Figure S1. Conformational equilibria of the Pt(DAB)$^{2+}$ moiety. A: Two stable conformations of the five-membered ring of the complex [PtCl$_2$(R,R-DAB)]. Top, two views of the conformation with equatorial positions of the methyl groups. Bottom, two views of the conformation with axial positions of the methyl groups. B: Plot of the C-C-C-C dihedral angle (along the bonds shown in orange thick sticks) in the Pt(R,R-DAB)$^{2+}$-**TGGT** (left) and Pt(S,S-DAB)$^{2+}$-**TGGT** (left) adducts as a function of the simulation time. The equatorial-axial transitions were less frequent in the case of the Pt(S,S-DAB)$^{2+}$-**TGGT** adduct, therefore, a longer simulation was necessary for an equivalent sampling.

Table S1 : Protocol for MD simulation of the intrastrand crosslink Pt(DAB)-DNA. Groups defintions : A = DNA (platinum-DNA adduct), B= counter ions, C = all Watson-Crick hydrogen bonds (WC) and D = terminal WC. Additional harmonic restraint on dihedral angles alpha (reference value : 180°) and gamma (reference value : 180°) of 5' platinated guanine during the first nine equilibration steps for alpha *trans*/gamma *trans* restrained DM simulations (2ns production period).

Stage	Time (ps)	Harmonic restraints on cartesian coordinates	Distances restraints	Remarks
Heating 1	5	25Kcal.mol-1 on A, 25Kcal.mol-1 on B	25Kcal.mol-1 on C	0K-150K
Heating 2	5	25Kcal.mol-1 on A, 25Kcal.mol-1 on B	25Kcal.mol-1 on C	150K-300K
Equilibration 1	5	25Kcal.mol-1 on A, 25Kcal.mol-1 on B	25Kcal.mol-1 on C	
Equilibration 2	2,5	25Kcal.mol-1 on A, 25Kcal.mol-1 on B	25Kcal.mol-1 on C	Switch to constant P
Equilibration 3	5	20Kcal.mol-1 on A, 15Kcal.mol-1 on B	25Kcal.mol-1 on C	
Equilibration 4	2,5	15Kcal.mol-1 on A, 10Kcal.mol-1 on B	25Kcal.mol-1 on C	
Equilibration 5	2,5	10Kcal.mol-1 on A, 5Kcal.mol-1 on B	25Kcal.mol-1 on C	
Equilibration 6	2,5	5Kcal.mol-1 on A, 2,5Kcal.mol-1 on B	25Kcal.mol-1 on C	
Equilibration 7	10	2,5Kcal.mol-1 on A	25Kcal.mol-1 on C	
Equilibration 8	20		25Kcal.mol-1 on C	
Re-distribution	0,002	Redistribution of the velocities according to a Maxwellian distribution		
Equilibration 9	20		25Kcal.mol-1 on D	
Re-distribution	0,002	Redistribution of the velocities according to a Maxwellian distribution		
Equilibration 10	20		25Kcal.mol-1 on D	
Re-distribution	0,002	Redistribution of the velocities according to a Maxwellian distribution		
Production	5000		25Kcal.mol-1 on D	