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

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ABSTRACT

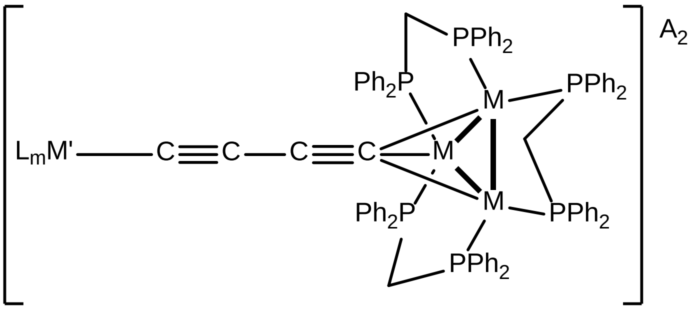
In this review the molecular structures of a series of trinuclear alkynyl and diynyl Group 11 cations $[\{M_3(\mu\text{-dppm})_3\}(X)_n]^{(3-n)+}$ (M = Cu, Ag; n = 1, 2; where X is an alkynyl or diynyl group, an inorganic anion or solvent) are considered from the points of view of (i) the dimensions and geometries of the $M_3(P\text{-}P)_3$ 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.

1. Introduction

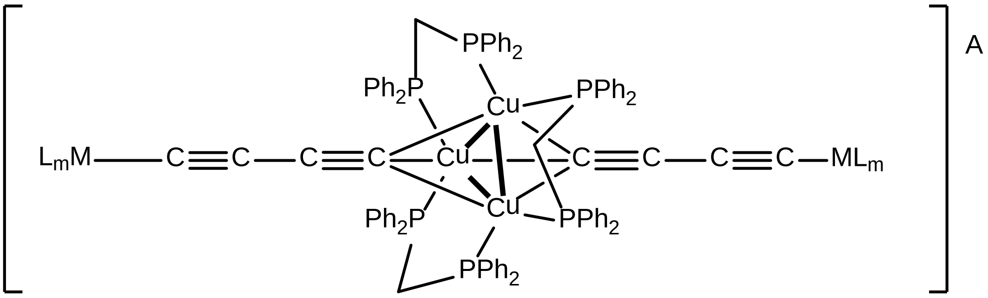
Numerous examples of trinuclear Group 11 complexes containing $M_3(\mu\text{-dppm})_3$ [M = Cu, Ag; dppm = $CH_2(PPh_2)_2$] moieties are known, more than 65 structural studies of which are listed in the Cambridge Structural Database (CSD). An extensive survey to 2005 of complexes $[M_3(\mu\text{-dppm})_3(\mu_3\text{-}A^1)(\mu_3\text{-}A^2)]^+$ in which A^1, A^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 $M'L_m$ = $Re(CO)_3(Bu^t{}_2\text{-bpy})$, M = Cu, n = 2 (**4**) (Chart 1) [6]. Several related cations with alkynyl or diynyl ligands on Re or Au, $[Cu_3(\mu\text{-dppm})_3\{\mu_3\text{-}C{\equiv}CC_6H_4C{\equiv}C[Re(CO)_3(bpy)]\}]^+$ (**5**) [7c], $[Ag_3(\mu\text{-dppm})_3\{\mu_3,\mu_3\text{-}C{\equiv}C(bpy)C{\equiv}C\}Ag_3(\mu\text{-dppm})_3]^{4+}$ (**6**) [8], $[M_3(\mu\text{-dppm})_3\{\mu_3\text{-}C{\equiv}C[Re(CO)_3(bpy)]\}_2]^+$ [M = Cu (**7**), Ag (**8**)] [9c], $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}I)\{\mu_3\text{-}C{\equiv}CC{\equiv}C[Au(C{\equiv}CC{\equiv}CH)]\}]^+$ (**9**) [10] have also been prepared and structurally characterised.

< Chart 1 here >



M = Cu **1**, Ag **3**; $M'L_m$ = Ru(dppe)Cp*



ML_m = Ru(dppe)Cp* **2**; $Re(CO)_3(Bu^t_2\text{-bpy})$ **4**

A = BF_4, PF_6

Chart 1. Structures of cations $[\{M_3(\mu\text{-dppm})_3\}\{\mu\text{-C}\equiv\text{CC}\equiv\text{C}[M'L_m]\}_n]^{(3-n)+}$ [M = Cu, Ag; n = 1, 2; $M'L_m$ = $Re(CO)_3(Bu^t_2\text{-bpy})$, Ru(dppe)Cp*].

In the course of that study, several interesting structural features relating to the geometries of the $M_3(dppm)_3$ clusters and the interactions of the diynyl ligand(s) with the clusters prompted us to review the reported structures of related alkynyl and diynyl complexes, of which some 39 (27 with M = Cu, 12 with M = Ag) are available in CSD (v. 1.19). All these compounds are listed in Table 1, while Figures 1-7 and Figures S1-S6 in the supporting information contain plots of the various cations of interest; important bond parameters are contained in Table S1. Following is a brief survey of their molecular structures, many of which are of unusual interest. In the discussions below, the various structures are indicated as M / X^1 / X^2 (Chart 2).

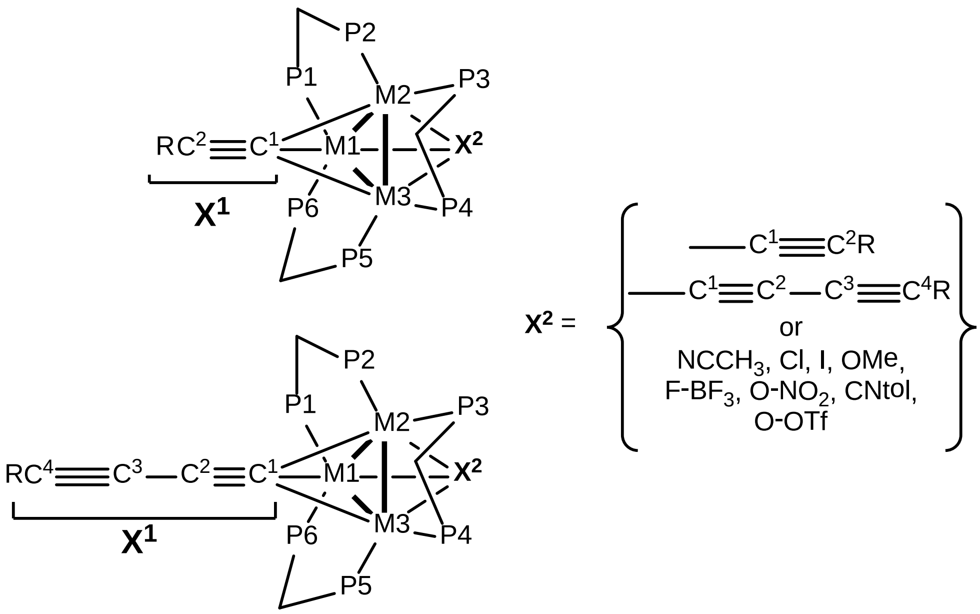


Chart 2. Generic molecular structures of the cations examined in this manuscript.

< Table 1 here >

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	$C{\equiv}CC{\equiv}C[Re(CO)_3(Bu^t{}_2\text{-bpy})]$	$C{\equiv}CC{\equiv}C[Re(CO)_3(Bu^t{}_2\text{-bpy})]$	IWAGAQ	6
5	Cu	$C{\equiv}CC_6H_4C{\equiv}C[Re(CO)_3(bpy)]$	$C{\equiv}CC_6H_4C{\equiv}C[Re(CO)_3(bpy)]$	SACFIL	7c
6	Ag	$C{\equiv}C\{bpy[ReCl(CO)_4]\}C{\equiv}C$	NCMe	YESXIE	8
7	Cu	$C{\equiv}CC{\equiv}C[Re(CO)_3(Me_2\text{-bpy})]$	$C{\equiv}CC{\equiv}C[Re(CO)_3(Me_2\text{-bpy})]$	ACAKUL	9c
8	Ag	$C{\equiv}CC{\equiv}C[Re(CO)_3(bpy)]$	$C{\equiv}CC{\equiv}C[Re(CO)_3(bpy)]$	ACALAS	9c
9	Cu	C≡CC≡C[Au(C≡CC≡CH)]	I	XIFWUE	10
10	Cu	$C{\equiv}CCO_2^-$	OMe	INOSOU	13
11	Ag	$C{\equiv}CCO_2^-$	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	$C{\equiv}CBu^t$	Cl	WARKEF	22
15	Cu	$C{\equiv}CBu^t$	-	TOGREM	23
16	Cu	C≡CPh	*F*-BF_3	JEBPAH10	3a,c
17	Ag	C≡CCMeEt(OH)	*O*-NO_2	JERVIM	24
18	Ag	$C{\equiv}CC_6H_4NO_2\text{-}4$	*F*-BF_3	RUMWOL	7b
19	Cu	$C{\equiv}CC_6H_4OMe\text{-}4$	$C{\equiv}CC_6H_4OEt\text{-}4$	GAMNEN	7d
20	Cu	$C{\equiv}CC_6H_4OMe\text{-}4$	$C{\equiv}CC_6H_4NO_2\text{-}4$	GAMNIR	7d
21	Cu	C≡CCOMe	C≡CCOMe	IXIDOJ	251
22	Cu	$C{\equiv}CCONH_2$	$C{\equiv}CCONH_2$	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	$C\equiv CC_6H_4OMe$-4	$C\equiv CC_6H_4OMe$-4	WIWZAD	15
27	Cu	$C\equiv C$(benzo-15-c-5)	$C\equiv C$(benzo-15-c-5)	XIBYUC	28
28	Ag	$C\equiv CC_6H_4NO_2$-4	$C\equiv CC_6H_4NO_2$-4	RUMWUR	7b
29	Ag	$C\equiv CPh$	$C\equiv CPh$	TEQSEN	29
30	Cu	$C\equiv CPh$	Cl	WARTIS	3c
31	Cu	-$C\equiv CC_6H_4C\equiv C$-	-	RUFREP	30
32	Ag	-$C\equiv CC_6H_4C\equiv C$-	-	RUFRIT	30
33	Ag	$C\equiv CFc$	O-OTf	MITLOQ	26
34	Cu	$C\equiv CC_6H_4${NHC(O)$C_6H_4NO_2$-4}-4	$C\equiv CC_6H_4${NHC(O)$C_6H_4NO_2$-4}-4	VUPZAJ[c] VUPZEN[d] VUPZIR[e]	31
35	Cu	$C\equiv CC_6H_4${NHC(O)$C_6H_4CF_3$-4}-4	$C\equiv CC_6H_4${NHC(O)$C_6H_4CF_3$-4}-4	VUPZOX	31
36	Cu	$C\equiv CC_6H_4${NHC(O)Ph}-4	$C\equiv CC_6H_4${NHC(O)Ph}-4	VUPZUD	31
37	Cu	$C\equiv CC_6H_4${NHC(O)C_6H_4OMe-4}-4	$C\equiv CC_6H_4${NHC(O)C_6H_4OMe-4}-4	VUQBAM[c] VUQBEQ[f]	31
38	Ag	-$C\equiv CC_{10}H_6C\equiv C$- (1,5)	-	TABBEG	32
39	Ag	$C\equiv CC\equiv C$[Re(CO)$_3$(Bu$^t{}_2$-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

2. Results and discussion

General comments

The species $[\{M_3(dppm)_3\}\{\mu_3\text{-}(C{\equiv}C)_nR\}(\mu_3\text{-}X^2)]^+$ (M = Cu, Ag; n = 1 or 2, X^2 = halide or other anion) consist of triangular $M_3(\mu\text{-dppm})_3$ cores in which the alkynyl (or diynyl) and X^2 groups approach the centroids of the M_3 triangles [the alkynyl (or diynyl) unit being end-on or η^1]. Their structures will be discussed particularly in respect of (i) the dimensions and geometries of the $M_3(P\text{-}P)_3$ cores, (ii) the arrays about the M_3 components and the conformations of the dppm ligands, and (iii) the attachment of the alkynyl (or diynyl) ligands. Table S1 presents a summary of presently available data for mono-alkynyl-, mixed mono-alkynyl / mono-halide- (or other ligand) and bis(alkynyl) (or diynyl, as appropriate) complexes. Interestingly, insofar as their geometric descriptions are concerned, these species can be divided into two categories, the major one containing 46 cluster valence electrons (cve) (Table 2), but a few containing 44 cve. These result from the attachment of two or one μ_3-X ligands, respectively.

< Table 2 here >

Table 2. M$_3$ central triangle distortions in order of increasing distortion for the [{M$_3$(dppm)$_3$}{μ$_3$-(X^1)(μ$_3$-X^2)}]$^{n+}$ cations (M / X^1 / X^2) ($|D| = [\Sigma(d_{mn} - \langle d_{mn}\rangle)^2]^{½}$; d_{mn} = intermolecular M$_m$···M$_n$ distance). For comparison the interatomic distances in copper and silver metal are 2.55 and 2.88 Å.

# (CCDC) [Ref]	M / X^1 / X^2	< d >/Å	$\vert D\vert$/Å
(a) 46-cve clusters[a]			
	M = Cu		
37 (VUPBEQ) [31]	Cu / C≡CC$_6$H$_4$NHC(O)C$_6$H$_4$OMe-4 / C≡CC$_6$H$_4$NC(O)C$_6$H$_4$OMe-4 (F)	2.6228	0.006
26 (WIWZAD) [15]	Cu / C≡CC$_6$H$_4$OMe-4 / C≡CC$_6$H$_4$OMe-4	2.605	0.025
25 (SITNIS10) [3c]	Cu / C≡CPh / C≡CPh	2.595	0.032
19 (GAMNEN) [7d]	Cu / C≡CC$_6$H$_4$OMe-4 / C≡CC$_6$H$_4$OEt-4	2.601	0.035
30 (WARTIS) [3c]	Cu / C≡CPh / Cl	2.820	0.037
37 (VUQBAM) [31]	(cations 1,2)	2.5962	0.040
	Cu / C≡CC$_6$H$_4$NHC(O)C$_6$H$_4$OMe-4 / C≡CC$_6$H$_4$NC(O)C$_6$H$_4$OMe-4 (BF$_4$)	2.5919	0.033
36 (VUPZUD) [31]	(cations 1,2,3,4)	2.5993	0.048
	Cu / C≡CC$_6$H$_4$NHC(O)Ph / C≡CC$_6$H$_4$NC(O)Ph	2.6140	0.124
		2.6145	0.118
		2.6086	0.071
23 (MITLUW) [26]	Cu / C≡CFc / C≡CFc	2.623	0.059
9 (XIFWUE) [10]	(cations 1,2)	2.734	0.061
	Cu / C≡CC≡C[Au(C≡CC≡CH)] / I	2.727	0.062
27 (XIBYUC) [28]	Cu / C≡C(benzo-15-crown-5) / C≡C(benzo-15-crown-5)	2.618	0.072
7 (ACAKUL) [9c]	Cu / C≡CC≡C[Re(CO)$_3$(Me$_2$-bpy)] / C≡CC≡C[Re(CO)$_3$(Me$_2$-bpy)]	2.595	0.079
34 (VUPZIR) [31]	Cu / C≡CC$_6$H$_4$NHC(O)C$_6$H$_4$NO$_2$-4 /	2.623	0.084

	$C\equiv CC_6H_4NHC(O)C_6H_4NO_2$-4		
5 (SACFIL) [7c]	Cu / $C\equiv CC_6H_4C\equiv C[Re(CO)_3(bpy)]$-4 / $C\equiv CC_6H_4C\equiv C[Re(CO)_3(bpy)]$-4	2.635	0.096
10 (INOSOU) [13]	Cu / $C\equiv CCO_2$ / OMe	2.651	0.098
2 (**IWAKUO**) [6]	Cu / $C\equiv CC\equiv C[Ru(dppe)Cp^*]$ / $C\equiv CC\equiv C[Ru(dppe)Cp^*]$	2.591	0.103
13 (EZUHAI) [14]	Cu / $C\equiv CC\equiv CPh$ / $C\equiv CC\equiv CPh$	2.653	0.108
4 (IWAGAQ) [6]	Cu / $C\equiv CC\equiv C[Re(CO)_3(Bu^t{}_2\text{-bpy})]$ / $C\equiv CC\equiv C[Re(CO)_3(Bu^t{}_2\text{-bpy})]$	2.624	0.120
21 (IXIDOJ) [25]	Cu / $C\equiv CCOMe$ / $C\equiv CCOMe$	2.665	0.121
14 (WARKEF) [22]	Cu / $C\equiv CBu^t$ / Cl	2.824	0.129
22 (IXIDUP) [25]	Cu / $C\equiv CCONH_2$ / $C\equiv CCONH_2$	2.662	0.131
20 (GAMNIR) [7d]	Cu / $C\equiv CC_6H_4OMe$-4 / $C\equiv CC_6H_4NO_2$-4	2.674	0.149
34 (VUPZAJ) [31]	Cu / $C\equiv CC_6H_4NHC(O)C_6H_4NO_2$-4 / $C\equiv CC_6H_4NC(O)C_6H_4NO_2$-4 ($BF_4$)	2.6153	0.152
34 (VUPZEN) [31]	Cu / $C\equiv CC_6H_4NHC(O)C_6H_4NO_2$-4 / $C\equiv CC_6H_4NC(O)C_6H_4NO_2$-4 ($ClO_4$)	2.6216	0.154
34 (VUPZIR) [31]	Cu / $C\equiv CC_6H_4NHC(O)C_6H_4NO_2$-4 / $C\equiv CC_6H_4NC(O)C_6H_4NO_2$-4 ($PF_6$)	2.6233	0.176
15 (TOGREM) [23]	Cu / $C\equiv CBu^t$ / -	3.008	0.208
12 (EZUHEM) [14]	Cu / $C\equiv CC\equiv CH$ / $C\equiv CC\equiv CH$	2.736	0.212
31 (RUFREP) [30]	$\{Cu / - / C\equiv C\}_2C_6H_4$	2.996	0.302
35 (VUPZOX) [31]	Cu / $C\equiv CC_6H_4NHC(O)C_6H_4CF_3$-4 / $C\equiv CC_6H_4NC(O)C_6H_4CF_3$-4	2.6769	0.326
16 (JEBPAH10) [3c]	Cu / $C\equiv CPh$ / ($F\text{-}BF_3$)	2.997	0.345
1 (**IWAFAP**) [6]	Cu / $C\equiv CC\equiv C[Ru(dppe)Cp^*]$ / -	2.815	0.351
24 (NEVWUG) [27]	Cu / $C\equiv Ctol$-4 / $C\equiv Ntol$-4	2.863	0.570
	M = Ag		
39 (IWAFOD) [6]	Ag / $C\equiv CC\equiv C[Re(CO)_3(Bu^t{}_2\text{-bpy})]$ / Cl	3.129	0.055

8 (ACALAS) [9c]	(cations 1,2)	2.94	0.091
	Ag / C≡CC≡C[Re(CO)$_3$(bpy)] / C≡CC≡C[Re(CO)$_3$(bpy)]	2.94	0.091
29 (TEQSEN) [29]	Ag / C≡CPh / C≡CPh	2.944	0.096
11 (INOSUA) [13]	Ag / C≡CCO$_2$ / Cl	3.080	0.117
28 (RUMWUR) [7b]	Ag / C≡CC$_6$H$_4$NO$_2$-4 / C≡CC$_6$H$_4$NO$_2$-4	3.015	0.228
32 (RUFRIT) [30]	{Ag / - / C≡C}$_2$C$_6$H$_4$	3.193	0.352
(b) 44-cve clusters[a]			
6 (YESXIE) [8]	{Ag / (NCMe) / C≡C }$_2$ / {(bpy)[ReCl(CO)$_3$]}	3.069	0.058
33 (MITLOQ) [26]	Ag / C≡CFc / *O*-OTf	3.247	0.094
38 (TABBEG) [32]	{Ag / - / C≡C }$_2$C$_{10}$H$_6$	3.113	0.101
3 (**IWAKOI**) [6]	Ag / C≡CC≡C[Ru(dppe)Cp*] / *F*-BF$_3$	3.117	0.115
17 (JERVIM) [24]	Ag / C≡CMeEt(OH) / (O-NO$_2$)	3.192	0.269
18 (RUMWOL) [7b]	Ag / C≡CC$_6$H$_4$NO$_2$-4 / (F-BF$_3$)	3.160	0.307
3 (**IWADUH**) [6]	Ag / C≡CC≡C[Ru(dppe)Cp*] / -	3.095	0.322

[a] cve = cluster valence electron count

Structural discussion

(i) Geometries of the M_3 cores

In discussing these systems we comment first that while the M_3 core of the cation has often been drawn with persuasive lines connecting the metal atoms, the degree of metal-metal bonding in such clusters is considered to be small [11,12], so that they are often only indicative of the overall geometries. The structural framework of the three metal atoms, three bridging dppm ligands and the X^1/X^2 component(s) might be expected to have some flexibility. As such, for M = Cu, computationally [6] and experimentally (Table 2, Table S1; cf. also Table 1 of ref. [1]), the Cu···Cu separations differ significantly among themselves within each set, perhaps reflecting the 'soft bonding interactions between the d^{10} metal centers in those systems which result from a mixing of the s, p and d levels' [11,12] and their susceptibility to intercomponent interactions.

A useful and interesting perception of the distortions in the cationic core array may be obtained from Table 2 wherein a distortion parameter $|D| = [\Sigma(d_{mn} - \langle d \rangle)^2]^{½}$ is presented, together with the average $M_m \cdots M_n$ distances $\langle d \rangle$, d_{mn} being the three individual distances. These data suggest that, in the diverse array of $[M_3(\mu\text{-dppm})_3 / X^1 / X^2]^{n+}$ forms listed (more emphatically for M = Cu than for Ag), the nature of the X component(s) has a considerable bearing on the size and shape of the M_3 triangle [note in particular the simpler C≡CPh, C≡CC≡CR (R = H, Ph) arrays]. The shortest M···M distance is that subtending the unique 'U' methylene group (see below), associated with the smallest of the three P-C-P angles, a tendency firmer for M = Cu over Ag. The distortion of the system correlates broadly with the size of the core (Table 2), and diminishes on replacement of alkynyl by a larger halide, regardless of increase in core size. Substitution of a halide (Cl or I) by alkynyl has the effect of enlarging the M_3 triangle and drawing the opposing bonded alkynyl carbon atoms closer; M-P distances may be slightly shortened, and the M_3 triangle distortion is diminished (Table 2, Table S1). Unsurprisingly, core sizes and distortions tend to be greater in the examples where only one ligand interacts with the core. The cve counts correspond broadly to a demarcation in terms of M···M distances (more clearly defined for the more numerous examples with M = Cu), albeit not monotonically so.

(ii) Geometries of the dppm ligands

For these complexes, there is little systematic behaviour of the dppm ligand geometries and many of the following points are approximate rather than exact observations. In overview, the phosphorus atoms can deviate appreciably from the M_3 plane, overwhelmingly to the same side as their associated methylene carbon atom, but by less than the latter. There appear to be no systematic correlations between M…M distances and associated M-P distances.

A pervasive feature of all of the $[M_3(dppm)_3 / X^1 / X^2]^{n+}$ arrays is that, for the three dppm ligands, two methylene C atoms lie to one side of the M_3 plane ('D', -) and one to the other ('U', +), providing ad hoc reference points for the more detailed descriptors in the Figures. A (pseudo)mirror plane may be drawn normal to the M_3 plane through the $M_3(P\text{-}C\text{-}P)_3$ array and the U methylene group, which may persist approximately or (sometimes) exactly for the remainder of the cation (e.g., **10**, **11**).[13]

As shown in the Figures, there are close approaches of the H atoms of the Ph groups of the dppm ligands to M and / or alkyne C atoms, which may determine cation conformation. There are also close approaches of H atoms either to the peripheral C atoms of substantial alkyne substituents (particularly found with mono-alkyne ligands), or intermolecularly. Where there are two alkynyl substituents, i.e., one on each side of the M_3 plane, anion locations are generally well-removed from the cation core; where there is only one alkynyl group, approaches of the anions, particularly halide and BF_4, may be intimate and interactive. Further, projections of the two examples of the cation of **3**, given in Figs. 6(b), 7, [6] show that the dispositions of the Ph rings may vary widely, in some cases conforming rather closely, even exactly, to m-symmetry, in other cases being much more random.

(iii) Geometries of the alkynyl ligands

The structure of the 'baseline' compound $[\{Cu_3(dppm)_3\}(C{\equiv}CC{\equiv}CH)_2]^+$ (**12**) [14] [Fig. 5(b)] with linear diynyl ligands provides a useful starting point for broader considerations. Uninhibited by substitution of the ligands, the deviation from linearity is the largest [125.2(1)º] among the compounds considered in Table S1, suggesting that, either the terminal H atoms of the ligands interact strongly with neighbouring molecules and / or that the constraints imposed by the array of phenyl- and methylene-H atoms within which the diynyl ligand nestles may accommodate diverse interactions of many types. The ligand to the 'D' side of the core [away from the reader, Fig. 5(b)] makes close C···H contacts extending across all four carbon atoms at distances of between 2.8-3.1 Å from U- or D-phenyl and D-methylene-H atoms; there are also close Cu···H contacts (< 3 Å) with phenyl-H atoms. For the other ligand ('U') there are no close methylene-H contacts, but a number of close phenyl-H contacts; again close Cu···phenyl-H approaches < 3 Å are found. These contacts are shown in Fig. 5; they do not appear to impact upon the linearity of the C_4 strings.

In general, the axis of the alkynyl ligand X is quasi-normal to the M_3 plane, but deviations can be considerable (Table S1), e.g., nearly 40º from the normal in one of the ligands of $[\{Cu_3(dppm)_3\}(\mu_3\text{-}C{\equiv}CC{\equiv}CH)_2]^+$ (**12**) [14], and the approach of the two ligands may be far from colinear - as much as 125.2(1)º in that example. Indeed, in that example the inclinations of the pair of alkynes, coupled with their displacements, is such as to suggest a change in the nature of their interaction with the M_3 cluster from *sym*- to *asym*-μ_3, even in extreme cases μ_2 (**13** [14] perhaps), with the divergence of the three metal atoms from the C_n axis of the ligand varying correspondingly. The erratic nature of the two forms of bonding and the observation of both in different components of the same crystal of **8** [9c], suggests very little difference in energy between the two modes and little or no barrier between them.

Of passing interest are the dimensions of the C≡C triple bonds found within the alkynyl or diynyl ligands. In all cases (except for six outlying values), these bonds range between 1.180 and 1.240 Å [average values 1.210 (Cu-alkynyl), 1.201 (Ag-alkynyl), 1.213 (Cu-diynyl), 1.218 Å (Ag-diynyl)], there being no apparent correlation between metals or alkynyl / diynyl substituents. These values also suggest that there is little or no back-bonding from the M_3 cluster into the C≡C triple bond orbitals.

Complexes containing a single μ_3-ligand

A minority of systems contain only one μ_3-alkynyl or μ_3-diynyl ligand on the $M_3(\mu\text{-dppm})_3$ core, and have a reduced cve count of 44. In these, M···M separations are somewhat greater and M-P distances are shorter, than in the bis(alkynyl) complexes. The M-C distances are appreciably shorter, the alkynyl C atom approaching closer to the M_3 plane.

Only in five of the 44-cve examples (**1**, **3** (acetone solvate), [6] **15**, [23] **31** [30] and **32** [30]) does it seem that the 'second' side of the M_3 plane is truly devoid of any anion approach. For **17** [24] the situation is more equivocal, one of the NO_3 groups clearly being associated with the cation but in a manner suggesting that surrounding phenyl-H interactions are influential [Fig. S2(b)], with Ag···O as short as 2.625(5) Å, the other Ag···O distances being longer, at 2.700(5), 2.783(5) Å (see Fig. 3 of ref. [24]). Similarly, in **16** [3a,c] and **18** [7b], the approach of one of the BF_4 counterions (as F-BF_3) may be considered to significant (more so than mentioned in the original report of the latter [Ag···F 2.923(4) Å] [Fig. 2(a)]), while the description of **6** [8] similarly overlooks the approach of MeCN to the other face [Table S1; Fig. S2(a)]; Ag-NCMe distances are 2.697(7), 2.706(6), 3.444(8) Å, i.e., a μ_2-Ag_3 approach. In these, phenyl-H···anion interactions may materially assist the associations.

As supported by DFT calculations on model cations $[\mathbf{1\text{-}H}]^{n+}$ and $[\mathbf{3\text{-}H}]^{n+}$ [n = 2,1; containing $CH_2(PH_2)_2$ (dpHm) in place of dppm] [6], the cve counts are important in governing the M…M separations in these species. Although the Ru-C_4-Cu_3 core of geometry-optimised cation $[\mathbf{1\text{-}H}]^{2+}$ (44-cve) is less distorted than experimentally observed in $[\mathbf{1}]^{2+}$ (|D| = 0.002 vs 0.351), the computed Cu-C and Cu…Cu distances are significantly shorter and longer, respectively (av. 2.011, 3.033 Å, resp.; cf. calcd 2.151 Å for Cu-C, 2.621 Å for Cu…Cu). Notably, the M-C separations differ from each other more in $[\mathbf{3\text{-}H}]^{2+}$ than in $[\mathbf{1\text{-}H}]^{2+}$, as observed for the structurally characterised bis(alkynyl) complexes (see Table 2), while oxidation of [**1-H**]$^+$ and [**3-H**]$^+$ (46-cve) increases the asymmetry of the M_3 unit. A further interesting factor, however, is the remarkable change in the conformations of the dppm ligands (Table 2, Figs. 1-7), resulting from a variety of significant agostic interactions between phenyl-H atoms and the M_3 ring, as well as with the diynyl group. This may account for the difficulty of formation of bis(diynyl) complexes as described above, although similar changes in conformation are perceptible to a similar or lesser degree in numerous other examples. There are wide divergences in the P-C-P angles of the ligands – in the cation **7** [9c], all are > 115°, while in the closely related complex **5** [7c], all are < 110°, there being no obvious correlation with other cation parameters.

Related complexes

Interestingly, in the cubane complexes $\{Cu(\mu_3\text{-}C{\equiv}CR)(PR_3)\}_4$ [15-21], the sets of Cu-P distances also exhibit considerably diverse spreads, much greater than those in $Cu_3\{\mu\text{-}CCH[Co_2(CO)_6]\}_3$, [12] for example. Added point is given to these considerations by the observation of the formation of $[Cu_3(dppm)_3(\mu\text{-}Cl)_2Cl]\cdot 2C_2H_4Cl_2$ [21] in which a pair of μ_2-Cl atoms, on either side of the Cu_3 plane, bridge a pair of Cu atoms. One of these has a long interaction to the third copper atom, which also carries a terminal Cl atom on the other side. Considering further the dichloro and diiodo analogues $[Cu_3(\mu\text{-}dppm)_3(\mu_3\text{-}X)_2]^+$ (X = Cl, I) (as exemplified in their $[CuX_2]^-$ salts) [1,2], there is considerable asymmetry in the Cu_3Cl_2 array [Cu-Cl range: 2.372(4)-2.793(3) Å], with Cu···phenyl-H approaches < 3 Å, and Cl···phenyl-H contacts as short as 2.6 Å. In the iodide, the Cu-I range is much tighter [2.699(1)-2.787(2) Å]; the shortest Cu···phenyl-H contact is 2.9 Å, with a number of phenyl-H···iodine contacts in the range 3.0-3.3 Å.[1a] These effects are carried over to a degree in adducts where only one face carries an alkynyl carbon, with Cl, I or OMe on the other face, as in **9** [10], **10** [13], **11** [20] and **14** [22] (Table S1) [Figs. 6(a), 3(a), S3(a) and 3(b), respectively].

Specific complexes

Plots of these cations are included in Figures 1-7 and Figures S1-S6 (supplementary information). Some correlations of structural parameters with specific substitution types are noted as follows:

1. Complexes with monoalkynyl (C≡CR) ligands

(a) $X^1 / X^2 = (C{\equiv}CAr)_2$. *M = Cu:* **5** [7c], **19** [7d], **20** [7d], **21** [25], **22** [25], **23** [26], **24** [27], **25** [3c], **26** [15], **27** [28]; *M = Ag:* **28** [7b], **29** [29].

In these arrays, the cation components are disposed with a fair approximation to m-symmetry. To the 'U' side of the Cu_3 plane the phenyl rings of the dppm ligands and of the alkyne (separated from the Cu_3 plane only by the C_2 component) are quasi-parallel, lying quasi-normal to the mirror plane; to the 'D' side they are quasi-parallel to the mirror plane [Fig. 1], perhaps directed by interactions between themselves, and with the methylene-H atoms, and by phenyl *ortho*-H…metal interactions. Although the approaches of the alkyne groups to the M_3 plane are quasi-normal, significant lateral displacements (evident among the M…C bond lengths) and / or tiltings are found in most of these examples, particularly in the D-substituents, so as to perturb the interactions towards *asym*-μ_3. This interaction is usually with M1,2 (i.e., away from M3), unhindered by the U disposition of the associated methylene 1, although in examples such as **28** [7b], where the U-substituent is *asym*-μ_3 toward Ag2,3, U and D-approaches may be oblique (Fig. 1, S1). Deviation of the phosphorus atoms associated with methylene 1 (U) are, like it, positive, those associated with methylenes 2,3 being, like them, negative, all deviations being less than 1 Å (M = Cu), 1.35 Å (M = Ag).

< Figure 1 here >

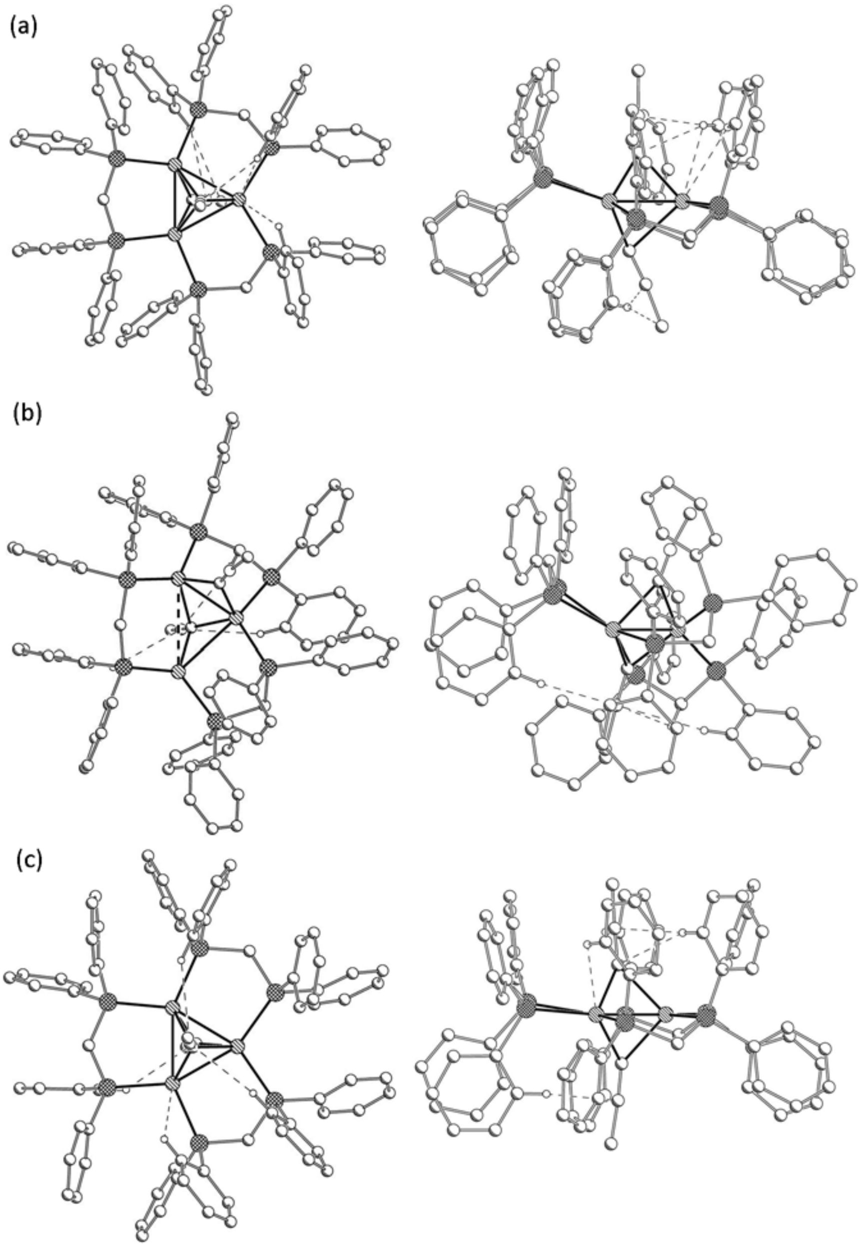


Fig. 1. Cation projections for representatives of the form $[M_3(dppm)_3(C{\equiv}CR)_2]^+$. M = Cu: (a) **5** [7c], (b) **24** [27], and (c) **26** [15]. In all Figures, which show the cations projected (left) normal to the M_3 plane and (right) normal to the mirror plane, the U-methylene group lies to the left, between M^1 and M^2. The examples show (a) pronounced tilting of one of the μ_3-C≡CR strings, (b) distortion of the M_3 core and (c) a relatively undistorted $[M_3(dppm)_3(C{\equiv}CR)_2]^+$ entity for comparison.

(b) X^1 / X^2 = C≡CAr / inorganic anion or neutral solvent. M = Cu: **16** [3a,c], **30** [3c]; *M = Ag:* **6** [8], **17** [24], **18** [7b].

These may be divided into two classes: (i) X^2 is strongly bound, interacting *sym*-μ_3 with the three metal atoms, as in X^2 = halide in **30** [3c] [Fig. 2(b)]; (ii) X^2 does not bind with the metal atoms, but is held in proximity to the face by interactions with the phenyl and methylene H atoms (a number of these interactions are not commented upon in the original descriptions of some of these structures) (X^2 = BF_4 in **16** [3a,c] [Fig. 2(a)], **18** [7b] [Fig. S2(c)], NO_3 in **17** [24] [Fig. S2(b)], and (neutral) MeCN in **6** [8] [Fig. S2(a)]. There are no examples thus far in which the X^2 site is vacant. In all of these cases, the alkyne ligand lies U, with an ambience of phenyl rings directed similarly to those of class (a), the ligand aromatic ring being directed likewise. Except in the case of the strongly bound X^2 = Cl, asymmetries in the μ_3 binding of the alkyne ligand are less pronounced and the directions of any perturbations are more random. There is a very marked difference in Cu-C distances between **30** [3c] (strongly bound X = Cl) and **16** [3a,c] (F-BF_3), despite the close approach of the one of the copper atoms in the latter. In **6** [8], the (previously unremarked) MeCN…Ag interaction is notable, albeit rather distant, being μ_2 on Ag(1,2). In the compounds of this group (both families), the asymmetry of the ligand dispositions is reflected in that of the phosphorus atoms in some of the complexes; unlike the pattern described in (a), we find that in **16** [3a,c] and **18** [7b] (both with BF_4 approaches opposed to the alkyne), there are pronounced twists in some of the chelate rings, such that one phosphorus atom lies U, one D, most notably in ligand 1 in each case (Fig. 2, SI 2).

< Figure 2 here >

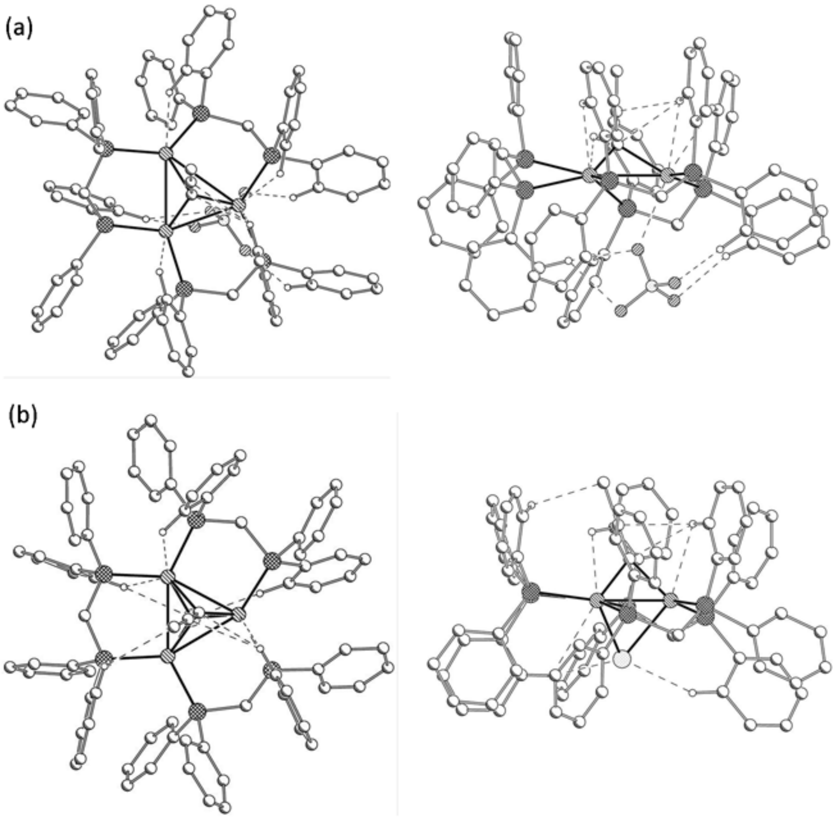


Fig. 2. Projections for representatives of the $[\{M_3(dppm)_3\}(\mu_3\text{-}X^1)(X^2)]^{n+}$ cations for M = Cu: (a) **16** [3a,c], (b) **30** [3c] where X^2 is an inorganic anion or neutral solvent. The figure shows exemplars (i) where X^2 does not bind with the metal atoms, but is held in proximity to the face by interactions with the phenyl and methylene H atoms and (ii) where X^2 is strongly bound, interacting *sym*-μ_3 with the three metal atoms, as in X^2 = halide in **30**. The extent of distortions of the M_3 core or the displacement/tilting of the X^1 group from normal to the plane appear to be independent of the placement of X^2.

(c) X^1 */* X^2 *= C≡CR / inorganic anion or methoxide. M = Cu:* **10** [13], **14** [22]; *M = Ag:* **11** [13], **33** [26].

A number of complexes have been defined with R other than phenyl, which exhibit features of interest related to the above: (i) **14** [22], **10** and **11** [13] (both isomorphous, with crystallographic m-symmetry) (see Figs. 3, SI 3) or (ii) **33** [26]. In all of these, the alkyne is D; although the array still has quasi-m symmetry, the central phenyl groups about the alkyne now lie quasi-normal to the mirror plane; on the other side (U), they are directed similarly, with inclinations toward the anion directed by hydrogen-bonding. In the isomorphous examples with R = CO_2 **10** and **11** [13], the CO_2 substituent of the alkyne lies within the aggregate, across the (crystallographic) mirror plane, interacting with nearby phenyl-H atoms. The inclinations of the alkyne groups in the latter are large with essentially μ_2 bonding to M1,2; in **14** [22], the inclination is much less, with no close phenyl-H contacts either to the C≡C triple bond or the Cu core, perhaps shielded by the 'umbrella' of the Bu^t group. As regards the phosphorus atom dispositions, while those of **10** and **11** [13] are 'normally' behaved [as in (a)], in **14** [22] (M = Cu) we find that in each of ligands 2 and 3 one phosphorus is D, and the other U.

< Figure 3 here >

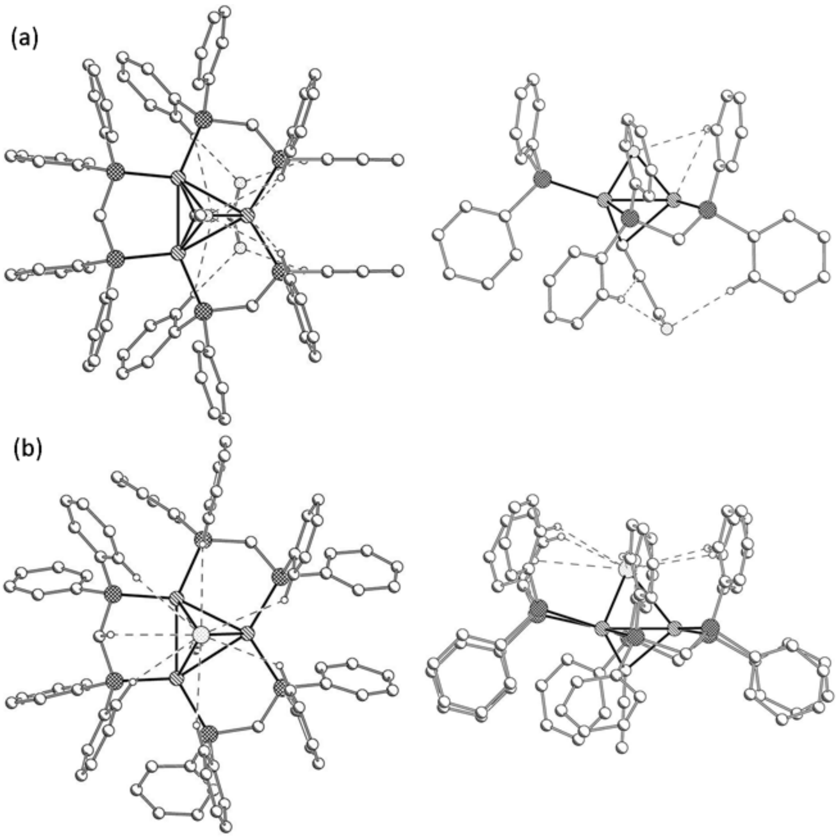


Fig. 3. Projections for representatives of the $[\{M_3(dppm)_3\}(\mu_3\text{-}X^1)(\mu_3\text{-}X^2)]^{n+}$ cations for M = Cu: (a) **10** [13], and (b) **14** [22] where X^2 is methoxide or chloride respectively.

(d) X^1 / X^2 = (C≡CR) / -: M = Cu: **15** [23], **31** [30]; *M = Ag:* **32** [30].

There are three representatives of this type, **15** [23] (Fig. 4), the alkyne being D, along with **31** and **32** [30] where a dialkynyl ligand bridges two $M_3(dppm)_3$ cations. As in **14** [22], there are no close approaches between phenyl-H atoms and the C≡C triple bond; there is a pair of symmetrical interactions with Cu1,2 on that side, facilitated by the U disposition of the methylene group in-between; as in **14** [22] also, we find unusual phosphorus dispositions, so that all phosphorus atoms except one in ligand 3 are U.

< Figure 4 here >

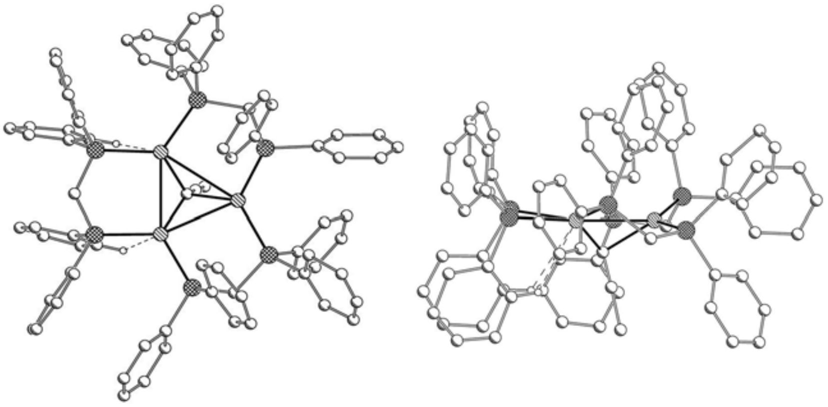


Fig. 4. Projections of the $[\{M_3(dppm)_3\}(\mu_3\text{-}X^1)]^{2+}$ cation for **15** [23] (no X^2 group).

2. *Complexes with diynyl ligands* ($C{\equiv}CC{\equiv}CR$)

(a) X^1 / X^2 = $(C{\equiv}CC{\equiv}CR)_2$. *M = Cu:* **2** [6], **7** [9c], **12** [14], **13** [14]; *M = Ag:* **8** [9c].

In these systems, the diynyl substituent is now well-removed from both the cation core and from any dppm phenyl-H atoms, this feature seemingly removing associated conformational constraints (Figs. 5 and SI 5). Although there is quasi-m symmetry to either side of methylene 1 in all cations here, any tendency toward m-symmetry among the remainder of the core periphery is lost, with the dispositions of those phenyl groups seemingly random, controlled by 'lattice forces'. The same is also true of the diynyl dispositions, in particular in the approaches of the D-ligands in **8** [9c], where, despite a rather imprecise determination, it seems fairly clear that they approach the Ag1…Ag2 line quite directly (μ_2), with little or no interaction with Ag_3. Despite the symmetry of the ligand complement, the phosphorus dispositions are in some cases erratic: in **13** [14] and **8** [9c] one of the phosphorus atoms of one of the D ligands in each case is U, while in **12** [14], all phosphorus atoms except one (associated with a D ligand) are D.

< Figure 5 here >

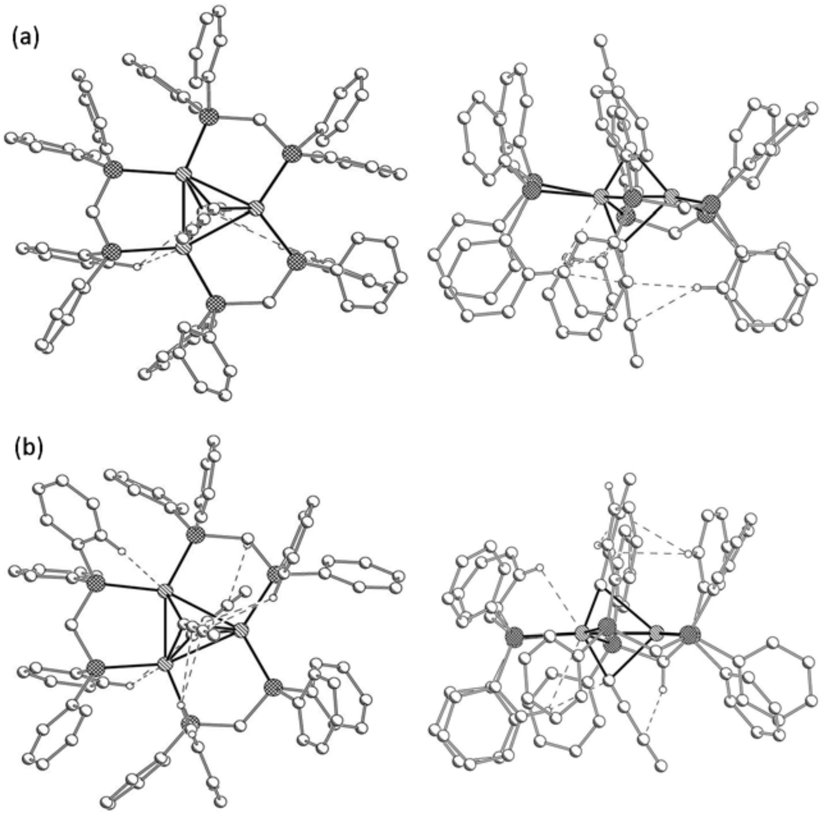


Fig. 5. Cation projections for representatives of the form $[M_3(dppm)_3(C{\equiv}CC{\equiv}CR)_2]^+$. M = Cu: (a) **7** [9c] and (b) **12** [14]. That for **12** shows phenyl-H···C_4 ligand and ···Cu_3 core approaches. Note also the inclination of the approaching C≡CC≡CH ligands to the Cu_3 ring (this being the most extreme example), indicative of a change in bonding mode, from *sym*-μ_3 towards *asym*-μ_3.

(b) X^1 / X^2 *= C≡CC≡CR / inorganic anion: M = Cu:* **9** (*mols. 1, 2*) [10]; *M = Ag:* **3** (*THF solvate*) [6].

For **9** the approaches of the hydrogen atoms about the iodine atom are quasi-symmetrical, but that tendency is not reflected about the diynyl ligand; the phosphorus atom dispositions are 'normal' (Figs. 6, SI 6). The THF solvate of **3** contains an invasively interacting BF_4 anion, with Ag1,2,3···F contacts 2.801(1), 2.787(3), 2.913(4) Å, the remainder of the fluorine atom dispositions broadly conforming to quasi-m symmetry, as also do the phenyl substituents; all phosphorus atoms lie to the same side of the M_3 plane (D) as the anion.[6]

< Figure 6 here >

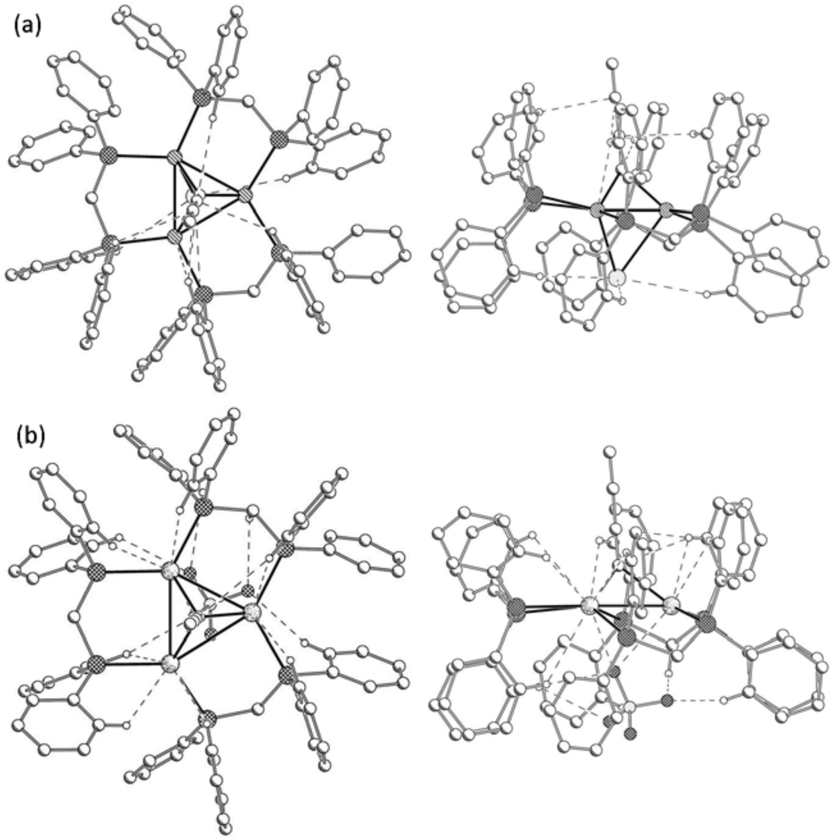


Fig. 6. Projections of the $[\{M_3(\mathrm{dppm})_3\}(\mu_3\text{-}X^1)(\mu_3\text{-}X^2)]^{n+}$ cations for M = Cu: (a) **9** (mol. 1) [10]; M = Ag: (b) **3** (THF solvate) [6].

(c) X^1 / X^2 *= C≡CC≡CR / -. M = Cu:* **1** [6]; *M = Ag:* **3** (*acetone solvate)* [6].

The acetone solvate of **3** [6] and its isomorphous M = Cu counterpart **1** [6] are devoid of any anion approach, and, beyond the surrounds of methylene 1, the phenyl dispositions are random; the phosphorus atom dispositions are 'normal' (Fig. 7). Cations of this group have no close phenyl-alkyne approaches.

< Figure 7 here >

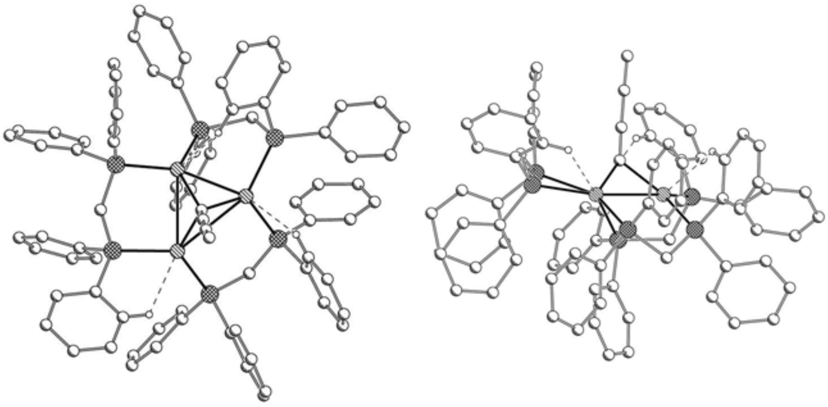


Fig. 7. Projections of the isomorphous $[\{M_3(dppm)_3\}(\mu_3\text{-}X^1)]^{n+}$ cations. M = Cu: **1** [6]; M = Ag: **3** (acetone solvate) [6], (no X^2 group).

A final note concerns possible interactions of ligand substituents with the remainder of the M_3 cluster, in particular those of the rather numerous ligands of the form C≡CAr, where the Ar group has *ortho*-H atoms not far removed from the cluster. In general, these H atoms are too far distant to interact with any of the three metal atoms, regardless of whether the ligand binding is μ_2 or μ_3. However, in many cases these H atoms do approach some of the H atoms associated with the dppm ligands, and, while we do not explore these in further detail, we note that their effect frequently appears to be instrumental in determining that the ligand aromatic plane lies normal to the previously noted quasi-mirror plane which bisects the M_3 core.

5. Conclusions

In summary, among the cations of the structurally characterised complexes of the form $[M_3(dppm)_3(\mu_3\text{-}C{\equiv}CR)(\mu_3\text{-}X)]^{n+}$ (M = Cu, Ag) that we and others have studied, the $M_3(dppm)_3$ core is crowded so that the dppm ligands are always arranged with one CH_2 group up and the other two down (1U + 2D or 1D + 2U, allowing a datum for the remaining ligands), to give mirror symmetry. The phenyl rings appear to be arranged to minimise steric interactions with each other. With a pair of arylalkynyl ligands bound to either side of the M_3 plane, a remarkably persistent aggregate is obtained, of quasi-m symmetry, the phenyl rings on the U side of the plane lying quasi-parallel to the mirror plane, and those below (D) quasi-normal. However, the alkyne approaches to the M_3 cluster are extremely variable, ranging from *sym*-μ_3 to almost purely μ_2.

There may also be extra C-H···M agostic interactions which influence the final conformations. This arrangement tends to persist when one of the alkynyl or diynyl ligands is replaced by an anion, or is removed completely. With replacement of ligands of this form by (a) two with more distant substituents or (b) one diynyl ligand, the steric constraints imposed within the aggregate, complemented by phenyl-H···metal / alkyne approaches, are more relaxed and, in the absence of metal-metal bonding, the chelate rings may adopt much more variable (twisted) dispositions, especially in the one-ligand situation in the presence of the invasive and less symmetrical approaches found with BF_4 as counterion, for example.

The presence of one or two alkynyl ligands exercises a significant influence over the geometry of the trinuclear cation core; with only one ligand, and a feebly-bound or non-existent donor to the other face, agostic interactions between dppm phenyl-H atoms and the M_3 core may produce unusual conformational changes in the dppm chelate rings, including twisting that takes the P atoms out of the M_3 plane. Both the conformations of the phenyl rings and the inclination of the alkynyl group are affected by various C-H···X interactions.

Acknowledgements

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References

[1] (a) C. Di Nicola, Effendy, F. Fazaroh, C. Pettinari, B.W. Skelton, N. Somers, A.H. White, Inorg. Chim Acta 358 (2005) 720, in particular, for $[Cu_3(\mu\text{-}dppm)_3(\mu_3\text{-}X)_2]^+$, L = Cl (**DAQPUH**) (solvated $[CuCl_2]^-$ salt); X = I (**DAQQES**) ($[CuCl_2]^-$ salt).

(b) For X = Cl, a later study is available: E. Colacio, R. Cuesta, J.M. Moreno, Inorg. Chem. 36 (1997) 1084 (**RIPHON**) (xanthine anion salt).

[2] For X = I, see also (a) Q. Yuan, H. Zhao, S-H. Zuang, Henan Daxue Xuebao, Ziran Kexueban 35 (2005) 45 (**VOKKEM**) (iodide salt);

(b) W-B. Zhou, Z-C. Dong, J-L. Song, H-X. Zeng, R. Cao, G-C. Goo, J-S. Huang, J. Li, J. Cluster Sci. 13 (2002) 119 (**WOYZUF**) (iodide salt);

(c) J.K. Bera, M. Nethaji, A.G. Samuelson, Inorg. Chem. 38 (1999) 218 (**HOMVAG**) (solvated iodide salt);

(d) Y-Q. Song, D-Y. Ma, S-Z. Zhan, J-Y. Su, J-W. Xu, J. Coord. Chem. 61 (2008) 4004 (**TOJZAU**) (hydrated $TCNQ^-$ salt).

[3] (a) M.P. Gamasa, J. Gimeno, E. Lantra, A. Aguirre, S. García-Granda, J. Organomet. Chem. 378 (1989) C11 (**16 JEBPAH**)

(b) J. Diéz, M.P. Gamasa, J. Gimeno, A. Aguirre, S. García-Granda, Organometallics 10 (1991) 380 (**25 SITNIS**).

(c) J. Diéz, M. P. Gamasa, J. Gimeno, E. Lastra, A. Aguirre, S. García-Granda, Organometallics 12 (1993) 2213 (**16 JEBPAH10, 25 SITNIS10, 30 WARTIS**).

[4] V.W.-W. Yam, W.-Y. Lo, N. Zhu, Chem. Commun. (2003) 2446.

[5] M.I. Bruce, P.J. Low, B.K. Nicholson, B.W. Skelton, N.N. Zaitseva, X.-l. Zhao, J. Organomet. Chem. 695 (2010) 1569.

[6] M.I. Bruce, B.G. Ellis, J.-F. Halet, B. Le Guennic, B.K. Nicholson, H. Sahnoue, N. Scoleri, B.W. Skelton, A.N. Sobolev, C.J. Sumby, A.H. White, N.N. Zaitseva, Inorg. Chim. Acta 453 (2016) 654 (**1 IWAFAP, 2 IWAKUO, 3 IWADUH, IWAKOI, 4 IWAGAQ, 39 IWAFOD**)

[7] (a) V.W-W. Yam, W.K-M. Fung, M-T. Wong, Organometallics 16 (1997) 1772;

(b) V.W-W. Yam, W.K-M. Fung, K-K. Cheung, Organometallics 16 (1997) 2032 (**18 RUMWOL**, **28 RUMWUR**).

(c) V.W-W. Yam, W.K-M. Fung, K.M-C. Wong, V.C-Y. Lau, K.K. Cheung, Chem. Commun. (1998) 777 (**5 SACFIL**).

(d) V.W-W. Yam, W.K-M. Fung, K-K. Cheung, Organometallics 17 (1998) 3293 (**19 GAMNEN**, **20 GAMNIR**).

[8] Q.-H. Wei, G.-Q. Yin, L.-Y. Zhang, Z.-N. Chen, *Inorg. Chem.* 45 (2006) 10371 (**6 YESXIE**).

[9] (a) V.W-W. Yam, K.K-W. Lo, Chem. Soc. Rev. 28 (1999) 323.

(b) V.W-W. Yam, Chem. Commun. (2001) 789.

(c) V.W-W. Yam, W-Y. Lo, C-H. Lam, W.K-M. Fung, K.M-C. Wong, V.C-Y. Lau, N. Zhu, Coord. Chem. Rev. 245 (2003) 39 (**7 ACAKUL, 8 ACALAS**).

[10] M.I. Bruce, B.C. Hall, B.W. Skelton, M.E. Smith, A.H. White, J. Chem. Soc., Dalton Trans. (2002) 995 (**9 XIFWUE**).

[11] P.K. Mehrotra, R. Hoffmann, Inorg. Chem. 17 (1978) 2187;

[12] A. Vega, V. Calvo, E. Spodine, A Zárate, V. Fuenzalida, J.-Y. Saillard, Inorg. Chem. 41 (2002) 3389 (**XOGBEA**).

[13] H.-Y. Chao, L. Wu, B.-C. Su, X.-L. Feng, Inorg. Chem. Commun. 14 (2011) 122 (**10 INOSOU, 11 INOSUA**).

[14] W-Y. Lo, C-H. Lam, V.W-W. Yam, N. Zhu, K-K. Cheung, S. Fathallah, S. Messaoudi, B. Le Guennic, S. Kahlal, J.-F. Halet, J. Am. Chem Soc. 126 (2004) 7300 (**12 EZUHEM**, **13 EZUHAI**).

[15] V.W-W. Yam, W.K-M. Fung, K-K. Cheung, J. Cluster Sci. 10 (1999) 37 (**26 WIWZAD**) (also contains the cubanoid **WIWZEH**).

[16] M.P. Gamasa, J. Gimeno, E. Lastra, X. Solans, J. Organomet. Chem. 346 (1988) 277 (**JEFSOC**).

[17] L. Naldini, F. Demartin, M. Manassero, M. Sansoni, G. Rassu, M.A. Zoroddu, J. Organomet. Chem. 279 (1985) C42 (**CUJLUO**); this note briefly reports the structure of $[\{(Ph_3P)Cu(C{\equiv}CPh)\}_4]$ for which no coordinates are available. A redetermination in our laboratories offers an improved record: $C_{104}H_{80}Cu_4P_4$, $M_r = 1707.7$. Monoclinic, space group $C2/c$ (#15), $a = 14.8400(10)$, $b = 24.540(2)$, $c = 23.331(2)$ Å, $\beta = 95.991(2)°$, $V = 8450.1.(12)$ Å^3 (T *ca* 293 K). D_c ($Z = 4$) = 1.34_2 g cm^{-3}. $\mu_{Mo} = 1.12$ mm^{-1}; specimen: 0.20 x 0.09 x 0.08 mm; '$T_{min/max} = 0.70$. $2\theta_{max} = 58°$; $N_{tot} = 47333$, $N = 10816$, ($R_{int} = 0.067$), $N_o = 4888$; $R1 = 0.041$, $wR2 = 0.099$ (a = 0.046); $S = 0.81$. $|\Delta\rho_{max}| = 0.35$ e Å^{-3}. Cu···Cu are

2.5123(5)-2.6649(5); Cu-P 2.2221(8), 2.2336(8); Cu-C 2.048(3)-2.336(3) Å. CCDC 668723; the assistance of N. Somers is acknowledged.

[18] (a) V.W-W. Yam, W-K. Lee, K-K. Cheung, J. Chem. Soc., Dalton Trans. (1996) 2335 (**TEPGIE**).
(b) V.W-W. Yam, V. C-Y. Lau, N. Zhu, Inorg. Chim. Acta 331 (2002) 239 (**XIXXUX**).

[19] F. Olbrich, J. Kopf, E. Weiss, Angew. Chem. Int. Ed. Engl. 32 (1993) 1077 (**WARMAD**).

[20] K. Osakada, T. Takizawa, T. Yamamoto, Organometallics, 14 (1995) 353 (**ZEPZID**);

[21] S. Daly, M.F. Haddow, A.G. Orpen, G.T.A. Rolls, D.F. Wass, R.L. Wingad, Organometallics 27 (2008) 3196 (**VOFWAP).**

[22] V.W-W. Yam, W-K. Lee, T-F. Lai, Organometallics, 12 (1993) 2383 (**14 WARKEF**).

[23] V.W-W. Yam, W-K. Lee, K-K. Cheung, B. Crystall, D. Phillips, J. Chem. Soc., Dalton Trans. (1996) 3283 (**15 TOGREM**).

[24] R. Aroz, F. Mohr, E. Cerrada, E.R.T. Tiekink, M. Laguna, Polyhedron 25 (2006) 3066 (**17 JERVIM**).

[25] M. Zhang, B-C. Su, C-L. Li, Y. Shen, C-K. Lam, X-L. Feng, H-Y. Chiao, J. Organomet. Chem. 696 (2011) 2654 (**21 IXIDOJ**, **22 IXIDUP**).

[26] J.H.K. Yip, J. Wu, K-Y. Wong, K.-W. Yeung, J.J. Vittal, Organometallics 21 (2002) 1612 (**23 MITLUW**, **33 MITLOQ**).

[27] J. Díez, M. Pilar Gamasa, J. Gimena, A. Aguirre, S. Garcia-Grande, Organometallics 16 (1997) 3684 (**24 NEVWUG**).

[28] V.W-W. Yam, C-H. Lam, K-K. Cheung, Inorg. Chim. Acta 316 (2001) 19 (**27 XIBYUC**).

[29] C-F. Wang, S-M. Peng, C-K. Chan, C-M. Che, Polyhedron 15 (1996) 1853 (**29 TEQSEN**).

[30] V. W-W. Yam, W.K-M. Fung, K-K. Cheung. Chem. Commun. (1997) 963 (**32 RUFREP**, **33 RUFRIT**).

[31] H.-Y. Shi, Y.-L. Huang, J.-K. Sun, J.-J. Jiang, Z.-X. Luo, H.-T. Ling, C.-K. Lam, H.-Y. Chao, RSC Adv. 5 (2015) 89669. (**34**, **35**, **36**, **37**)

[32] H.-S. Lo, E. C.-C. Cheng, H.-L. Xu, W. H. Lam, N. Zhu, V. K.-M. Au, V. W.-W. Yam, J. Organomet. Chem. 812 (2016) 43. (**38 TABBEG**)