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$_3$O$_9$$^{3-}$, P$_4$O$_{12}$$^{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 cyclophosphate 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)$_2$]$_2$ (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 [Cp*Ru(MeCN)$_3$]$_2$ (Cp* = η$^5$-C$_5$H$_5$), [Rh(cod)(acetone)$_n$]$_2$ (cod = 1,5-cyclooctadiene), and [Pd(η$_3$-C$_3$H$_5$)(acetone)$_n$]$_2$ give the heterotrinuclear complexes [(Cp*Ir)$_2$(ML)(µ$_3$-NCN)$_2$]$_2$ (ML = Cp*Ru, 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)$_4$]$_4$ (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$_4$O$_{12}$$^{4-}$) with [Cp*TiCl$_2$] gives [(Cp*Ti)$_2$(P$_4$O$_{12}$)$_2$]$_2$ where the P$_4$O$_{12}$ ligands adopt a saddle conformation, while that with [(Cp*TiCl)$_3$(µ-O)$_3$] leads to [(Cp*Ti)$_3$(µ-O)$_3$(P$_4$O$_{12}$)]$^-$ containing a crown form P$_4$O$_{12}$ ligand; both products feature their unique cage structures. The latter complex is fluxional in solution, and the variable temperature $^1$H NMR study has revealed that the Ti$_3$O$_3$ unit is rotating on the P$_4$O$_{12}$ platform. On the other hand, the reactions of the cyclotriphosphate ion (P$_3$O$_9$$^{3-}$) with [(Cp*TiCl)$_2$(µ-O)] and [(Cp*TiCl)$_3$(µ-O)$_3$] afford [(Cp*Ti)$_2$(µ-O)(P$_3$O$_9$)$_2$]$^-$ and [(Cp*Ti)$_3$(µ-O)$_3$Cl(P$_3$O$_9$)$_2$]$^-$, 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.

$^1$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$_3$O$_9$$^{3-}$) with [(Cp*TiCl)$_2$(µ-O)] and [(Cp*TiCl)$_3$(µ-O)$_3$] afford [(Cp*Ti)$_2$(µ-O)(P$_3$O$_9$)$_2$]$^-$ and [(Cp*Ti)$_3$(µ-O)$_3$Cl(P$_3$O$_9$)$_2$]$^-$, 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.