The Reactivity of Phosphanyldiphosphinidene Complexes of Transition Metals Toward Terminal Dihaloalkanes

Anna Ordyszewska[a], Natalia Szynkiewicz[a], Jarosław Chojnacki[a], Jerzy Pikies[a] and Rafał Grubba*[a]

[a] Department of Inorganic Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 11/12 Gabriela Narutowicza Str. 80-233 Gdańsk, Poland

Supplementary Information

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1. Crystallographic details

Diffraction intensity data for 1b, 1c, 1e, 2a, 2b, 2c, 3a and 3c were collected on an IPDS 2T dual beam diffractometer (STOE & Cie GmbH, Darmstadt, Germany) at 120.0(2) K with MoKα radiation of a microfocus X-ray source (GeniX 3D Mo High Flux, Xenocs, Sassenage, 50 kV, 1.0 mA, and λ = 0.71069 Å). Investigated crystals were thermostatted under a nitrogen stream at 120 K using the CryoStream-800 device (Oxford CryoSystem, UK) during the entire experiment.

Data collection and data reduction were controlled by using the X-Area 1.75 program (STOE, 2015). An absorption correction was performed using integrated reflections by a combination of frame scaling, reflection scaling and a spherical absorption correction. The structures were solved using intrinsic phasing implemented in SHELXT and refined anisotropically using the program packages Olex21 and SHELX-20152,3. Positions of the C–H hydrogen atoms were calculated geometrically taking into account isotropic temperature factors. All H-atoms were refined as riding on their parent atoms with the usual restraints.

Special treatment. Tungsten complexes. Structure 1b was refined with substitutional disorder of Br1/Cl1 atoms with site occupation factors of 0.650(5)/0.350(5), respectively. Several intensities (namely 11 reflections) were affected by beamstop and were excluded from the refinement. The same kind of substitutional disorder was found in 1c where Br1/Cl1 atoms have site occupation factors of 0.308(5)/0.692(5), respectively, and in 1e where Br1/Cl1 atoms have site occupation factors of 0.319(7)/0.681(7), respectively. Structure 1e contains the main molecule sitting on the rotational 2-fold axis, with the centre of the alkyl chain disordered. Additionally, disordered eight solvent molecules of pentane were excluded from the refinement using the SQUEEZE procedure.

Platinum complexes. Structure 2a did not require any special conditions. Structure 2b also was solved and refined by routine methods, however it contained a strong electron density peak between P1 and Pt1 atoms. In our opinion it is an artefact (e.g. due to cut of Fourier series), since no atom can be present at that location. Hydrogen atom presence must be excluded based on 1H and 31P NMR spectra. Structure 2c required to keep three carbon atoms C12, C13 and C14 in isotropic model to avoid abnormal expansion of the displacement ellipsoids. As a side effect two electron holes were created in neighbourhood of bromine atoms, which are hard to remove and most probably are just artefacts. Structural analysis for 3a produced a result with electron density map affected by minor disorder/twinning. As a result six strong residual electron density peaks are present in vicinity of I2 and carbon atoms rising A-level alerts by the checkcif procedure. We repeated the diffraction experiment thrice with different crystal specimens with the same result. Probably the twinning or disorder has minor contribution so it is hard to model, nevertheless the heaviest atoms, platinum and iodine, give relatively high distortion of the resultant electron density map at their new positions. Structure 3c was solved and refined using classical methods with four reflections omitted from the refinement as being affected by beamstop and being outliers not reproducing the actual reciprocal space.

Crystallographic data for all structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1963412-1963419. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; E mail: deposit@ccdc.cam.ac.uk).
### Table S1. Crystal data and structure refinement for 1b, 1c and 1e.

|                | 1b                | 1c                | 1e                |
|----------------|-------------------|-------------------|-------------------|
| CCDC no.       | 1963412           | 1963419           | 1963417           |
| Empirical formula | C₃₆H₅₈Br₁.₆₂Cl₀.₃₈N₆P₂W | C₆₇H₁₁₂Br₀.₆₂Cl₁.₃₈Na₄P₄W₂ | C₇₀H₁₁₆Br₀.₆₂Cl₁.₃₈Na₄P₄W₂ |
| M_r/g mol⁻¹    | 896.88            | 1575.21           | 1604.60           |
| Temperature/K  | 120 K             | 120 K             | 120 K             |
| Crystal system | Triclinic         | Monoclinic        | Monoclinic        |
| Space group    | P1̅               | P2/n              | C2/c              |
| a/Å            | 9.7463 (9)        | 10.2230 (4)       | 22.6588 (9)       |
| b/Å            | 10.1656 (11)      | 16.5252 (10)      | 36.2759 (13)      |
| c/Å            | 21.452 (2)        | 21.5979 (8)       |                   |
| α/°            | 99.019 (8)        |                   |                   |
| β/°            | 91.086 (8)        | 98.813 (3)        |                   |
| γ/°            | 115.565 (7)       | 90                |                   |
| Volume/Å³      | 1884.6 (3)        | 3605.6 (3)        | 8732.2 (5)        |
| Z              | 2                 | 2                 | 4                 |
| ρ_cal g/cm³    | 1.580             | 1.451             | 1.220             |
| Crystal size/mm³ | 0.32 × 0.15 × 0.06 | 0.38 × 0.13 × 0.05 | 0.28 × 0.15 × 0.04 |
| Radiation      | Mo Kα (λ = 0.71073) | Mo Kα (λ = 0.71073) | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 6.6–52.0 | 3.8–58.6 | 4.0–51.0 |
| Reflections collected/unique | 14945/7357 | 47018/9738 | 20742/8080 |
| Completeness to θ_max (%) | 99.3 | 98.9 | 99.5 |
| Data/restraints/parameters | 7357/397/0 | 9738/379/0 | 8080/392/10 |
| Goodness-of-fit on F² | 1.039 | 1.088 | 1.070 |
| Final R indexes [I>2σ (I)] | R₁ = 0.0356, wR₂ = 0.0846 | R₁ = 0.0503, wR₂ = 0.1144 | R₁ = 0.0626, wR₂ = 0.1353 |
| Final R indexes [all data] | R₁ = 0.0486, wR₂ = 0.0938 | R₁ = 0.0597, wR₂ = 0.1193 | R₁ = 0.0921, wR₂ = 0.1519 |
| Largest diff. peak/hole / e Å⁻³ | 1.31/-2.02 | 1.60/-3.24 | 1.33/-1.82 |

### Table S2. Crystal data and structure refinement for 2a, 2b and 2c.

|                | 2a                | 2b                | 2c                |
|----------------|-------------------|-------------------|-------------------|
| CCDC no.       | 1963416           | 1963414           | 1963413           |
| Empirical formula | C₃₀H₄₂IP₃Pt     | C₃₉H₃₉I₂Pt₃Pt    | C₃₅H₃₉Br₂Pt₃Pt   |
| M_r/g mol⁻¹    | 817.57            | 929.40            | 919.57            |
| Temperature/K  | 120 K             | 120 K             | 120 K             |
| Crystal system | Triclinic         | Triclinic         | Triclinic         |
| Space group    | P1̅               | P1̅               | P1̅               |
| a/Å            | 10.6050 (5)       | 10.6685 (7)       | 10.8798 (7)       |
| b/Å            | 11.0201 (6)       | 11.0177 (7)       | 10.9788 (7)       |
|                | 3a                              | 3c                              |
|----------------|---------------------------------|---------------------------------|
| CCDC no.       | 1963418                         | 1963415                         |
| Empirical formula | C_{124}H_{173}I_{3}O_{4}P_{12}Pt_{3} | C_{72}H_{62}Br_{2}Cl_{6}P_{8}Pt_{2} |
| M_r/g mol$^{-1}$ | 3065.22                         | 2038.81                         |
| Temperature/K  | 120 K                           | 120 K                           |
| Crystal system | Monoclinic                      | Monoclinic                      |
| Space group    | $P2_1/c$                        | $P2_1/n$                        |
| a/Å            | 40.6131 (8)                     | 15.9484 (6)                     |
| b/Å            | 9.7743 (2)                      | 15.1930 (4)                     |
| c/Å            | 33.3460 (14)                    | 17.0397 (7)                     |
| $\alpha^{\circ}$ | 90                             | 90                              |
| $\beta^{\circ}$ | 106.913 (2)                     | 97.380 (3)                      |
| $\gamma^{\circ}$ | 90                             | 90                              |
| Volume/Å$^3$   | 12664.6 (7)                     | 4094.6 (3)                      |
| Z              | 4                               | 2                               |
| $\rho_{\text{calc}}$ g/cm$^3$ | 1.608                          | 1.654                           |
| Crystal size/mm$^3$ | 0.12 × 0.05 × 0.03              | 0.34 × 0.23 × 0.09               |
| Radiation      | Mo Kα ($\lambda = 0.71073$)     | Mo Kα ($\lambda = 0.71073$)     |
| 2Θ range for data collection/$^\circ$ | 4.2-58.6                      | 4.2-58.6                        |
| Reflections collected/unique | 133338/34185                  | 33339/10840                     |

Table S3. Crystal data and structure refinement for 3a and 3c.
| Completeness to θ<sub>max</sub> (%) | 98.7 | 97.4 |
|-----------------------------------|------|------|
| Data/restraints/parameters        | 34185/1321/1 | 10840/421/0 |
| Goodness-of-fit on F<sup>2</sup>   | 1.027 | 1.051 |
| Final R indexes [I>=2σ (I)]       | R<sub>1</sub> = 0.0692, wR<sub>2</sub> = 0.1695 | R<sub>1</sub> = 0.0368, wR<sub>2</sub> = 0.0859 |
| Final R indexes [all data]        | R<sub>1</sub> = 0.1064, wR<sub>2</sub> = 0.1902 | R<sub>1</sub> = 0.0488, wR<sub>2</sub> = 0.0895 |
| Largest diff. peak/hole / e Å<sup>3</sup> | 6.27 / -3.03 | 1.29 / -2.03 |

**Figure S1.** Molecular structure of complex 1e. Ellipsoids are shown at 50% probability. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1-W1 2.516(2), P2-W1 2.400(2), P1-P2 2.150(4), C1-P1 1.873(8), ΣP1 284.2, ΣP2 341.7 (with neglecting P2-W1 bond), C1-P1-P2 112.6(3), C1-P1-P2-C4 -17.0(6).

Primed atoms are symmetry equivalents generated by symmcode (1-x, y, ½-z) i.e. 2-fold rotation.

**Figure S2.** Space filling model for 1c.
2. NMR SPECTROSCOPIC DATA

Figure S3. $^{31}$P{$^1$H} NMR spectrum of crude reaction mixture 1c.

Figure S4. $^{31}$P{$^1$H} NMR spectrum of 1b.

Figure S5. $^1$H NMR spectrum of 1b.
Figure S6. $^{13}$C ($^1$H) NMR spectrum of 1b.

Figure S7. 2D NMR COSY of 1b.

Figure S8. 2D NMR HMQC of 1b.

Figure S9. 2D NMR HMBC of 1b.
Figure S10. $^{31}$P($^1$H) NMR spectrum of crude reaction mixture 1c.

Figure S11. $^{31}$P($^1$H) NMR spectrum of 1c.

Figure S12. $^1$H NMR spectrum of 1c.
Figure S13. $^{13}$C ($^1$H) NMR spectrum of 1c.

Figure S14. 2D NMR COSY of 1c.
Figure S15. 2D NMR HMQC of 1c.

Figure S16. 2D NMR HMBC of 1c.

Figure S17. $^{31}$P($^1$H) NMR spectrum of 1c-Br/1c-Cl in DME after addition of three-fold excess of anhydrous LiCl.

Figure S18. $^{31}$P($^1$H) NMR spectrum of 1d.
Figure S19. $^{31}$P($^1$H) NMR spectrum of crude reaction mixture 1e.

Figure S20. $^{31}$P($^1$H) NMR spectrum of 1e.

Figure S21. $^1$H NMR spectrum of 1e.
Figure S22. $^{13}$C ($^1$H) NMR spectrum of $1e$.

Figure S23. 2D NMR COSY of $1e$.

Figure S24. 2D NMR HMQC of $1e$.

Figure S25. 2D NMR HMQC of $1e$. 
Figure S26. $^{31}$P($^1$H) NMR spectrum of crude reaction mixture 2a.

Figure S27. $^{31}$P($^1$H) NMR spectrum of 2a.

Figure S28. $^1$H NMR spectrum of 2a.
Figure 29. $^{13}$C ($^1$H) NMR spectrum of 2a.

Figure S30. 2D NMR COSY of 2a.

Figure S31. 2D NMR HMQC of 2a.

Figure S32. 2D NMR HMBC of 2a.
Figure S33. $^{31}\text{P}[^1\text{H}]$ NMR spectrum of crude reaction mixture 2b.

Figure S34. $^{31}\text{P}[^1\text{H}]$ NMR spectrum of 2b.

Figure S35. $^1\text{H}$ NMR spectrum of 2b.
Figure S36. $^{13}$C ($^1$H) NMR spectrum of 2b.

Figure S37. 2D NMR COSY of 2b.

Figure S38. 2D NMR HMQC of 2b.

Figure S39. 2D NMR HMBC of 2b.
Figure S40. $^{31}$P($^1$H) NMR spectrum of crude reaction mixture 2c.

Figure S41. $^{31}$P($^1$H) NMR spectrum of 2c.

Figure S42. $^1$H NMR spectrum of 2c.
Figure S43. $^{13}$C ($^1$H) NMR spectrum of 2c.

Figure S44. 2D NMR COSY of 2c.

Figure S45. 2D NMR HMQC of 2c.

Figure S46. 2D NMR HMBC of 2c.
Figure S47. $^{31}$P($^1$H) NMR spectrum of crude reaction mixture 3a.

Figure S48. $^{31}$P($^1$H) NMR spectrum of 3a.

Figure S49. $^1$H NMR spectrum of 3a.
Figure S50. $^{13}$C [$^1$H] NMR spectrum of 3a.

Figure S51. 2D NMR COSY of 3a.

Figure S52. 2D NMR HMQC of 3a.

Figure S53. 2D NMR HMBC of 3a.
Figure S54. $^{31}$P($^1$H) NMR spectrum of crude reaction mixture 3c.

Figure S55. $^{31}$P($^1$H) NMR spectrum of 3c.

Figure S56. $^1$H NMR spectrum of 3c.
3. IR SPECTROSCOPIC DATA

The FTIR spectra of crystalline products were recorded using a Nicolet iS50 FT-IR spectrometer equipped with the Specac Quest single-reflection diamond attenuated total reflectance (ATR) accessory. Spectral analysis was carried out by using the OMNIC software package.
Figure S60. IR spectrum of solid 1e.

Figure S61. IR spectrum of solid 2a.

Figure S62. IR spectrum of solid 2b.
4. COMPUTATIONAL DETAILS

All calculations were performed using Amsterdam Density Functional (ADF) package (version 2017.101)\(^4\)-\(^6\). Calculations were carried out with the General Gradient Approximation (GGA) functional BLYP (Becke\(^7\) for the exchange part and Lee, Young, Parr\(^8\) for the correlation part) with Grimme’s dispersion correction with additional Becke and Johnson damping functions (-D3BJ)\(^9\). All atoms were described by a Slater-type triple-\(\zeta\) quality basis set with two polarization functions, corresponding to TZ2P basis set\(^{10}\) in the ADF package. Relativistic effects were included using scalar Zeroth Order Regular Approximation (scalar ZORA) model\(^{11\text{-}13}\). The functional and basis set were chosen according to our experience.\(^{14\text{-}16}\) Moreover, results of this work may be compared with the one previously published by our group as the same basis set and functional were used.

Starting geometries for all compounds were taken from experimental crystallographic data. Starting geometries for non-coordinated molecules TBu\(_2\)PMe, TBu\(_2\)PPI and TBu\(_2\)PPPPTBu\(_2\) were taken from complexes 2a, 2b and 3c, respectively. Then the geometries were optimized for each spin state (singlet and triplet) and charge (+1 and -1). Geometries of complexes 1a, 2a, 2b were not optimized and experimental coordinates were used for further calculations.
As we were not able to perform calculations for 3c due to the size of the system, we have replaced Ph substituents with methyl groups (3c’) in phosphine ligands and then optimized such obtained structure. On optimized geometries of tBu2PPMe, tBu2PPI, tBu2PPPPP-tBu2 and 3c’ and non-optimized geometries of 1a, 2a, 2b a series of other calculations were conducted – Natural Bonding Orbitals (NBO), Hirshfeld population analysis17, Mayer Bond Order analysis18. Natural Bonding Orbitals (NBO, version 6.0)19 analysis was performed for all systems including calculations of Natural Localized Molecular Orbitals (NLMO)20 and Natural Population Analysis (NPA)21. Condensed Fukui functions were obtained using Hirshfeld Population Analysis to quantitatively assign properties of atoms.

To elucidate diversified reactivity of phosphanylphosphinidene tungsten complexes towards dihalogenalkanes, we propose simple model estimating energetic effects associated with formation of four-, five-, six- and seven-membered rings products as presented in Figure S49. To this end, we have optimized structures of respective reagents and performed harmonic frequency calculations to obtain values of free energy of reactions. The result are presented in Table S4. All calculations for compounds c-CnP and n-CnP (N = number of carbon atoms in aliphatic chain) presented in the paper were performed using the Gaussian 0922 program package. Molecular geometries were optimized by using the ωB97XD functional by Head-Gordon23 with 6-31+G(d,p) basis set. Nature of the final gas phase geometries as a local minima (no imaginary frequencies) on the potential energy surface was then validated by harmonic frequency calculations at the same level of theory. Values of calculated energies, enthalpies and free energies derived from thermochemical calculations were corrected for the zero-point energy (ZPE).

![Figure S65. Simplified model of reactions leading to formation of cyclic diphosphanes](image)

**Table S4.** Values of free-energy of reaction: formation of four-, five-, six- and seven-membered rings diphosphanes

| Compound | ΔG [kJ/mol] |
|----------|-------------|
| c-CnP   | 43.8        |
| 4        | -4.8        |
| 5        | 1.0         |
| 6        | 34.3        |

**Table S5.** Selected computational parameters obtained for systems involved in formation of cyclic diphosphanes (in atomic units A.U.): $\varepsilon_0$ - electronic energy; $\varepsilon_0 + \ldots$ - sum of electronic and: $\varepsilon_{\text{ZPE}}$ - zero-point energies, $E_{\text{therm}}$ - thermal energies, H – thermal enthalpies, G - thermal free energies calculated in the gas phase at ωB97XD/6-31+G(d,p) level of theory

| No. | Compound | $\Delta E_{\text{elec}}$ [A. U.] | $\Delta E_{\text{ZPE}}$ [A. U.] | $\Delta E_{\text{therm}}$ [A. U.] | H [A. U.] | G [A. U.] |
|-----|----------|---------------------------------|---------------------------------|---------------------------------|-----------|-----------|
| 1   | c-C3P    | -1116.203248                    | -1115.868549                    | -1115.851432                    | -1115.850488 | -1115.911163 |
| 2   | n-C3P    | -3688.579890                    | -3688.234087                    | -3688.214478                    | -3688.213534 | -3688.282330 |
| 3   | c-C4P    | -1155.530477                    | -1155.166212                    | -1155.148090                    | -1155.147146 | -1155.209652 |
| No. | Compound | \(E_{\text{elec}}\) [A. U.] |
|-----|----------|-----------------------------|
| 1   | \([\text{tBu}_2\text{P}-\text{PMe}]^+\) (singlet) | -1038.046188 |
| 2   | \([\text{tBu}_2\text{P}-\text{PMe}]^+\) (triplet) | -1038.011887 |
| 3   | \([\text{tBu}_2\text{P}-\text{PMe}]^-\) (singlet) | -1038.312616 |
| 4   | \([\text{tBu}_2\text{P}-\text{PMe}]^-\) (triplet) | -1038.231406 |
| 5   | \([\text{tBu}_2\text{P}-\text{PI}]^+\) (singlet) | -7918.065668 |
| 6   | \([\text{tBu}_2\text{P}-\text{PI}]^+\) (triplet) | -7918.019293 |
| 7   | \([\text{tBu}_2\text{P}=\text{P}=\text{P}]=\text{P}\text{tBu}_2]^2-\) (singlet) | -1996.237398 |
| 8   | \([\text{tBu}_2\text{P}=\text{P}=\text{P}]=\text{P}\text{tBu}_2]^2-\) (triplet) | -1995.819557 |

Table S6. Electronic energy of considered ligands

Figure S66. Hirshfeld atomic charges of ligand \([\text{tBu}_2\text{P}-\text{PMe}]^+\) (singlet).
Figure S67. Hirshfeld atomic charges of ligand [tBu₂P-PMe⁺](triplet).

Figure S68. Hirshfeld atomic charges of ligand [tBu₂P-PMe⁻](singlet).
Figure S69. Hirshfeld atomic charges of ligand \([\text{fBu}_2\text{P} \cdot \text{PMe}]\) (triplet).

Figure S70. Hirshfeld atomic charges of ligand \([\text{fBu}_2\text{P} \cdot \text{PI}]^+\) (singlet).
Figure S71. Hirshfeld atomic charges of ligand $[\text{tBu}_2P\text{=P}=\text{P}\text{=P}t\text{Bu}_2]^2+$ (singlet).

Figure S72. Hirshfeld atomic charges of complex 1a.
Figure S73. Hirshfeld atomic charges of complex 2a.

Figure S74. Hirshfeld atomic charges of complex 2b.
Figure S75. Hirshfeld atomic charges of complex 3c'.

Table S7. Cartesian coordinates of the optimized structure of ligand [(Bu₃P-PMe)⁺ (singlet).

|  |  |  |  |
|---|---|---|---|
| H | 3.66137778 | 5.18100007 | 5.59670660 |
| H | 5.29959748 | 4.70497729 | 5.11948848 |
| P | 5.41670329 | 1.52587342 | 2.88411904 |
| P | 4.85212476 | 3.43611213 | 2.46145044 |
| H | 4.05160648 | 3.47067061 | 5.41599860 |
| C | 4.78335967 | 1.52129026 | 4.58990025 |
| H | 4.89095156 | 0.03458936 | 4.68193969 |
| H | 5.40810779 | 1.59460262 | 5.35518155 |
| H | 3.73615977 | 1.39133470 | 4.74299166 |
| C | 5.27797835 | 3.93047821 | 0.68177780 |
| C | 6.01371419 | 2.75031435 | 0.07868633 |
| H | 6.95710893 | 2.50891322 | 0.50736389 |
| H | 5.39587711 | 1.84855163 | -0.04291927 |
| H | 6.24828875 | 3.05535190 | -1.01934534 |
| C | 6.20120985 | 5.17470221 | 0.69431213 |
| H | 5.71031191 | 6.02010999 | 1.09641605 |
| H | 7.12119776 | 4.98926461 | 1.25849903 |
| H | 6.48244242 | 5.39190405 | -0.34354426 |
| C | 3.94884616 | 4.21137991 | -0.06564707 |
| H | 3.30764016 | 3.32400955 | -0.09487848 |
| H | 3.38480551 | 5.04146923 | 0.36702427 |
| H | 4.19633064 | 4.48446046 | -1.09902881 |
| C | 3.77503214 | 4.59155691 | 3.53232756 |
| C | 3.93043089 | 6.06064263 | 3.08326319 |
| H | 4.95455317 | 6.42312614 | 3.21143300 |
| H | 3.61419142 | 6.22873709 | 2.05171477 |
| H | 3.28079359 | 6.66612304 | 3.72459717 |
| C | 2.31022745 | 4.11461360 | 3.36143954 |
| H | 1.96405167 | 4.21172108 | 2.32773642 |
| H | 2.17639682 | 3.07536297 | 3.67902585 |
| H | 1.67191595 | 4.74657597 | 3.99251938 |
| C | 4.23832339 | 4.46188246 | 5.00206656 |
**Table S8.** Cartesian coordinates of the optimized structure of ligand $[tBu_2P-PMe]^- \text{ (triplet).}$

|    | X (Å)       | Y (Å)       | Z (Å)       |
|----|-------------|-------------|-------------|
| H  | 3.21845159  | 5.04391973  | 5.54457961  |
| H  | 4.95283171  | 4.7576613   | 5.30579093  |
| P  | 4.58349402  | 1.49224777  | 3.01989179  |
| P  | 5.02121785  | 3.60068157  | 2.61245974  |
| H  | 3.80107029  | 3.39634257  | 5.26780501  |
| C  | 6.05287107  | 0.93567347  | 4.01878588  |
| H  | 3.05287107  | 4.27807669  | 5.26780501  |
| H  | 1.52984904  | 4.93470564  |
| C  | 3.88721025  | 0.76890094  |
| H  | 2.69536995  | 0.30643498  |
| H  | 3.80107029  | 3.39634257  | 5.26780501  |
| C  | 6.05287107  | 0.93567347  | 4.01878588  |

**Table S9.** Cartesian coordinates of the optimized structure of ligand $[tBu_2P-PMe]^- \text{ (singlet).}$

|    | X (Å)       | Y (Å)       | Z (Å)       |
|----|-------------|-------------|-------------|
| H  | 3.05836352  | 6.08410389  | 0.91209767  |
| H  | 7.09397715  | 5.18889520  | 1.20037801  |
| H  | 6.43267515  | 5.31977764  | 0.43816128  |
| C  | 4.04245376  | 3.93999489  | 0.02779266  |
| H  | 3.44996920  | 3.02717289  | 0.09559444  |
| H  | 4.29634537  | 4.03560914  | 1.09250879  |
| C  | 3.72410708  | 4.67885941  | 3.47330887  |
| H  | 3.94334488  | 6.16483686  | 3.11763959  |
| H  | 4.96252260  | 6.49916643  | 3.33881666  |
| H  | 3.71851754  | 6.37496402  | 2.06836395  |
| H  | 3.25654046  | 6.76443439  | 3.72852238  |
| C  | 2.2991123   | 4.21782007  | 3.06909176  |
| H  | 2.10445676  | 4.43703232  | 2.00189721  |
| H  | 2.11566491  | 3.17261014  | 3.3380773  |
| H  | 1.58179429  | 4.80427552  | 3.62121563  |
| C  | 3.95147013  | 4.44626017  | 4.98857216  |

H: Hydrogen, P: Phosphorus, C: Carbon
Table S10. Cartesian coordinates of the optimized structure of ligand [fBu₂P-PMe₃] (triplet).

|   |      |      |      |
|---|------|------|------|
| C | 3.91267622 | 4.73094167 | 3.46415263 |
| C | 4.42805050 | 6.18395030 | 3.53977690 |
| H | 5.43926161 | 6.21122348 | 3.96847763 |
| H | 4.46695177 | 6.6667942 | 2.55828156 |
| H | 3.76795474 | 6.79275073 | 4.18278233 |
| C | 2.53917275 | 4.6639401 | 2.7785815 |
| H | 2.55269199 | 5.14220093 | 1.79109676 |
| H | 2.23201635 | 3.61810947 | 2.66198915 |
| H | 1.77360322 | 5.18522138 | 3.38422871 |
| C | 3.76497346 | 4.19775843 | 4.90677766 |

Table S11. Cartesian coordinates of the optimized structure of ligand [fBu₂P-PI]⁺ (singlet).

|   |      |      |      |
|---|------|------|------|
| H | 3.41594944 | 5.12949024 | 5.5930889 |
| H | 5.16941221 | 5.04807834 | 5.25510768 |
| P | 4.97772350 | 1.46133271 | 2.71521745 |
| P | 5.33024941 | 3.60714741 | 2.68373567 |
| H | 4.23152227 | 3.55502292 | 5.4422507 |
| C | 4.66331182 | 1.04350583 | 4.52949061 |
| H | 4.73939520 | -0.0536733 | 4.6176244 |
| H | 5.41188108 | 1.50821997 | 5.18833399 |
| H | 3.65802725 | 1.35076474 | 4.86385214 |
| C | 5.29042462 | 3.93870273 | 0.72221417 |
| C | 6.22951816 | 2.88726569 | 0.08910822 |
| H | 7.22139925 | 2.89688881 | 0.5592989 |
| H | 5.82645717 | 1.87316310 | 0.17380531 |
| H | 6.35425749 | 3.12141804 | -0.98073199 |
| C | 5.90440095 | 5.32998350 | 0.45279318 |
| H | 5.27760513 | 6.14744155 | 0.81851304 |
| H | 6.89400712 | 5.42502723 | 0.9185425 |
| H | 6.02561578 | 5.47074297 | -0.63734321 |
| C | 3.90393357 | 3.83313222 | 0.06119383 |
| H | 3.43199717 | 2.86682586 | 0.27417026 |
| H | 3.22462209 | 4.62689841 | 0.39123054 |
| H | 4.00516404 | 3.93022658 | -1.0401618 |
| C | 3.87710054 | 4.58898643 | 3.5330995 |
| C | 3.87460742 | 6.05939523 | 3.0597323 |
| H | 4.86834680 | 6.1954841 | 3.1637809 |
| H | 3.54696417 | 6.15955535 | 2.01772641 |
| H | 3.17341481 | 6.63666841 | 3.67905318 |
| C | 2.48893421 | 3.95617335 | 3.29672728 |
| H | 2.20991824 | 3.96500901 | 2.23729758 |
| H | 2.45821082 | 2.91660474 | 3.64735205 |
| H | 1.7241535 | 4.52442579 | 3.8542596 |
| C | 4.20004778 | 4.57354166 | 5.04669057 |

Table S10. Cartesian coordinates of the optimized structure of ligand [fBu₂P-PMe₃] (triplet).

Table S11. Cartesian coordinates of the optimized structure of ligand [fBu₂P-PI]⁺ (singlet).
Table S12. Cartesian coordinates of the optimized structure of ligand [tBu₂P=PI]^+ (triplet).

|      | x    | y    | z     |
|------|------|------|-------|
| H    | 7.98310449 | 6.92517689 | -0.48974006 |
| H    | 9.16139394 | 7.25161395 | 0.79031020  |
| I    | 6.42218676 | 5.51761111 | 3.99385558  |
| P    | 8.38788811 | 7.01613476 | 0.401521904 |
| P    | 7.53980071 | 6.84845909 | 2.8242138  |
| H    | 7.7722391 | 6.1746584 | 1.10061089 |
| C    | 6.4069730 | 9.8375888 | 3.77504556 |
| C    | 5.07460942 | 9.13589999 | 4.14294215 |
| H    | 4.51828413 | 8.80467564 | 3.26291084 |
| H    | 4.45611563 | 9.86985571 | 4.67298282 |
| H    | 5.23557574 | 8.2834816 | 4.80471215 |
| C    | 6.15093051 | 11.08969724 | 2.90642249 |
| H    | 7.08148055 | 11.5833922 | 2.60815699 |
| H    | 5.57491908 | 11.8008184 | 3.51209294 |
| H    | 5.56075483 | 10.86562247 | 2.01349337 |
| C    | 7.18597417 | 10.21972821 | 5.0666424 |
| H    | 7.38701746 | 9.34859120 | 5.6890464 |
| H    | 6.56757838 | 10.91749370 | 5.63495678 |
| H    | 8.13472994 | 10.7147704 | 4.82814953 |
| C    | 2.73651083 | 8.30858904 | 0.97866111 |
| C    | 5.73377985 | 8.02274494 | 0.74591800 |
| H    | 5.39205308 | 7.15601077 | 1.31931262 |
| H    | 5.60034670 | 7.80124174 | -0.32170985 |
| H    | 5.10252302 | 8.88290978 | 0.98533041 |
| C    | 7.70231797 | 9.55548092 | 0.18324954 |
| H    | 7.11682481 | 10.44731367 | 0.41674086 |
| H    | 7.56805322 | 9.33650760 | -0.88396542 |
| H    | 8.76251984 | 9.77282824 | 0.3510974 |
| C    | 8.09714704 | 7.08649706 | 0.5897715 |

Table S13. Cartesian coordinates of the optimized structure of ligand [tBu₂P=P=P=PrBu₂]^2- (singlet).

|      | x    | y    | z     |
|------|------|------|-------|
| H    | -3.67951412 | 2.6463867 | -1.7011274 |
| P    | -0.06162256 | 1.04702611 | -0.21264180 |
| P    | -1.18124984 | 1.00520552 | -1.93713835 |
| H    | -3.55438859 | 2.25856785 | -3.4338642 |
| C    | -3.15904959 | 2.88204065 | -2.63560107 |
| H    | -3.52990766 | 0.21891367 | -3.83572228 |
| P    | 1.52807547 | -1.06364156 | 1.82931461 |
| C    | 2.00929533 | 0.48520171 | 2.84566171 |
### Table S14. Cartesian coordinates of the optimized structure of ligand [tBu₂P=P=P=tBu₂]²⁺ (triplet).

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | 2.77112781 | 1.43337885 | 1.88671097 |
| H    | 3.68701279 | 0.97417202 | 1.50084832 |
| H    | 2.15885058 | 1.76043333 | 1.04376226 |
| H    | 3.05617482 | 2.32405910 | 2.46138359 |
| C    | 0.68127769 | 1.10479079 | 3.35208642 |
| H    | 0.01576292 | 1.39945420 | 2.5510306 |
| H    | 0.14143954 | 0.54968210 | -4.84553979 |
| C    | -2.56183406 | -0.17842508 | -4.14820850 |
| H    | -2.08665467 | 0.51496821 | -2.56352057 |
| C    | -2.11741133 | 3.76007630 | -1.41642026 |
| C    | -2.31804440 | -1.48777945 | -1.99252257 |
| H    | -0.58654959 | -2.07246777 | -4.01556523 |
| C    | -0.33287746 | -1.17461330 | -3.44809777 |
| H    | -1.12073969 | 4.04009919 | -4.14790614 |
| H    | 0.32700275 | -1.46675011 | -4.69511852 |
| C    | 0.20201087 | 2.93757766 | -3.72532275 |
| C    | 0.88523658 | 3.01485846 | -3.83310883 |
| H    | -2.75182815 | -1.11069121 | -4.69511852 |
| C    | -1.61939544 | 2.76818282 | -2.48804058 |
| H    | -1.21683944 | 2.34938441 | -4.62860144 |
| H    | -3.35143855 | -1.02616178 | -1.61850989 |
| C    | -1.82731700 | -1.81391398 | -1.14341115 |
| H    | -1.37694974 | 4.76850021 | -1.76246085 |
| C    | 2.91780422 | 0.11587179 | 4.03584616 |
| H    | -2.45077844 | -0.58497057 | 4.73131764 |
| H    | 3.88646430 | -0.27379750 | 3.71480337 |
| H    | 3.10500701 | 1.04572917 | 4.58777459 |
| C    | 1.96008775 | -2.82781329 | 2.37777920 |
| C    | 1.23287000 | -3.07634244 | 3.7293138 |
| H    | 1.56145981 | -2.40486669 | 4.51875021 |
| H    | 0.14506531 | -3.00259760 | 3.61480731 |
| H    | 1.47155710 | -4.10808088 | 4.03764116 |
| H    | 1.46359268 | -3.81766935 | 1.30507142 |
| H    | -1.60375218 | 3.60833865 | -0.44723907 |
| H    | 0.37639230 | -3.78563430 | 1.17976291 |
| H    | 1.94849637 | -3.66731137 | 0.33550511 |
| H    | 1.72468183 | -4.82651367 | 1.64895340 |
| C    | 3.50570433 | -2.94139429 | 2.52435556 |
| H    | 4.02577242 | -2.70233714 | 1.59053128 |
| H    | 3.90129701 | -2.32070140 | 3.32916521 |
| H    | 3.72905739 | -3.9675508 | 2.77247456 |
| H    | -0.03088533 | 3.72733507 | 1.28970217 |
| H    | 0.21319593 | -0.49701000 | -4.11568502 |
| P    | 0.39782321 | -1.10441570 | 0.11183095 |
| C    | -1.66147573 | -0.54578105 | -2.95129347 |

H  -4.33167842  0.89748624  -1.84127124
P  -0.37746349  0.45287308  0.03196980
P  -1.32957297  0.73569134  -1.82780810
H  -3.83952719  1.54748213  -3.42796691
C  -3.90372923  1.76148707  -2.36054993
H  -2.79605671  -0.05606483  -4.44185511
P  1.90749256  -1.22787913  1.68556124
C  3.08189113  0.17749167  2.19558096
Table S15. Cartesian coordinates of the optimized structure of complex 3c'.

|   |   |   |
|---|---|---|
| Pt | 3.94012604 | 8.47147080 | 8.81821976 |
| P  | 6.40189327 | 8.5555421 | 8.5858466 |
| P  | 5.1074849 | 6.0581467 | 6.8147198 |
| P  | 3.5631967 | 8.12613041 | 4.7614976 |
| H  | 0.94752434 | 3.49371829 | 4.55110967 |
| H  | -1.80402547 | 2.94476605 | 0.18925308 |
| H  | 0.68589823 | 1.44086729 | -3.91574780 |
| P  | 1.12465000 | -1.03134253 | -0.36781427 |
| C  | -0.82430498 | -0.10786869 | -3.46213679 |

|   |   |
|---|---|
| C  | 4.13201312 | 0.27328771 | 1.06166789 |
| H  | 4.70159684 | 0.65470152 | 0.9475004 |
| H  | 3.67618297 | 0.53259663 | 0.09846164 |
| H  | 4.83735171 | 1.07286418 | 1.32074012 |
| C  | 2.27346765 | 1.49122689 | 2.3120700 |
| H  | 1.81786707 | 1.7826184 | 1.35935376 |
| H  | 1.49660697 | 1.44350032 | 3.08207621 |
| H  | 2.79723377 | 2.28504734 | 2.9526636 |
| H  | -4.59642365 | 2.6033796 | -2.2326883 |
| C  | -1.77438512 | 0.29500599 | -4.60810482 |
| H  | -1.78181522 | 1.37041285 | -4.80049505 |
| H  | -0.60860727 | -2.12949188 | -4.16429189 |
| C  | -2.73368935 | 2.59695336 | -0.27285039 |
| H  | -0.90512035 | -2.12949188 | -3.22920114 |
| C  | 0.94419890 | -0.13410787 | -4.68880167 |
| H  | 0.62557703 | 0.35864633 | -3.76075782 |
| H  | -2.58660995 | 4.20118459 | -2.51611734 |
| H  | 1.32847422 | 0.07228599 | -2.97237071 |
| H  | -0.94353300 | 3.67199875 | -2.10662769 |
| C  | -1.89134370 | 3.35132002 | -2.55198572 |
| H  | -1.40123245 | -0.19625935 | -5.51577025 |
| C  | -2.54661156 | 2.19272319 | -1.75089223 |
| H  | -1.72944150 | 3.10436198 | -3.60424692 |
| H  | -1.92275100 | -1.96029556 | -2.98640876 |
| H  | -0.22548065 | -1.98394330 | -2.44545604 |
| H  | -3.44343689 | 3.43346446 | -0.25313059 |
| C  | 3.75194607 | -0.19010856 | 3.53687641 |
| H  | 3.04002355 | -0.21287034 | 4.36661188 |
| H  | 4.28343475 | -1.14566132 | 3.48751918 |
| H  | 4.49140915 | 0.58989548 | 3.7564546 |
| C  | 0.75274747 | -2.10185098 | 2.92589891 |
| H  | -0.0219938 | -1.01702023 | 3.70273650 |
| H  | 0.63404643 | -0.38900028 | 4.31769174 |
| H  | -0.61462568 | -0.36796933 | 3.04259839 |
| H  | -0.71884814 | -1.52709494 | 4.37824992 |
| H  | -0.2055142 | -2.99387352 | 2.10631127 |
| H  | -3.15979993 | 1.78790813 | 0.32987500 |
| H  | -0.87236979 | -2.40734127 | 1.46603016 |
| H  | 0.33196574 | -3.72567019 | 1.49326572 |
| H  | -0.83222526 | -3.55130052 | 2.81376716 |
| C  | 1.62542805 | -2.96485983 | 3.86831223 |
| H  | 2.20106593 | -3.71769557 | 3.31900600 |
| H  | 2.30699062 | -2.36638598 | 4.7614976 |
| H  | 0.94752434 | -3.49371829 | 4.55110967 |
| H  | -1.80402547 | 2.94476605 | 0.18925308 |
| H  | 0.68589823 | 1.44086729 | -3.91574780 |
| P  | 1.12465000 | -1.03134253 | -0.36781427 |
| C  | -0.82430498 | -0.10786869 | -3.46213679 |
C  9.05677132  8.86188686  11.01576676
H  10.05665081  8.89607428  10.57315277
H  8.34237994  9.21336432  10.26528140
H  9.03174283  9.55850746  11.86346753
C  6.55871886  7.73010632  11.38581110
H  7.02267153  6.44773922  12.52568550
H  7.25736742  6.44773922  12.52568550
C  4.03669743  9.22546793  12.34401560
C  9.69075297  7.83536088  5.99937085
H 12.79769465  8.28016137  6.29244520
C  9.72180839  4.94731210  5.01379379
C  13.10970379  6.67533095  9.66344030
C  12.26017330  6.22363430  5.79876342
H 12.63857403  6.34392528  4.77660880
H 12.50803191  5.20719069  6.12737185
C  12.87950293  7.28018171  6.73410573
H 13.94401646  7.07070524  6.88290944
C  13.01789877  8.20207494  9.57949476
C  1.51155313  8.38352023  11.19221509
H  1.12315213  7.80743622  12.04030412
H  9.4989951  4.94489496  11.4236966
C  0.79330116  8.01054941  9.88325901
C  1.14019107  3.65191125  9.10002440
H  0.86220597  8.01491815  6.95927246
H  7.65672889  3.75468736  8.7640519
H  9.35208656  3.97561800  8.28919882
C  8.88633112  2.58942482  9.2917738
C  10.41702523  4.16298038  10.8475947
H 11.12071571  4.47572995  10.06942789
H 10.67881405  4.66027826  11.78343718
H  5.4111423  3.08349144  10.9974644
Pt 9.70554855  7.0689452  8.06485172
P 10.41780795  6.27941600  5.69290364
P 11.98052013  7.30726208  8.35959380
C  4.95897766  7.11405537  5.62686811
C  4.38302073  5.94371506  6.4576842
C  3.39995730  6.19450658  6.8698461
H  5.03945560  5.66498502  7.28629751
H  4.27304650  5.07069776  5.80176819
C  6.32542371  6.71859609  5.03192899
H  7.02226000  6.40870643  5.8144660
H  6.77417302  7.53082995  4.45372920
H  6.17995113  5.86864700  4.35187524
C  3.97559134  7.44623242  4.48322674
H  4.38317354  8.18220153  3.78591021
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