Metallamacrocycle formation through dimerization of metal bioconjugates derived from amino acids and peptides.

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Supporting Information.
Figure S1. (above) $^1$H NMR in CDCl$_3$ (* represents residual solvent peak) of dimer 2c (aromatic region) showing the equivalence of the iminopyridine signals, which suggest that an effective centrosymmetric structure is maintained in solution. The assignments of the signals were carried out with the help of 2D experiments, $^1$H-$^1$H COSY (below left) and $^1$H-$^1$H NOESY (below right). The $^1$H-$^1$H NOESY NMR of 2c shows the spatial proximity of the $^6$ proton of the pyridine with one of the syn protons of the methallyl system, which indicates a relative trans conformation of the methallyl group and the chlorine. A crosspeak is also observed between the imine proton $C(H)=N$ and one of the protons of the NCH$_2$ group, confirming that this group is the one bonded to the imine nitrogen (see also figure S2)
Figure S2: $^1$H-$^1$H NOESY experiment showing spatial proximity between the H$^6$ proton and one H$_{syn}$ proton and between one proton of the NCH$_2$ group and the iminic proton. The distance between both sets of protons in the structure obtained by X-ray diffraction is 2.503 and 2.091 Å respectively, which is in agreement with the spatial proximity observed in solution.
Figure S3: $^1$H NMR DOSY of an approximately equimolar mixture of dimer 2c (upper line) and its monomeric precursor 1c (lower line) in CD$_2$Cl$_2$
Monitoring of formation of dimer 2c by $^1$H NMR.

An NMR tube was charged with 10 mg of 1c and CDCl$_3$ was added (0.6mL). To the resultant suspension 1.5 equivalents of NEt$_3$ were added (3 uL) to yield a purple solution. $^1$H NMR spectra showed broad signals suggesting some dynamic process. After 5 min at room temperature no changes were observed by $^1$H NMR and AgOTf was added (5 mg, 1.5 equivalents). The reaction was followed by $^1$H NMR. Several unidentified signals appeared and were evolving at room temperature in the $^1$H NMR spectra until after 3h at room temperature, the $^1$H NMR spectrum showed the formation of dimer 2c as the only iminopyridine compound of the reaction. Note: The same results were obtained by adding first AgOTf and subsequently NEt$_3$.

Figure S4. $^1$H NMR (room temperature) spectra in CDCl$_3$ showing the reaction of 1c (spectrum A) in the presence of AgOTf and NEt$_3$ to produce dimer 2c (spectrum E). From bottom to top: A) Compound 1c before the addition of any reagent, B) After the addition of 1.5 eqv of NEt$_3$, C) After the addition of 1.5 eqv of NEt$_3$ and AgOTf and 15min at room temperature, D) After 40min at room temperature, E) after 3h at room temperature