VIII-F Syntheses, Structures, and Reactivities of Multinuclear Transition Metal Complexes with *O*- and *N*-Donor Ligands

Organotransition metal complexes with *O*- and *N*-donor ligands have recently been attracting considerable attention, because they often show structures, reactivities, and physicochemical properties significantly different from those of the complexes with *P*- and *S*-donor ligands. In this project it has been disclosed that *O*- and *N*-donor ligands such as cyanamide (NCN^{2-}) and cyclophosphate ($P_3O_9{}^{3-}$, $P_4O_{12}{}^{4-}$) ions act as effective bridges to form multinuclear complexes with characteristic structures. The newly synthesized diiridium complex [Cp*Ir(μ-NCN-*N*,*N*)]$_2$ provides a versatile building block for the synthesis of a series of tri- and tetranuclear cyanamido clusters. On the other hand, di- and trinuclear Ti(IV) complexes built up with Cp*Ti units and cyclophosphato ligand(s) possess novel three-dimensional structures and exhibit unique fluxional behavior in solution.

VIII-F-1 A Cyanamido-Bridged Diiridium Complex: A Reactive Building Block for Polynuclear Cyanamido Complexes

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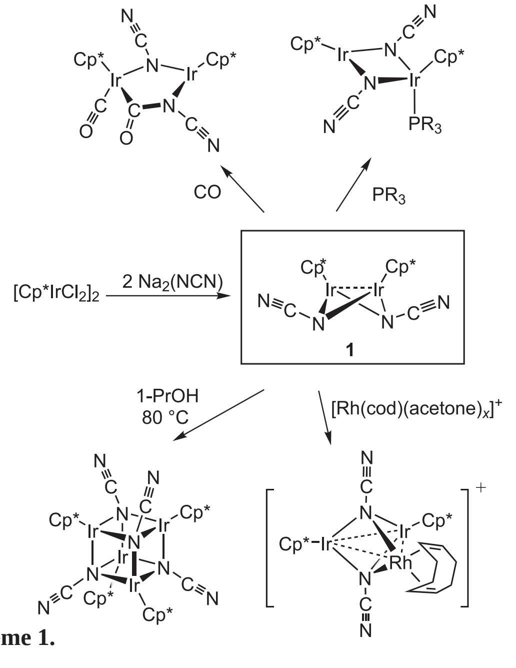
Treatment of diiridium complex [Cp*IrCl$_2$]$_2$ (Cp* = η^5-C$_5$Me$_5$) with 2 equiv of Na$_2$NCN has been found to afford the NCN–bridged diiridium complex [Cp*Ir(μ_2-NCN-*N*,*N*)]$_2$ (**1**), which undergoes further reactions with donor molecules such as CO and phosphines. Complex **1** works as an excellent building block for the synthesis of NCN-capped multinuclear complexes: its reactions with cationic group 8–10 metal complexes such as [CpRu(MeCN)$_3$]$^+$ (Cp = η^5-C$_5$H$_5$), [Rh(cod)(acetone)$_n$]$^+$ (cod = 1,5-cyclooctadiene), and [Pd(η^3-C$_3$H$_5$)(acetone)$_n$]$^+$ give the heterotrinuclear complexes [(Cp*Ir)$_2$(ML)(μ_3-NCN)$_2$]$^+$ (ML = CpRu, Rh(cod), Pd(η^3-C$_3$H$_5$)), while the dimerization of **1** leads to the cubane-type tetrairidium complex [Cp*Ir(μ_3-NCN)]$_4$ (Scheme 1).



Scheme 1.

VIII-F-2 Synthesis, Structures, and Solution Behavior of Di- and Trinuclear Titanium(IV)-Cyclophosphato Complexes

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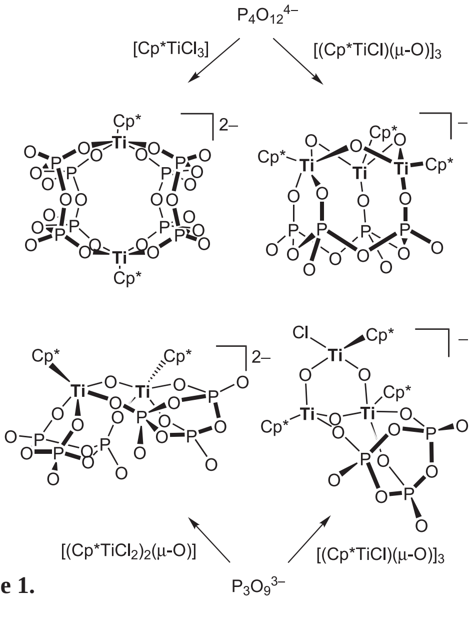
The reaction of the cyclotetraphosphate ion ($P_4O_{12}{}^{4-}$) with [Cp*TiCl$_3$] gives [(Cp*Ti)$_2$(P$_4$O$_{12}$)$_2$]$^{2-}$ where the P$_4$O$_{12}$ ligands adopt a saddle conformation, while that with [(Cp*TiCl)$_3$(μ-O)$_3$] leads to [(Cp*Ti)$_3$(μ-O)$_3$(P$_4$O$_{12}$)]$^-$ containing a crown form P$_4$O$_{12}$ ligand; both products feature their unique cage structures. The latter complex is fluxional in solution, and the variable temperature ^{1}H NMR study has revealed that the Ti$_3$O$_3$ unit is rotating on the P$_4$O$_{12}$ platform. On the other hand, the reactions of the cyclotriphosphate ion ($P_3O_9{}^{3-}$) with [(Cp*TiCl$_2$)$_2$(μ-O)] and [(Cp*TiCl)$_3$(μ-O)$_3$] afford [(Cp*Ti)$_2$(μ-O)(P$_3$O$_9$)$_2$]$^{2-}$ and [(Cp*Ti)$_3$(μ-O)$_3$Cl(P$_3$O$_9$)]$^-$, respectively, and in both cases the P$_3$O$_9$ ligands bridge the two titanium centers with an η^2:η^1 coordination mode (Scheme 1).



Scheme 1.