Supplementary

All quantum-chemical computations were carried out using the GAUSSIAN 03 [1] suite of programs. Calculations were performed with Becke's three parameter hybrid exchange functional [2] and the gradient-corrected nonlocal correlation functional of Lee et al. [3] (B3LYP) and OPBE density functional, which is Handy and Cohen's optimized exchange functional OPTX [4] in combination with Perdew–Burke–Ernzerhof (PBE) functional [5]. Standard 6-31G* [6] basis set was used for the ligand atoms (H, C, and N), while ECP LanL2DZ basis set [7] was used for Fe atoms. Complete structural optimization was carried out for the cations and neutral complexes in both high- and low-spin states. All stationary points were characterized as minima by analysis of the Hessian matrices. The calculated force fields were transformed to internal coordinates, and SQM scaling procedure [8] was applied using the program described in Refs. [9]. The transferable scaling factors employed in this work are summarized in Table 1. The total energies were corrected for zero-point vibrational energy, calculated at the optimized geometries without scaling. The atomic partial charges have been estimated with the NBO method [10].

Table 1. Scaling factors for the force fields of the compounds studied.

Scaling factor		Value	References
Stretch	CC, CN	0.9207	[8]
Stretch	CH (arom.)	0.915	[11]
Stretch	CH (aliph.)	0.889	[11]
Bend	NCN, CNN, CCC	1.0144	[8]
Bend	CCH, NCH	0.950	[8]
Bend	HCH	0.9016	[8]
Torsion	All	0.9523	[8]

1 Frisch, M.J. et al., GAUSSIAN 03, Revision B.05, Gaussian, Inc., Wallingford, CT, 2004.

2 Becke, A. D. (1993). Density-functional thermochemistry. III. The role of exact exchange. The Journal of Chemical Physics, 98(7), 5648–5652; https://doi.org/10.1063/1.464913

3 Lee, C., Yang, W., & Parr, R. G. (1988). Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Physical Review B, 37(2), 785–789; https://doi.org/10.1103/PhysRevB.37.785

4 Handy, N. C., Cohen, A. J. (2001). Left-right correlation energy. Molecular Physics, 99(5), 403–412., https://doi.org/10.1080/00268970010018431

5 Perdew, J. P., Burke, K., & Ernzerhof, M. (1996). Generalized Gradient Approximation Made Simple. Physical Review Letters, 77(18), 3865–3868, https://doi.org/10.1103/PhysRevLett.77.3865. Perdew, J. P., Burke, K., & Dunning Jr., P.J. Hay, Moder Ernzerhof, M. (1997). Generalized Gradient Approximation Made Simple [Phys. Rev. Lett. 77, 3865 (1996)]. Physical Review Letters, 78(7), 1396–1396, https://doi.org/10.1103/PhysRevLett.78.1396

6 Hariharan, P. C., Pople, J. A. (1973). The influence of polarization functions on molecular orbital hydrogenation energies. Theoretica Chimica Acta, 28(3), 213–222, https://doi.org/10.1007/BF00533485

7 Hay, P. J., Wadt, W. R. (1985). Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. The Journal of Chemical Physics, 82(1), 270–283, https://doi.org/10.1063/1.448799 ; Wadt, W. R., Hay, P. J. (1985). Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. The Journal of Chemical Physics, 82(1), 284–298, https://doi.org/10.1063/1.448800 ; Hay, P. J., Wadt, W. R. (1985). Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. The Journal of Chemical Physics, 82(1), 299–310, https://doi.org/10.1063/1.448975.

8 Baker, J., Jarzecki, A. A., Pulay, P. (1998). Direct Scaling of Primitive Valence Force Constants: An Alternative Approach to Scaled Quantum Mechanical Force Fields. The Journal of Physical Chemistry A, 102(8), 1412–1424, https://doi.org/10.1021/jp980038m

9 Sipachev, V. A. (2001). Local centrifugal distortions caused by internal motions of molecules. Journal of Molecular Structure, 567-568, 67–72, https://doi.org/10.1016/S0022-2860(01)00534-8 ; Sipachev, V. A. (2000). Anharmonic Corrections to Structural Experiment Data. Structural Chemistry, 11(2/3), 167–172, https://doi.org/10.1023/A:1009217826943 .

10 Reed, A. E., Curtiss, L. A., Weinhold, F. (1988). Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. Chemical Reviews, 88(6), 899–926, https://doi.org/10.1021/cr00088a005

11 Katsyuba, S., Schmutzler, R., Grunenberg, J. (2005). Binding energies, vibrations and structural characteristics of small polyphosphorus molecules from quantum chemical computations. Dalton Transactions, (9), 1701-1706, https://doi.org/10.1039/B417922F