

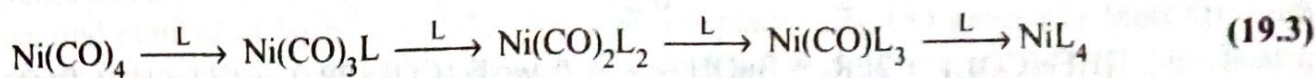
Reactions of Organometallic Complexes

Substitution Reactions in Carbonyl Complexes¹

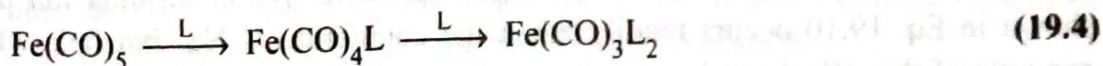
The earliest methods of replacing one or more carbonyl ligands from a complex relied on brute force (heat or light) to break the M—CO bond.² The idea was that once the gaseous CO had dissociated, it would escape easily from solution and thus have minimal chances of recombining with the metal. The departure of CO from a complex leaves a vacant coordination site and in general an unstable metal fragment which is electron deficient. The fragment can then react with a nucleophile such as a phosphine, R₃P, to produce a substituted metal carbonyl. The entire dissociative process can be described as follows.³



Of course some complexes lose CO more readily than others. For example, it is rather easy to displace all four CO groups of $\text{Ni}(\text{CO})_4$ with L ($\text{L} = \text{R}_3\text{P}$) in stepwise fashion:

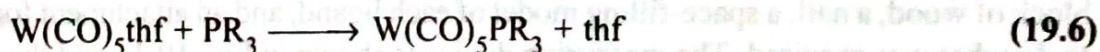
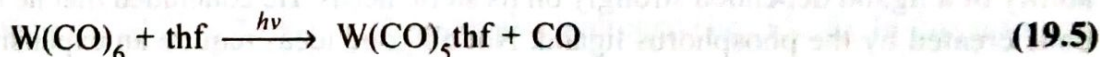


The task is much more difficult for $\text{Fe}(\text{CO})_5$, which has a large energy of activation for substitution and requires high temperatures. At these temperatures side reactions are significant and yields of substituted products are low:



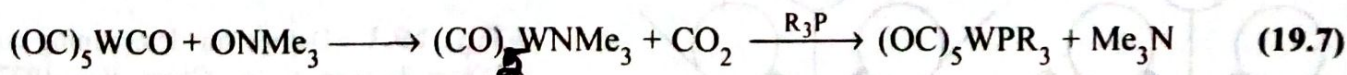
Notice that Eq. 19.4 shows only two CO ligands being displaced. Each time CO is replaced by R_3P , the complex becomes more electron rich and the remaining CO groups receive more π electron density. This means that in general the M—CO bond strength increases and CO becomes more resistant to dissociation. Of course the steric requirements of the phosphine may limit the degree of substitution as well (see cone angles).

The thermal and photolytic reactions described above usually give a mixture of products and therefore are not as popular as they once were. Reactions have now been developed which give a good yield of the particular product of interest. For example, if one wishes to prepare $\text{W}(\text{CO})_5\text{PR}_3$, one would not heat $\text{W}(\text{CO})_6$ with PR_3 at high temperatures or irradiate the reaction mixture with ultraviolet light because both of these methods would give mixtures of $\text{W}(\text{CO})_5\text{PR}_3$, *cis*- $\text{W}(\text{CO})_4(\text{PR}_3)_2$, *trans*- $\text{W}(\text{CO})_4(\text{PR}_3)_2$, and perhaps facial or meridional trisubstituted products as well. A preferable approach would be to first prepare $\text{W}(\text{CO})_5\text{thf}$ by photolysis of $\text{W}(\text{CO})_6$ in thf and then, without isolation of this complex, displace the thf with the phosphine in a subsequent room-temperature reaction:

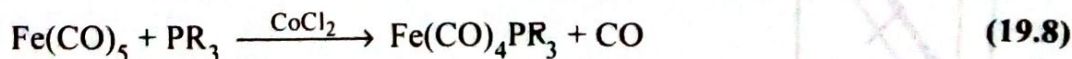


Tetrahydrofuran is a sufficiently poor ligand that it seldom displaces more than one CO group in the photolysis step and thus the reaction yields the monosubstituted product exclusively.

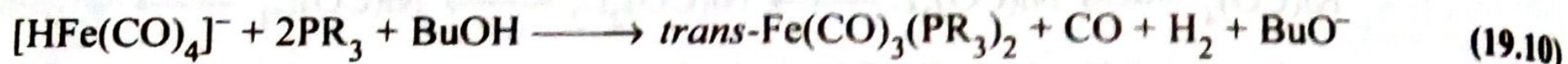
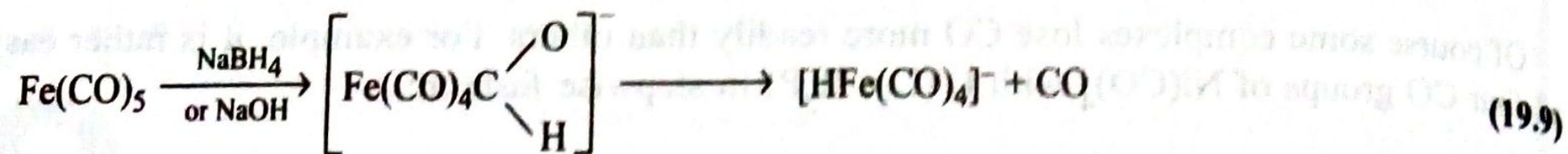
Another twist is to add Me_3NO which attacks the carbon a coordinated CO, leading to eventual loss of CO_2 and formation of an unstable trimethylamine complex. The phosphine easily displaces the amine to form the final product:



The preparation of pure $\text{Fe}(\text{CO})_4\text{PR}_3$ and *trans*- $\text{Fe}(\text{CO})_3(\text{PR}_3)_2$ have long been frustrating because thermal and photolytic methods give mixtures of products which are not easy to separate. The monosubstituted complex may now be prepared by several routes, one of which involves cobalt(II) chloride as a catalyst:



The exact role of the catalyst in this reaction is unknown⁴. Alternatively, the reaction may be catalyzed by polynuclear iron anions, such as $[\text{Fe}_2(\text{CO})_8]^{2-}$ or $[\text{Fe}_3(\text{CO})_{11}]^{2-}$.⁵ A successful method for producing the *trans* disubstituted complex is to create $[\text{HFe}(\text{CO})_4]^-$ and allow it to react with PR_3 , in refluxing 1-butanol.⁶



The counterion is quite important to the outcome of this reaction. Ion pairs, which form between alkali metal ions and the complex, induce CO lability which aids in the substitution process.⁷ Large charge-delocalized cations such as PPN^+ are much less effective in forming ion pairs. The substitution process shown in Eq. 19.10 occurs readily when the counterion is Na^+ but fails when it is PPN^+ . Another good example of this effect can be seen by comparing $\text{Na}[\text{Co}(\text{CO})_4]$ and $\text{PPN}[\text{Co}(\text{CO})_4]$.⁸ The former is readily substituted by ^{13}CO , phosphines, and phosphites, while the latter is inert with respect to substitution.