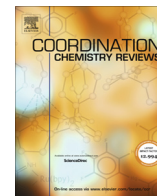




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## Review

## Six coordinate capped trigonal bipyramidal complexes

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## ABSTRACT

This review collects the examples of a rare, six-coordinate geometry, the capped trigonal bipyramid (CTB). Examples have been identified for  $d^0$  Sc(III), Y(III), Zr(IV), Ta(V),  $d^4$  Mo(II),  $d^2$  Mo(IV) and W(IV),  $d^2$  Re(V), and  $d^{10}$  Zn(II) and Cd(II). These distorted geometries are caused by bulky thiolate groups or tripodal tetradentate triamidoamine or tetraamine ligands that impose a pseudo  $C_3$  symmetry with two capping atoms that form a distorted Y shape with the metal and the axial donor ligand. The important angles of the structures are highlighted to illustrate this. The environment of the capping atoms is crowded and so the ligands that contribute these atoms have a small steric profile. These include hydrides, small alkyls, alkylidenes, alkyne, phosphines, azobenzene, CO and tetrahydrofuran and the bidentate anions benzamidinate, carbonate, hydrazide and nitrate. The metals that accommodate this crowding tend to be the larger 4d and 5d metals. Several of the complexes are hydrides with a small HML angle at the top of the Y-shape ranging from  $50^\circ$  to  $80^\circ$ . This results, in the case of phosphine complexes, in a large  $J_{PH}$  NMR coupling constant of 50–100 Hz between the *cis* hydride and phosphorus nuclei. An alkylidene–alkyl adduct from diphenylacetylene also has the CTB geometry as well as, possibly, a cationic lutidine adduct with an agostic methyl C–H...Mo bond. Zinc(II) and three cadmium(II) complexes with tripodal nitrogen-donor ligands and capping bidentate anions also have the CTB geometry. Several types of reactions have been observed at the capping position including Wittig-like reactions, protonation, reactions with dihydrogen, and reactions involving alpha and beta hydride elimination and addition. The observed reactions related to carbon dioxide fixation, dinitrogen reduction and hydrodesulfurization make such complexes worthy of further examination directed toward catalyst development.

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## 1. Introduction

The most common geometry of six coordinate metal complexes is octahedral or distorted octahedral [1,2]. A much less common second class of complexes with six ligands has the trigonal prismatic geometry and these are usually found for early transition metals in the  $d^0$ ,  $d^1$  or  $d^2$  electron configuration [3–7]. A search of the 2016 Cambridge Structural Database (CSD) revealed that of the 113,000 structures with a transition metal bonded to six main group elements, only about 200 (approx. 2%) have a regular trigonal prismatic geometry with metals mainly of groups 6 and 12. The main group compound  $\text{XeOF}_5$  has a pentagonal pyramidal geometry [8]. This review considers a fourth, very rare six-coordinate geometry, the capped trigonal bipyramid (CTB). Only about 25 X-ray structures (approx. 0.2%) of six-coordinate complexes of transition metals were found in the CSD with the CTB geometry as is reviewed here. They have the interesting property of forcing a capping ligand quite close to a second ligand and this results in unusual NMR and reactivity patterns.

The CTB geometry is identified by donor atoms taking up one apex and three equatorial positions of a trigonal bipyramid (TBP) (Fig. 1). The remaining two coordination sites  $R^1$  and  $R^2$  form the

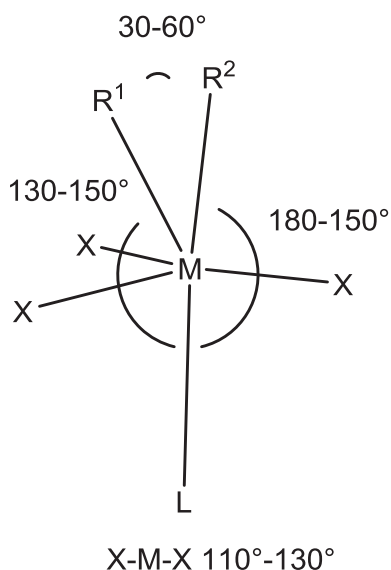


Fig. 1. Angles of an idealized capped trigonal bipyramidal geometry.

top of a distorted Y shape around the opposite apex, effectively adding a capping atom to a TBP with a  $R^1MR^2$  angle of  $50\text{--}80^\circ$ . The  $R^2ML$  angle (Fig. 1) ideally is close to  $180^\circ$  but in practice can be as small as  $150^\circ$ . The  $R^1ML$  angle falls in the range of  $150\text{--}130^\circ$ . The capping atoms of  $R^1$  and  $R^2$  along with M form a plane that is sometimes almost coplanar with one of the M–L–X planes. The dihedral angle  $MLX/MR^2R^1$  is calculated in this review to check for this feature. In some cases this angle is closer to  $30^\circ$ , the angle that allows the maximum staggering of these two planes to minimize steric interactions between the groups. The groups occupying the two sites  $R^1$  and  $R^2$  appear to be mobile, often resulting in NMR spectra consistent with structures having an averaged  $C_3$  symmetry.

This geometry has been identified for complexes of  $d^0$  scandium(III), yttrium(III), zirconium(IV), tantalum(V),  $d^2$  molybdenum(IV) and tungsten(IV),  $d^4$  molybdenum(II) and  $d^2$  rhenium(V) and  $d^{10}$  zinc(II) and cadmium(II). The geometry can be imposed by tripodal triamidoamine  $\text{NN}_3$  ligands for Ta(V), W(IV) and Re(V) or by sterically demanding thiolate ligands for Mo(II), Mo(IV) and W(IV). The group 6 and group 7 metal complexes have the general formula  $[\text{MRX}_3\text{L}_2]^{n+}$ ,  $n = 0$  for M(IV) and  $n = 1$  for Re(V) where the metal has a formal  $d^2$  electronic configuration with one non-bonding electron pair, 4 M–X covalent bonds with some  $X \rightarrow M$  pi bonding and 2  $L \rightarrow M$  dative bonds. They are formally coordinatively unsaturated. When R is a hydride these tend to be fluxional around the capped face since they have spectroscopic properties that indicate pseudo  $C_3$  symmetry.

## 2. Group 3 metal complexes

The yttrium(III) complex (Fig. 2) is a representative from group 3; the corresponding Sc(III) complex is isomorphous [9]. The geometry around this  $d^0$  metal is imposed by a bisamido amine pyridine tripodal ligand and a benzamidinate capping ligand that has a small N–Y–N bite angle of  $57.14(2)^\circ$ . The  $23.9^\circ$  dihedral angle between the planes specified in Fig. 2 allows the capping groups to avoid the tripodal ligand.

## 3. Group 4 metal complexes

The CTB zirconium(IV) complex of Fig. 3 is cyclometallated at a silyl methylene group of the trisamidoamine ligand forcing this carbon close to the neighboring tetrahydrofuran ligand with a O–Zr–C angle of  $81.43(6)^\circ$ . The capping oxygen and carbon are almost in a plane with the zirconium and nitrogen  $N^3$  as indicated

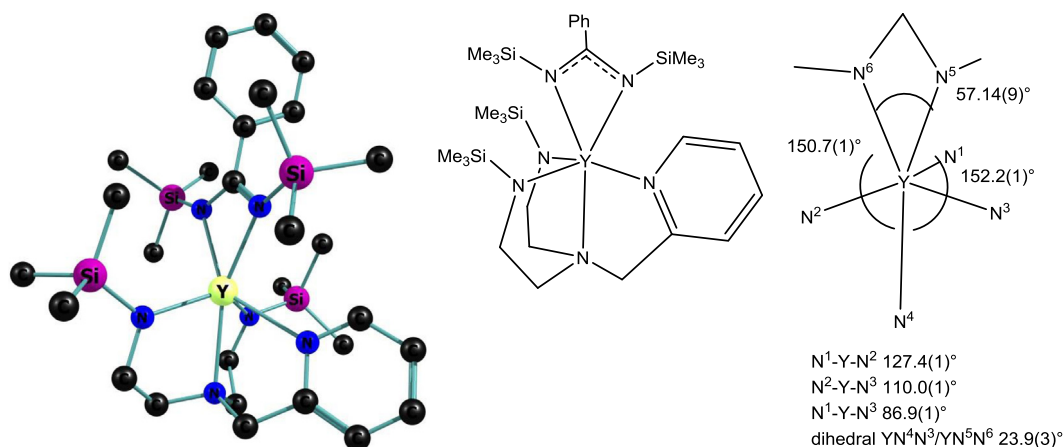


Fig. 2. The Y(III) complex with CSD code AFUFIQ. The hydrogens have been omitted for clarity.

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