

2,2',6,6'-Tetrasubstituted 1,1'-biphenyls as bridging fragments in dinuclear transition metal complexes

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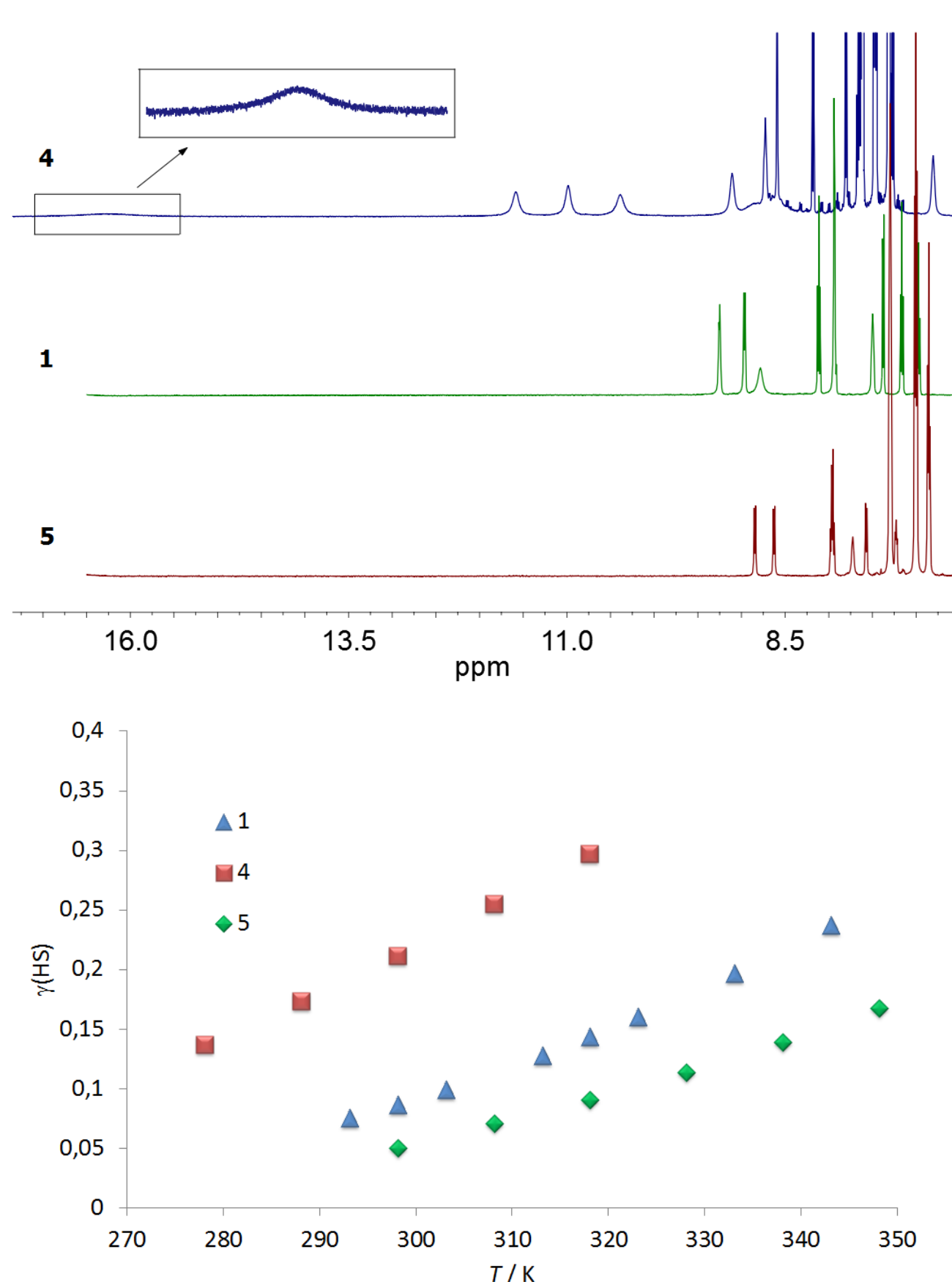
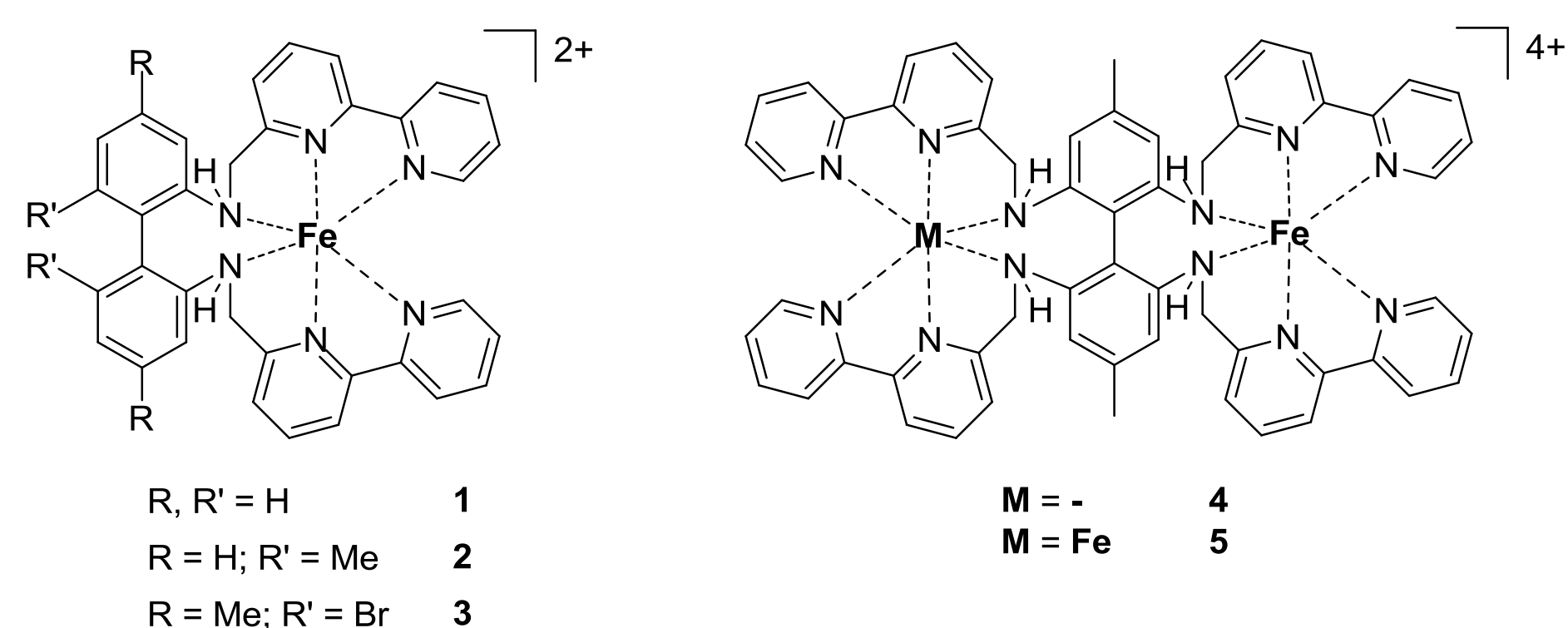
Biphenyls are long-known organic compounds that show high stability due to their two aromatic rings, starting with the first reports the question of the molecular structure arose. A co-planar structure would allow resonance stabilization, a twisted structure would reduce the steric repulsion between the *ortho* hydrogen atoms. At the moment researchers agreed to a torsion angle of about 44°, a fine balance between attraction and repulsion of the *ortho* hydrogen atoms, and a barrier of about 6 kJ/mol for the torsion of the aromatic rings.[1] As we can see that even in this simple case the interaction between the four *ortho* hydrogen atoms is an interesting object to study. We have started to look at biphenyls that bear four functional groups in the *ortho* positions.

Due to their d⁶ electron configuration octahedral Fe²⁺ complexes can exist in a diamagnetic low-spin or a paramagnetic high-spin form. In the case of a critical value of the ligand field splitting, an equilibrium between these two spin-states can be present, yielding so called Spin-Crossover (SCO) complexes. Those have ever since been promising candidates for several applications as data storage, new displaying devices or for sensors.[2] We have used a 2,2',6,6'-tetraaminobiphenyl as bridge between two SCO Fe(II) centers. In this system the biphenyl moiety transmits the change in ion diameter through the torsion angles and allows a cooperative behavior.

Although 2,2'-diphosphino biphenyls are well known and widely used as supporting ligands in asymmetric catalysis[3] due to their C₂-symmetry, the higher symmetric 2,2',6,6'-tetraphosphinobiphenyls were until last year unknown.[4] This class of bridging ligands also couples two transition metal centers through allosteric interaction, the impact on the reactivity and catalytic activity is not yet explored.

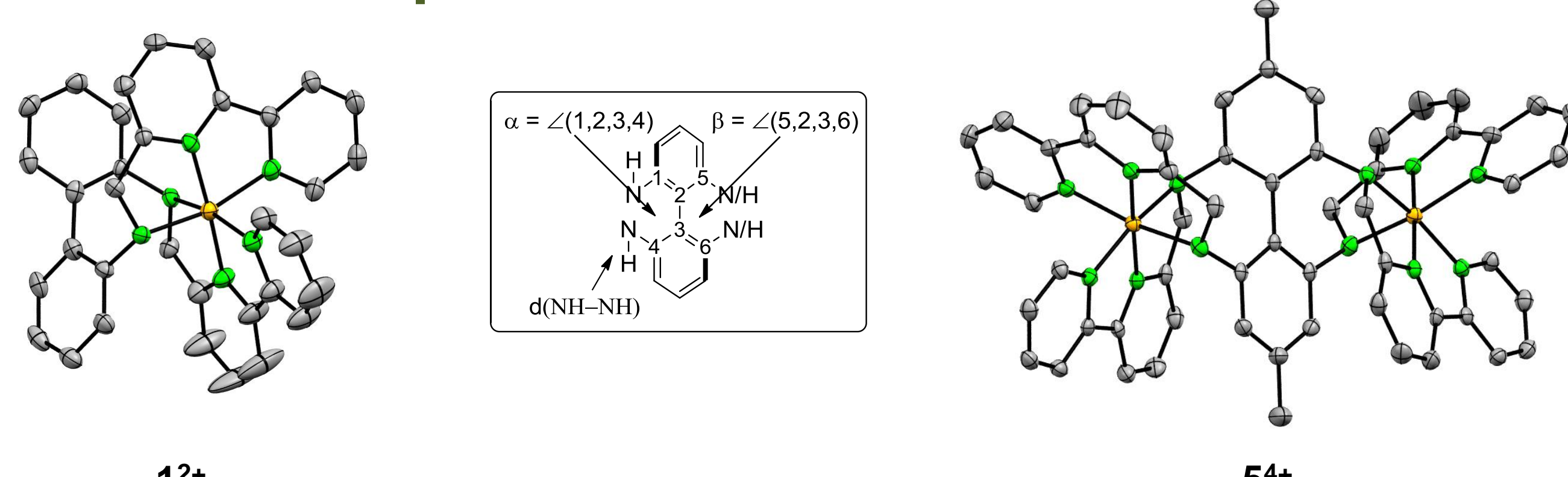
At least 2,2',6,6'-biphenyls may not only be functional bridging ligands: in the last year we were able to prepare the first 4,9-Dibora-5,10-diaza-4,5,9,10-tetrahydropyrene that couples two Lewis acid and base adducts through a biphenyl bridge. These compounds may find some application as emitters due to their high stability and their unique quadrupole moment.

Mono- vs. Dinuclear Complexes



Although the forces on donor atoms induced by the torsion of biphenyl are rather small they can be exploited to tune an SCO equilibrium in a wide range. In the series of complexes 1–3 which only differ in size of R' groups on the left side of the bridge we observe a difference of 62 K for the equilibrium temperature $T_{1/2}$ (1, 2, 3, $T_{1/2}$ = 403K, 375K, 341K; $|\Delta(\alpha-\beta)|$ = 2.8(10)°, 5.0(4)°, 7.8(4)°).[5] When we expanded this system to the dinuclear complex 5, we found that in this $T_{1/2}$ is the highest among this series of complexes. Interestingly, complex 4 that possesses the same organic backbone as complex 5 but only one metal follows the rule that bulky substituents lower $T_{1/2}$. On the upper left figure the proton NMR spectra of 4, 1, and 5 are shown. Clearly shifts and line broadening correspond to the mole fraction of HS vs. LS complex. By applying a calibration function the mole fraction of 1, 4, 5 were determined.

Comparison of Solid State Structures



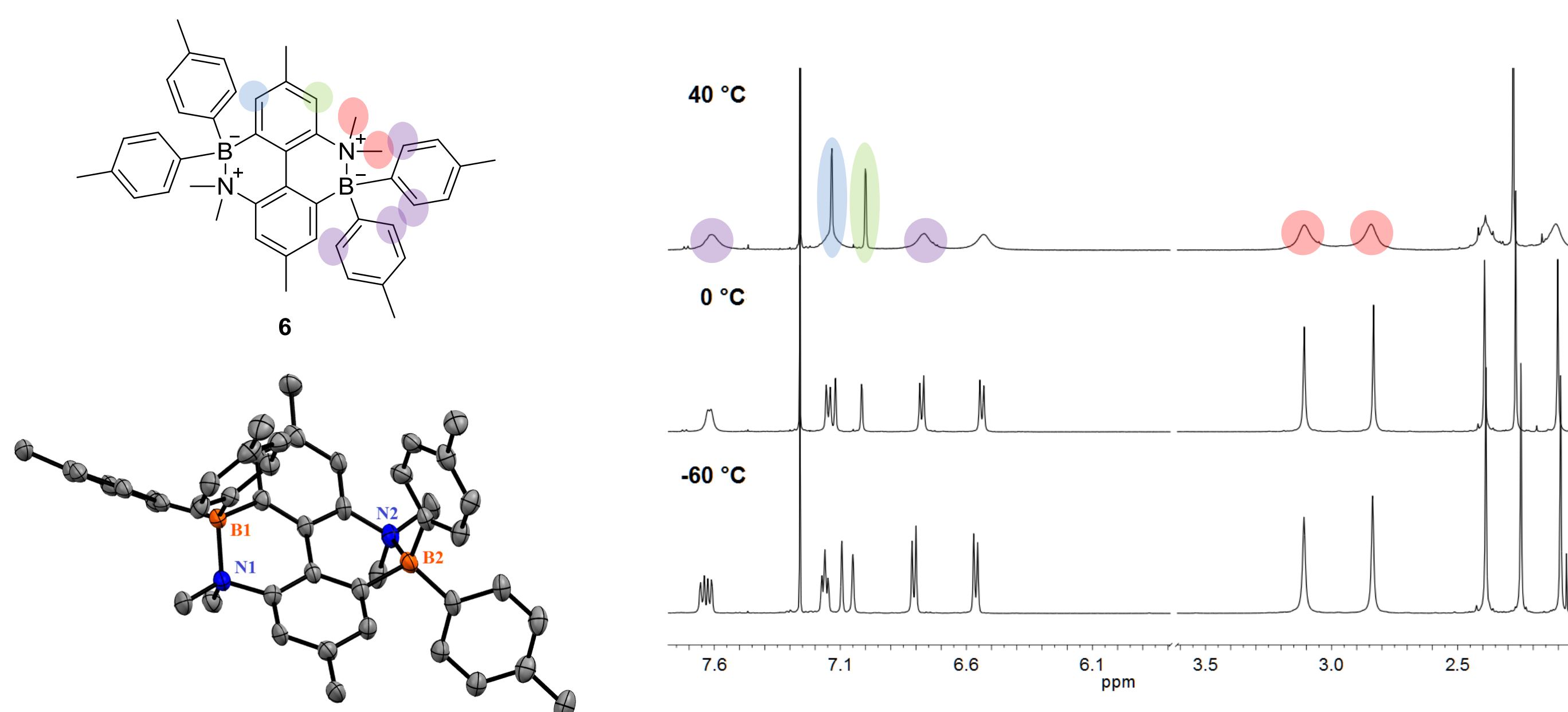
Complex	M–N (Å) (solid @ 110K)	d(NH...NH) (Å) (solid @ 110K)	$ \Delta(\alpha-\beta) $ (°) (solid @ 110K)	Spin State (solid @ 110K)
[5][BPh ₄] ₄	1.8884(17) – 2.0553(17)	2.9629(27)	0	Low-Spin
[1][Cl] ₂	1.883(4) – 2.059(4)	3.0068(62)	2.8(10)	Low-Spin
[1-Zn][PF ₆] ₂	2.0621(16) – 2.3123(17)	3.3255(26)	1.3(4)	Model for High-Spin Fe ²⁺

In the solid state structures several indicators for the low-spin state can be found. First, the Fe–N bond lengths of ca. 1.9 to 2.1 Å clearly demonstrate the low spin configuration of these complexes.

Due to change of the spin-state from low-spin to high-spin, the Fe²⁺ ion is enlarged which results in elongation of Fe–L bond lengths. For having a qualitative glance on the structure of the respective high-spin complex of 1, the Zn²⁺ complex akin to 1 was investigated by X-Ray analysis (radii of Zn²⁺ and Fe²⁺_{hs} are very similar). The most striking change is the elongation of the M–N bond lengths by ca. 0.2 Å and a subsequently increasing N...N distance of the amino nitrogen atoms by 0.3 Å.

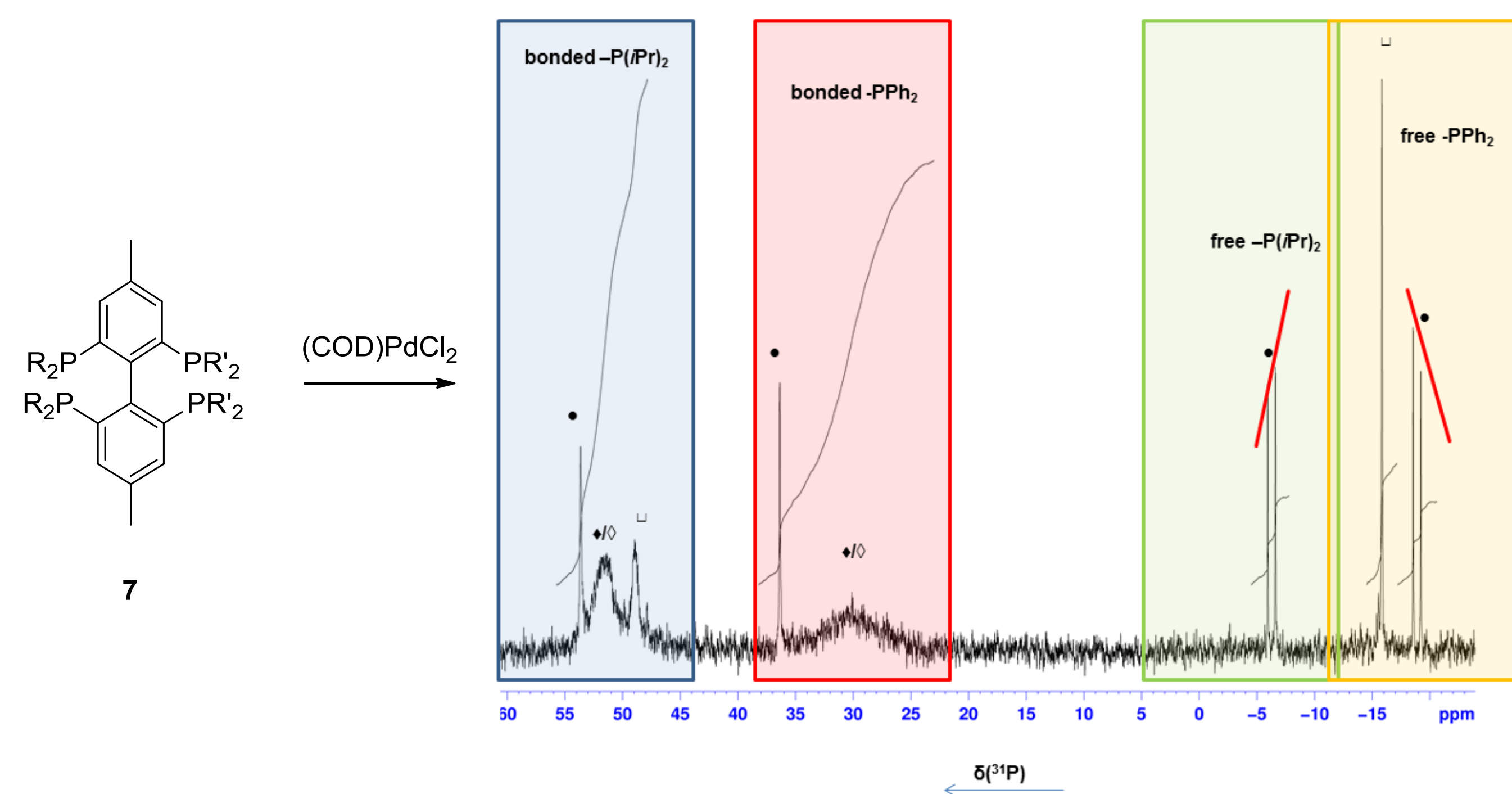
The difference of the torsion angles (α , β) can be used as a measure for the steric strain in these biphenyl based compounds. In an unstrained biphenyl bridge $\Delta(\alpha-\beta)$ should be zero. We have recently shown that placing substituents R' in the 6,6'-positions can increase this steric strain and hence lower the spin transition temperature $T_{1/2}$ according to size (1, 2, 3; $T_{1/2}$ = 403K, 375K, 341K; $|\Delta(\alpha-\beta)|$ = 2.8(10)°, 5.0(4)°, 7.8(4)°).[5]

A 4,9-Dibora-5,10-diaza-4,5,9,10-tetrahydropyrene



The parent 4,9-Dibora-5,10-diaza-4,5,9,10-tetrahydropyrene is, as the name already tells, isoelectronic to tetrahydropyrene, but due to the polar B–N bond it is also much more polar. We have recently synthesized the first example of a 4,9-dibora-5,10-diaza-4,5,9,10-tetrahydropyrene. Interestingly, by closer inspection of the structure of 6 it becomes clear that the two polar bonds and their resulting dipole moment in this formal C_{2h} symmetric molecule equal each other resulting in a molecule with zero dipole moment, solely a quadrupole moment will result. Taking in account the solid state structure and the torsion angle of 17° around the central C–C bond a small dipole moment can be found, perpendicular to the aromatic system along the C₂ axis. If we look at temperature dependent proton NMR spectra we observe a slow inversion of the C₂ axis and with accompanied with this an inversion of the dipole moment. The consequences on the photophysical properties on this fluorescent compound is under exploration in our group.

2,2',6,6'-Tetraphosphinobiphenyl



The first example of a 2,2',6,6'-tetraphosphinobiphenyl was recently presented by our group.[4] The improved protocol now allows us to prepare a variety of alkyl or aryl substituted symmetric as well as asymmetric 2,2',6,6'-tetraphosphinobiphenyls. These ligands have unique properties as the coordination of one complex fragment in a κ^2 -P₂P₂ fashion changes the molecular structure of the remaining chelate dramatically. In the figure above a typical ³¹P{¹H} spectrum is given for the reaction product of tetraphosphane 7 (R = Ph; R' = *i*-Pr) with a PdCl₂ precursor. From the spectrum we learn that symmetric (□) and asymmetric (●) mononuclear as well as the dinuclear (♦, ♦) complexes were formed. Only one of the five possible complexes is not observed, which one is it?

Conclusion

The 2,2',6,6'-biphenyl bridge is a useful building block for construction of molecules with new properties. In this account we have shown the first dinuclear SCO complex with a single bridging ligand that is capable to induce a positive cooperativity between the two iron SCO centers. This cooperativity is mainly transmitted through the torsion between the two aromatic rings in the biphenyl bridge. In contrast, the reactivity of 2,2',6,6'-tetraphosphino biphenyls towards Pd(II) salts is dominated by the repulsion of the substituents of the phosphino moieties. At last, the first 4,9-Dibora-5,10-diaza-4,5,9,10-tetrahydropyrene is isoelectronic to tetrahydropyrene but possesses a quadrupole moment with a small slowly inverting dipole moment. In the future, we would like to expand the series of functionalized 2,2',6,6'-substituted biphenyls. We hope that this poster gave you a little insight into this adventure at its beginning.

References

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