For model organisms such as *E. coli* and *S. cerevisiae*, a large number of protein-protein interactions have been identified both by conventional small-scale experiments over the decades, and more recently by large-scale functional genomics experiments. The mechanisms that underlie the evolution of networks and complexes are largely unknown. We have studied the role of different duplication scenarios in the evolution of interactions in the protein-protein interaction network and in sets of protein complexes. The duplication of a protein that engages in protein-protein interactions raises issues about the stoichiometry and equilibrium of protein complexes when the quantities of one component increases. Simultaneous duplication of all components involved in an interaction or a protein complex is predicted by the gene dosage balance hypothesis. In contrast, our results indicate that most interactions and complexes have evolved by step-wise partial duplications. We show that duplicated complexes retain the same overall function, but have different binding specificities and regulation, revealing that duplication of these modules is associated with functional specialization. We distinguish between duplications that result in a new, alternative protein complex and duplications that result in additional components of an existing complex, and quantify events of both types. The evolutionary analyses described above provide insight into affinities and specificities of interactions, and indicate ways in which prediction of these properties may be possible.