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Review

Structural systematics of some trinuclear alkynyl and diynyl Group 11 complexes containing dppm [dppm = $CH_2(PPh_2)_2$]

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ABSTRACT

In this review the molecular structures of a series of trinuclear alkynyl and diynyl Group 11 cations $[\{M_3(\mu\text{-dppm})_3\}(X)_n]^{(3-n)+}$ (M = Cu, Ag; n = 1, 2; where X is an alkynyl or diynyl group, an inorganic anion or solvent) are considered from the points of view of (i) the dimensions and geometries of the $M_3(P–P)_3$ cores, (ii) the conformations of the dppm ligands, and (iii) the attachment of the alkynyl and diynyl ligands. In the crowded $[M_3(\mu\text{-dppm})_3]^{3+}$ core, the dppm ligands are arranged so that there is always one CH_2 group up and two down, to give pseudo mirror symmetry perpendicular to the M_3 plane (crystallographic in some cases). Attachment of the alkynyl or diynyl substituent(s) occurs roughly normal to the M_3 plane; according to their perpendicularity, the C(1) atom may be μ_2 or μ_3. In most cases where only one alkynyl or diynyl ligand is present, a second ligand is also attached to the M_3 core. Unusual and interesting dispositions/conformations of the dppm ligands are widespread, among the mono–diynyl complexes in particular, whereby some phosphorus donor atoms lie at unusual distances out of the M_3 planes, a concomitant of strong agostic interactions between phenyl H atoms and the atoms of the open M_3 face, and weak M···M interactions. With one X group, C—H···M interactions persist on the other face, with C—H···X interactions with the alkyne affecting the inclination of the alkyne and the conformation of the Ph rings. With two substituents (one of which may be a loosely bound anion), similar interactions may occur, accompanied by twisting of the dppm chelate ring to displace P atoms from the M_3 plane. These factors possibly inhibit formation of the bis(diyndiyl) complexes, which are only obtained under more strongly basic conditions.

Contents

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1. Introduction

Numerous examples of trinuclear Group 11 complexes containing $M_3(\mu\text{-dppm})_3$ [M = Cu, Ag; dppm = $CH_2(PPh_2)_2$] moieties are known, more than 65 structural studies of which are listed in the Cambridge Structural Database (CSD). An extensive survey to 2005 of complexes $[M_3(\mu\text{-dppm})_3(\mu_3\text{-}X^1)(\mu_3\text{-}X^2)]^+$ in which X^1, X^2 = halogen or other simple anion has been given previously [1], including a summary of cation core geometries presented in Tables 1 and 2 therein. Several later individual studies have appeared [2]. A series of alkynyl- or diynyl-Group 11 complexes has been generally obtained from the reactions of $[M_2(\mu\text{-dppm})_2(NCMe)_n]A_2$ (M = Cu, n = 4; Ag, n = 2; A = BF_4, PF_6) with a terminal alkyne or diyne in the presence of an excess of KOH or dbu in refluxing CH_2Cl_2/MeOH [3]. Depending on the stoichiometry and reaction conditions, either mono- or bis-μ_3-alkynyl-Group 11 metal cluster compounds $[\{M_3(\mu\text{-dppm})_3\}(C{\equiv}CR)_n]^{(3-n)+}$ (n = 1, 2) may be obtained. In some cases, further reaction may occur to give bi-, tetra- or hexa-nuclear clusters [4,5], although these systems are not considered further here.

We have recently described the syntheses and properties of the diynyl complexes $[\{M_3(\mu\text{-dppm})_3\}\{\mu\text{-}C{\equiv}CC{\equiv}C[M'L_m]\}_n]^{(3-n)+}$ [M = Cu, Ag; n = 1, 2; $M'L_m$ = $Re(CO)_3(Bu^t_2\text{-bpy})$, Ru(dppe)$Cp^*$ (dppe = $Ph_2PCH_2CH_2PPh_2$)], including the single-crystal X-ray structures of those derivatives with $M'L_m$ = Ru(dppe)Cp^*, M = Cu, n = 1 (**1**), 2 (**2**) and M = Ag, n = 1 [**3** (two solvates)], and $M'L_m$ = $Re(CO)_3$

Table 1
Structures $[\{M_3(\mu\text{-dppm})_3\}(X^1/X^2)_n]^{(3-n)+}$ (n = 1, 2) (by #).

#	M	X^1	X^2	CCDC	Reference
1	Cu	C≡CC≡C[Ru(dppe)Cp^*]	–	IWAFAP	[6]
2	Cu	C≡CC≡C[Ru(dppe)Cp^*]	C≡CC≡C[Ru(dppe)Cp^*]	IWAKUO	[6]
3	Ag	C≡CC≡C[Ru(dppe)Cp^*]	–	IWAKOI[a] IWADUH[b]	[6]
4	Cu	C≡CC≡C[$Re(CO)_3(Bu^t_2\text{-bpy})$]	C≡CC≡C[$Re(CO)_3(Bu^t_2\text{-bpy})$]	IWAGAQ	[6]
5	Cu	C≡CC_6H_4C≡C[$Re(CO)_3$(bpy)]	C≡CC_6H_4C≡C[$Re(CO)_3$(bpy)]	SACFIL	[7c]
6	Ag	C≡C{bpy[$ReCl(CO)_4$]}C≡C	NCMe	YESXIE	[8]
7	Cu	C≡CC≡C[$Re(CO)_3(Me_2\text{-bpy})$]	C≡CC≡C[$Re(CO)_3(Me_2\text{-bpy})$]	ACAKUL	[9c]
8	Ag	C≡CC≡C[$Re(CO)_3$(bpy)]	C≡CC≡C[$Re(CO)_3$(bpy)]	ACALAS	[9c]
9	Cu	C≡CC≡C[Au(C≡CC≡CH)]	I	XIFWUE	[10]
10	Cu	C≡CCO_2^-	OMe	INOSOU	[13]
11	Ag	C≡CCO_2^-	Cl	INOSUA	[13]
12	Cu	C≡CC≡CH	C≡CC≡CH	EZUHEM	[14]
13	Cu	C≡CC≡CPh	C≡CC≡CPh	EZUHAI	[14]
14	Cu	C≡CBu^t	Cl	WARKEF	[22]
15	Cu	C≡CBu^t	–	TOGREM	[23]
16	Cu	C≡CPh	*F*-BF_3	JEBPAH10	[3a,c]
17	Ag	C≡CCMeEt(OH)	*O*-NO_2	JERVIM	[24]
18	Ag	C≡C$C_6H_4NO_2$-4	*F*-BF_3	RUMWOL	[7b]
19	Cu	C≡CC_6H_4OMe-4	C≡CC_6H_4OEt-4	GAMNEN	[7d]
20	Cu	C≡CC_6H_4OMe-4	C≡C$C_6H_4NO_2$-4	GAMNIR	[7d]
21	Cu	C≡CCOMe	C≡CCOMe	IXIDOJ	[25]
22	Cu	C≡C$CONH_2$	C≡C$CONH_2$	IXIDUP	[25]
23	Cu	C≡CFc	C≡CFc	MITLUW	[26]
24	Cu	C≡C(tol)	CNtol	NEVWUG	[27]
25	Cu	C≡CPh	C≡CPh	SITNIS10	[3c]
26	Cu	C≡CC_6H_4OMe-4	C≡CC_6H_4OMe-4	WIWZAD	[15]
27	Cu	C≡C(benzo-15-c-5)	C≡C(benzo-15-c-5)	XIBYUC	[28]
28	Ag	C≡C$C_6H_4NO_2$-4	C≡C$C_6H_4NO_2$-4	RUMWUR	[7b]
29	Ag	C≡CPh	C≡CPh	TEQSEN	[29]
30	Cu	C≡CPh	Cl	WARTIS	[3c]
31	Cu	—C≡CC_6H_4C≡C—	–	RUFREP	[30]
32	Ag	—C≡CC_6H_4C≡C—	–	RUFRIT	[30]
33	Ag	C≡CFc	O-OTf	MITLOQ	[26]
34	Cu	C≡CC_6H_4{NHC(O)$C_6H_4NO_2$-4}-4	C≡CC_6H_4{NHC(O)$C_6H_4NO_2$-4}-4	VUPZAJ[c] VUPZEN[d] VUPZIR[e]	[31]
35	Cu	C≡CC_6H_4{NHC(O)$C_6H_4CF_3$-4}-4	C≡CC_6H_4{NHC(O)$C_6H_4CF_3$-4}-4	VUPZOX	[31]
36	Cu	C≡CC_6H_4{NHC(O)Ph}-4	C≡CC_6H_4{NHC(O)Ph}-4	VUPZUD	[31]
37	Cu	C≡CC_6H_4{NHC(O)C_6H_4OMe-4}-4	C≡CC_6H_4{NHC(O)C_6H_4OMe-4}-4	VUQBAM[c] VUQBEQ[f]	[31]
38	Ag	—C≡C$C_{10}H_6$C≡C— (1,5)	–	TABBEG	[32]
39	Ag	C≡CC≡C[$Re(CO)_3(Bu^t_2\text{-bpy})$]	Cl	IWAFOD	[6]

[a] THF solvate.
[b] Acetone solvate.
[c] BF_4 salt.
[d] ClO_4 salt.
[e] PF_6 salt.
[f] F salt.

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