This thesis deals with outside options and centrality in cooperative games. First, the question whether outside options actually matter is investigated by a pilot experiment using glove games to model simple negotiation situations. The finding that outside options do matter is followed by the question of whether cooperative allocation rules can be supported by the data. Motivated by this experimental finding, a probabilistic cooperative forecasting model is used in theoretical support of the importance of outside options. Outside options are formalized and suitable axioms for a categorization into outside-optionsensitive and -insensitive allocation rules are suggested and applied. During this categorization it turns out that there is only one outside-option-sensitive allocation rule within the framework of networks. This and further issues arising from the analysis of the forecasting model lead to a deeper analysis of networks, especially the issue of centrality and power indices. A new approach for centrality measures and power indices is suggested which is based on the idea that not only the failure of a whole node is of interest, but rather the failure of a certain link. Axiomatic characterizations, a political application analyzing the performance for forecasting government formation and an application on centrality analyzing identification of top key nodes are provided. While existing cooperative allocation rules either lack sensitivity to outside options or ignore the difference in centralities of agents, a combination possibility of the previously analyzed issues follows. A new (axiomatically characterized) allocation rule for network structures accounting for both outside options and centrality is provided, enriched with an (axiomatically characterized) alternative variant being more suitable for applications in political networks due to moderate relative proportions and applicability in presence of incompatibilities. By the analysis of the explicit effect of outside options on these new allocation rules it is found that this effect is more complex for link-based allocation than for player-based allocation which finally provides a deep and detailed understanding of outside options and their effects.