound 2. CIF1 and 3 are fine and can be published without hesitation.

10) X-ray analysis: At CIF2 (compound 3) there are some problems. The Crystal was weakly diffracting (There are no reflexes with I/σ >3 after a resolution of 1.2 Å). This may cause the high Rint (15.6%) as well as the high wR2 (27.6%). Further a toluene molecule shares the same position with the 1,2-diflourobenzene (distribution is 38: 62), modelling this will cause the wR2 to drop to 23%. To solve the problem with the high R values I would suggest to collect a new data set with a better diffracting crystal or to switch from Mo to Cu radiation.

11) X-ray analysis: CIF4 (compound 4): The crystal was also weakly diffracting. Again no reflexes with I/σ >3 after a resolution of 1.1 Å. This again may cause the high R values (Rint: 8.73%; wR2: 26.97%). The original data should be checked again to exclude any other reason for this problem. If this does not help, I would again suggest to collect a new data set with a better diffracting crystal or to switch from Mo to Cu radiation.

12) X-ray analysis: CIF5 (compound 5): Here it is the same problem. The crystal was weakly diffracting and no reflexes with a I/σ higher 3 were collected after a resolution of 1.1 Å. This again may cause the high R values (Rint:6.4%; wR2: 34.3%). Further some atoms have isotropic ADPs (2 toluene molecules and C16C) without any comments regarding this. Again I would suggest to check the original data or to collect a new data set with a better diffracting crystal or to switch from Mo to Cu radiation, since a structure with a wR2 value of 34% can not be published!

Reviewer #3: I think the paper is unique with the isolation of the "half-naked" P2+ cation, as most other examples in the literature are either full sandwich complexes, or carbone/NHC stabilized dications. In terms of characterization, everything is well characterized by multinuclear NMR , DFT and X-ray however, no further characterization was used as they note that HRMS failed due to high moisture/air sensitivity. The literature cited is mostly consistent with the focus of the manuscript and supports the conclusions drawn from the work however, most of the sources provided are ca. 30 years old. The application of these cations is fairly limited with silane activation, ligand complexation and halide abstraction being shown however, this does give insight into the Lewis acidic properties of the dication with it being used to abstract fluoride from SbF6, leading to the assertion this can be classified as a super Lewis acid. Overall I think it is a solid piece of work.

Corrections:
-Page 3 "applicationin" should be "application in"
-Page 4 "diflurobenzene" should be "difluorobenzene"
-Page 5 "withη5" should be "with η-5'
-Ref 45 volume number is stated as 4, this should be 24.
-Figure 4 caption does not mention the omission of [SiEt3.tol][B(C6F5)4] ion pair from the cocrystal diagram.
-Perhaps some contemporary sources on main group Lewis super acids could be included such as Angew. Chem. Int. Ed. 2018, 57, 1717; Angew. Chem. Int. Ed. 2017, 56, 8578; Chem. Sci. 2018, 9, 245; ChemPhysChem 2017, 18, 683.
-The recent work by Chiu from NTU on Cp*BR cation could be cited.
-The coordination of bipy to P has been demonstrated by Burford for example in the case of P-Lewis acidic phosphadazonium (JACS 2005). This precedent could be quoted in the discussion.
In the SI.
-The POV-ray diagrams are squished/distorted.
-Figure S26 is somewhat drowned out by the use of protic solvent, an expansion on the relevant

aliphatic and aromatic regions would help the reader identify the major components.
-Some spectra have clearly labelled solvent peaks whilst others do not. It would be good to ensure all spectra (1H, 13C, 19F) have all solvent signals labelled to avoid confusion.

Reviewer #4: There are 5 Structures in this paper. We examined this file: combined
The structures have been provided as 5 separate files: 1.cif 2.cif 3.cif 4.cif 5.cif

All five structures have been determined and reported expertly. I could imagine a few (entirely inconsequential!) improvements for modelling the solvent disorder in structure **5** -- but nothing much could be learned from this.

I recommend publication of all five structures.