

# Group 6 metal complexes of 1,3,5-tri(4-pentynyl)-1,3,5-triazacyclohexane

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1,3,5-Tri(4-pentynyl)-1,3,5-triazacyclohexane (tptach), a 1,3,5-triazacyclohexane ligand with three pendant alkyne groups, was synthesized. The metal tricarbonyl adducts  $[\text{Cr}(\text{CO})_3(\text{tptach})]$  and  $[\text{Mo}(\text{CO})_3(\text{tptach})]$ , featuring a tptach co-ordinated to the metal centre *via* only the three nitrogen atoms, were prepared by reaction of tptach with reactive sources of “ $\text{M}(\text{CO})_3$ ”. The chromium trichloride adduct  $[\text{CrCl}_3(\text{tptach})]$  was synthesized in low yield *via* the reaction of tptach with  $[\text{CrCl}_3(\text{thf})_3]$ . Structural studies of  $[\text{CrCl}_3(\text{tptach})]$  and another chromium trihalide–tach adduct,  $[\text{CrBr}_3(\text{tmtach})]$  (tmtach = 1,3,5-trimethyl-1,3,5-triazacyclohexane), were made.

## Introduction

As part of an investigation into the co-ordination chemistry of 1,3,5-trialkyl-1,3,5-triazacyclohexanes with Group 6 metals, we recently reported the synthesis and characterisation of chromium complexes of hydroxyl-functionalised 1,3,5-trialkyl-1,3,5-triazacyclohexanes.<sup>1</sup> The presence of the pendant hydroxyl groups in these triazacyclohexanes complicates their co-ordination chemistry, but under certain conditions it has been possible to form complexes in which the three nitrogen atoms of the triazacyclohexane unit are bound to chromium while the hydroxyl groups remain free.

Here we report the synthesis and co-ordination chemistry of another functionalised triazacyclohexane, 1,3,5-tri(4-pentynyl)-1,3,5-triazacyclohexane (tptach). We are interested in intramolecular co-ordination of pendant alkynes to transition metal centres, an area which has received little attention to date. In view of the ease of synthesis of tptach and the variety of routes that have been established for the synthesis of complexes of tach ligands with Group 6 metals,<sup>1–8</sup> we felt that the tptach system would serve as an interesting starting point for an investigation of intramolecular co-ordination of pendant alkynes. Like the hydroxyl groups in the hydroxyl-functionalised 1,3,5-triazacyclohexanes, the alkynyl groups of tptach complicate the co-ordination of tptach to metal centres. Through the use of particular metal sources, however, it has been possible to bind tptach to metal centres *via* the three nitrogen atoms only. The complexes  $[\text{Cr}(\text{CO})_3(\text{tptach})]$ ,  $[\text{Mo}(\text{CO})_3(\text{tptach})]$  and  $[\text{CrCl}_3(\text{tptach})]$  each have three pendant alkyne groups not involved in co-ordination to a metal centre, a rare feature in metal–alkyne chemistry.

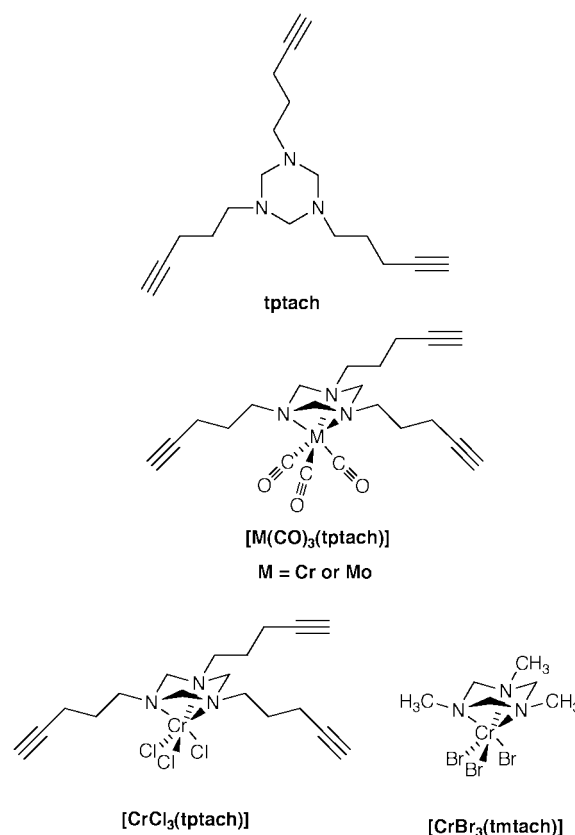
## Results and discussion

### 1,3,5-Tri(4-pentynyl)-1,3,5-triazacyclohexane

The compound tptach was synthesized in quantitative yield by treatment of 5-amino-1-pentyne with paraformaldehyde in diethyl ether at room temperature and was of sufficient purity for further use. The ligand is stable in benzene, acetone and chloroform. However, dissolution of tptach in  $\text{CD}_3\text{OD}$  initially leads to H/D exchange of the acetylenic protons, followed by a slower reaction with methanol that yields a mixture of unidentified products.

### Reaction of tptach with sources of $\text{M}(\text{CO})_3$ (M = Cr, Mo or W)

Several methods for the preparation of  $[\text{M}(\text{CO})_3(\text{tach})]$  (M =



Cr, Mo or W) complexes have been reported. The simplest method starts with the appropriate metal hexacarbonyl as the source of  $\text{M}(\text{CO})_3$ ,<sup>2,7,8</sup> and displacement of carbonyl groups from the hexacarbonyl is promoted by heating or photolysis. Other methods use less readily accessible metal sources such as  $[\text{Mo}(\text{CO})_3(\text{C}_7\text{H}_8)]$ ,<sup>5</sup>  $[\text{Cr}(\text{CO})_3(\text{CH}_3\text{CH}_2\text{CN})_3]$ <sup>1</sup> or  $[\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ <sup>6</sup> as starting materials, but have the advantage that the reactions can occur at ambient temperature. Earlier work from this laboratory<sup>7</sup> suggested that tach displacement reactions could also be used to synthesize tach complexes, since the 1,3,5-trimethyl-1,3,5-triazacyclohexane (tmtach) group in  $[\text{M}(\text{CO})_3(\text{tmtach})]$  is susceptible to displacement by tach ligands with larger alkyl substituents.

The complexes  $[\text{Cr}(\text{CO})_3(\text{tptach})]$  and  $[\text{Mo}(\text{CO})_3(\text{tptach})]$  were prepared by addition of tptach to acetone solutions of

$[\text{Cr}(\text{CO})_3(\text{CH}_3\text{CH}_2\text{CN})_3]$  and  $[\text{Mo}(\text{CO})_3(\text{CH}_3\text{CH}_2\text{CN})_3]$ . The reactions were rapid at room temperature and quantitative (as indicated by  $^1\text{H}$  NMR spectroscopy), and the yields of isolated products were good ( $M = \text{Cr}$ , 74%;  $M = \text{Mo}$ , 49%). The high yields for these reactions imply that there is little or no alkyne–metal interaction during the synthesis or isolation of the products. In line with corresponding complexes of tmtach,  $[\text{Cr}(\text{CO})_3(\text{tpach})]$  is orange and  $[\text{Mo}(\text{CO})_3(\text{tpach})]$  is yellow. Their respective infrared,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra show signals characteristic of  $[\text{M}(\text{CO})_3(\text{tach})]$  complexes in which the tach unit is facially co-ordinated through the three nitrogen atoms.<sup>8</sup> The infrared and  $^{13}\text{C}$  NMR signals for the tpach acetylenic groups are similar in the spectra for both free tpach and the  $[\text{M}(\text{CO})_3(\text{tpach})]$  ( $M = \text{Cr}$  or  $\text{Mo}$ ) complexes. These results indicate that in the  $[\text{M}(\text{CO})_3(\text{tpach})]$  complexes the alkyne groups are not involved in alkyne–metal bonding. Both complexes are oxygen sensitive in the solid state and in solution. Heating of solutions of either complex leads to rapid decomposition, producing brown, presumably polymeric products; attempts to grow crystals of either  $[\text{Cr}(\text{CO})_3(\text{tpach})]$  or  $[\text{Mo}(\text{CO})_3(\text{tpach})]$  gave similar results.

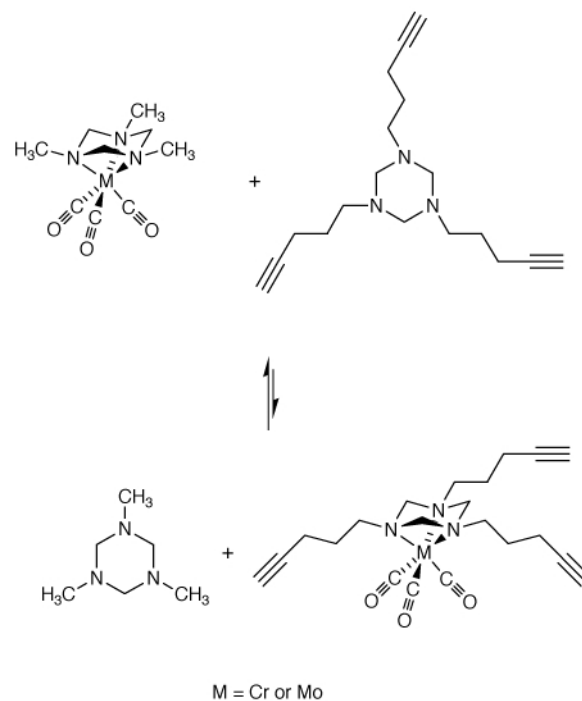
The reaction of tpach with  $[\text{W}(\text{CO})_3(\text{CH}_3\text{CH}_2\text{CN})_3]$  in acetone- $d_6$  solution afforded  $[\text{W}(\text{CO})_3(\text{tpach})]$  in quantitative yield (according to  $^1\text{H}$  NMR spectroscopy). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the sample showed signals characteristic of  $[\text{W}(\text{CO})_3(\text{tach})]$  complexes having a single type of CO group and an  $\eta^3$ -tach unit co-ordinated to W *via* the nitrogen atoms only.<sup>8</sup> Attempts to isolate the  $[\text{W}(\text{CO})_3(\text{tpach})]$  by concentration of the solution under vacuum or precipitation of the product by the addition of ether invariably resulted in degradation of the  $[\text{W}(\text{CO})_3(\text{tpach})]$  to a brown, insoluble material. The infrared spectrum of this material contained a large number of strong bands in the region 1700–2000  $\text{cm}^{-1}$ , suggesting the presence of CO groups in many different environments. This result, along with the colour of the material and its poor solubility, suggested that it was polymeric. Given that reactions of simple 1,3,5-trialkyl-1,3,5-triazacyclohexanes ( $\text{C}_3\text{H}_6\text{N}_3\text{-R}_3$ ,  $\text{R} = \text{CH}_3$  or *t*-Bu) with  $\text{W}(\text{CO})_3$  sources are not complicated by the formation of polymeric products,<sup>6,8</sup> the formation of polymeric material from  $[\text{W}(\text{CO})_3(\text{tpach})]$  is presumably due to the presence of the alkyne units. Polymeric products could form by polymerisation or intermolecular cyclotrimerisation of alkyne groups<sup>9,10</sup> or by pendant alkynes of  $[\text{W}(\text{CO})_3(\text{tpach})]$  becoming involved in intermolecular metal–alkyne interactions.

Our attempts to synthesize  $[\text{M}(\text{CO})_3(\text{tpach})]$  complexes by other methods were unsuccessful or not practical. The reaction of tpach with  $[\text{Cr}(\text{CO})_6]$  in refluxing light petroleum,  $[\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3]$  in refluxing thf, or  $[\text{Cr}(\text{CO})_3(\text{C}_7\text{H}_8)]$  in hot acetone led only to brown intractable products. The reaction of tpach with  $[\text{Cr}(\text{CO})_3(\text{C}_7\text{H}_8)]$  in acetone at room temperature produced  $[\text{Cr}(\text{CO})_3(\text{tpach})]$  very slowly (less than 50% yield after 1 week), but that with  $[\text{Mo}(\text{CO})_3(\text{C}_7\text{H}_8)]$  at ambient temperature produced  $[\text{Mo}(\text{CO})_3(\text{tpach})]$  in quantitative yield within 2 h. Isolation of either  $[\text{Cr}(\text{CO})_3(\text{tpach})]$  or  $[\text{Mo}(\text{CO})_3(\text{tpach})]$  from these reaction mixtures proved difficult due to the number of compounds present and the sensitivity of the tpach adducts.

Attempts to synthesize  $[\text{M}(\text{CO})_3(\text{tpach})]$  ( $M = \text{Cr}$  or  $\text{Mo}$ ) *via* displacement of tmtach from  $[\text{M}(\text{CO})_3(\text{tmtach})]$  in acetone- $d_6$  led to equilibrium mixtures (Scheme 1) within 15 h for  $M = \text{Cr}$  and within 30 min for  $M = \text{Mo}$ . In both cases, the equilibria favoured the  $[\text{M}(\text{CO})_3(\text{tpach})]$  complex, despite tpach having bulkier alkyl substituents than those of tmtach.<sup>7</sup> Owing to the presence of an excess of tpach, as well as  $[\text{M}(\text{CO})_3(\text{tmtach})]$  and free tmtach, we were unable to isolate the  $[\text{M}(\text{CO})_3(\text{tpach})]$  products from these reaction mixtures.

### Synthesis of $[\text{CrCl}_3(\text{tpach})]$

The complexes  $[\text{CrCl}_3(\text{C}_3\text{H}_6\text{N}_3\text{R}_3)]$  ( $\text{R} = \text{Me}$ , *i*-Pr,  $\text{CH}_2\text{Ph}$  or cyclohexyl) can be prepared in high yield *via* the reaction of the

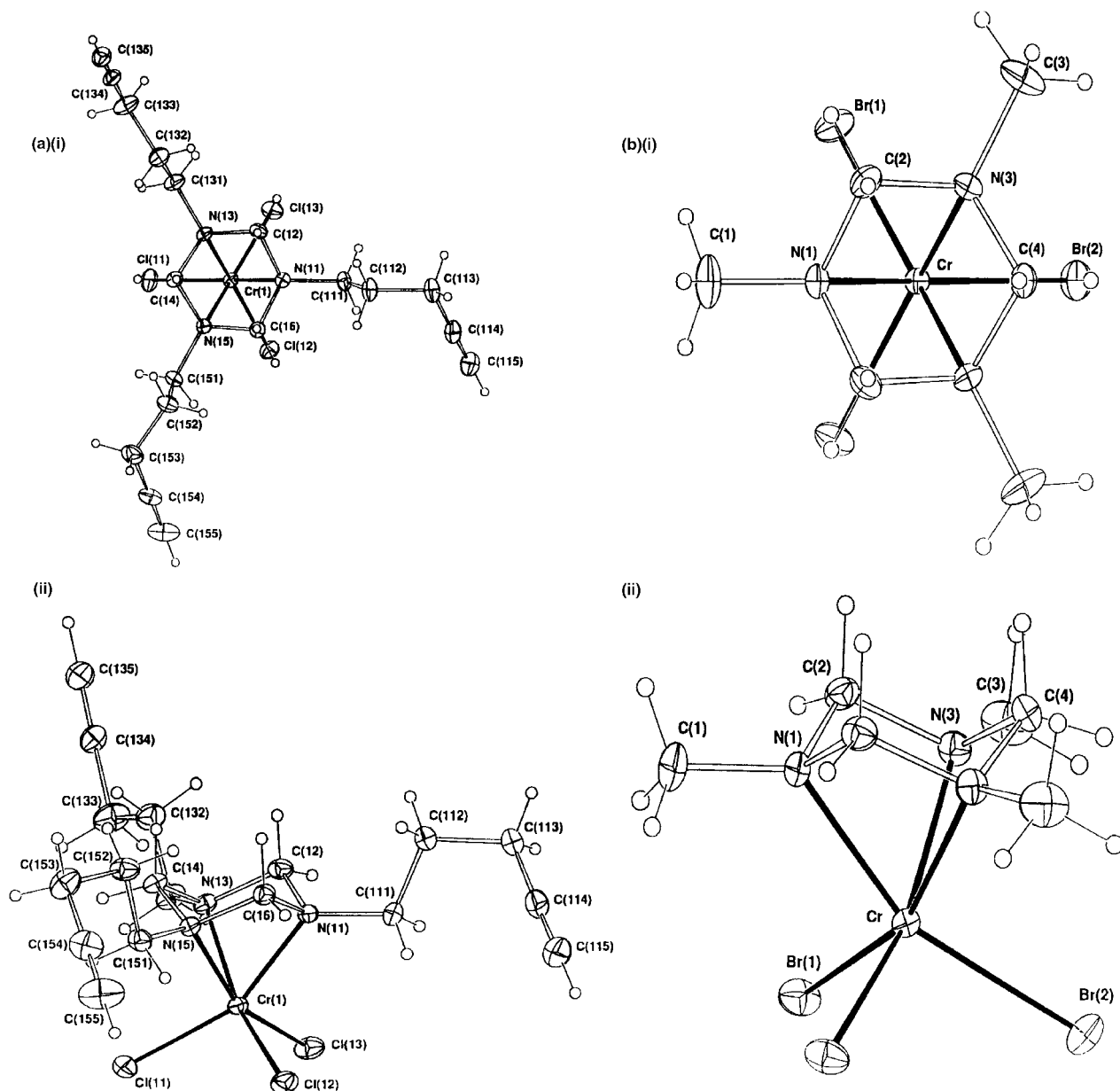


Scheme 1

corresponding tach with  $[\text{CrCl}_3(\text{thf})_3]$  in thf at room temperature.<sup>3,4</sup> Using this method, the alkynyl complex  $[\text{CrCl}_3(\text{tpach})]$  was obtained as a mauve powder, but the yield was pitiful (3–5%). Variation of the reaction conditions, including the use of different solvents, temperatures and concentrations, failed to increase the yield. In all cases the major product was an amorphous, green, water-soluble solid which was easily separated from the water-insoluble  $[\text{CrCl}_3(\text{tpach})]$  by filtration. The complex  $[\text{CrCl}_3(\text{tpach})]$  was stable towards air and water.

To test the possibility that the green product might arise by decomposition of the tpach due to ligand–metal interactions, a sample was treated with zinc and aqueous sodium cyanide (to strip chromium from any complex present), and the resulting mixture extracted with chloroform. Examination of the extract by NMR spectroscopy indicated the presence of many products, but neither tpach nor 5-amino-1-pentyne was present.

Oxidative halogenation of  $[\text{Cr}(\text{CO})_3(\text{tpach})]$  provided a possible alternative route to a tpach chromium trihalide adduct. *N*-Bromosuccinimide was tested as a reagent for this purpose; previously, *N*-bromosuccinimide has been used to oxidise tris(pyrazolyl)borate tungsten(0) tricarbonyl complexes to the seven-co-ordinate bromotricarbonyl tungsten(II) species.<sup>11</sup> Reaction of  $[\text{Cr}(\text{CO})_3(\text{tmtach})]$  with *N*-bromosuccinimide produced  $[\text{CrBr}_3(\text{tmtach})]$  as a purple powder, in 26% yield. The structure of this product was confirmed by a single crystal X-ray study. Reaction of  $[\text{Cr}(\text{CO})_3(\text{tpach})]$  with *N*-bromosuccinimide under similar conditions also afforded a pink-purple solid. The infrared spectrum of this solid showed no CO stretches, consistent with oxidative removal of CO from the metal under the reaction conditions. It appeared, however, that partial dibromination of the alkynyl substituents had also occurred; the  $^1\text{H}$  NMR spectrum of the tach ligand recovered from a sample of the pink-purple solid showed signals in the vinylic region which we tentatively attribute to dibromoalkenes. *N*-Bromosuccinimide reacts with alkynes to produce brominated olefins under certain conditions.<sup>12</sup> Treatment of 1-hexyne with *N*-bromosuccinimide under conditions similar to those used for the reaction with  $[\text{Cr}(\text{CO})_3(\text{tpach})]$  resulted in the slow formation of *E*-1,2-dibromo-1-hexene, which was identified by  $^1\text{H}$  NMR spectroscopy.<sup>13</sup>



**Fig. 1** Projections of (a)  $[\text{CrCl}_3(\text{tptach})]$  (molecule 1; molecule 2 is very similar) and (b)  $[\text{CrBr}_3(\text{tmtach})]$  (i) down and (ii) (approximately) normal to the quasi-3 axes of the chromium environments. 20% Thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

#### Attempts to induce co-ordination of pendant alkynes

During this work we found no evidence for the formation of any compounds in which an alkyne unit and the three nitrogen atoms in a tptach ligand are simultaneously co-ordinated to a single metal centre, and attempts to induce intramolecular displacement of CO by one or more of the pendant alkynyl groups in the  $[\text{M}(\text{CO})_3(\text{tptach})]$  complexes have so far been unsuccessful. 4-Methylmorpholine *N*-oxide, a reagent used to remove co-ordinated CO groups by oxidation to  $\text{CO}_2$ , resulted in the decomposition of  $[\text{M}(\text{CO})_3(\text{tptach})]$  ( $\text{M} = \text{Cr}$  or  $\text{Mo}$ ). Attempts to displace a CO ligand by an alkyne group under photochemical conditions yielded only unchanged starting material with small amounts of decomposition products. Attempts to labilise the carbonyl groups by oxidation of the metal centre in  $[\text{Mo}(\text{CO})_3(\text{tptach})]$  using  $\text{I}_2$ , as recently reported for  $[\text{Mo}(\text{CO})_3(\text{t-Bu}_3\text{tach})]$ ,<sup>14</sup> resulted in a complex that decomposed to insoluble, presumably polymeric products, within 30 min. These results suggest that in the  $[\text{M}(\text{CO})_3(\text{tptach})]$  system the M–CO bonding is too strong and/or the M–tptach bonding is too weak for this system to be useful for examination of intramolecular metal–alkyne interactions. The small quantities in which

$[\text{CrCl}_3(\text{tptach})]$  could be synthesized prevented studies of Cr–alkyne co-ordination in this system.

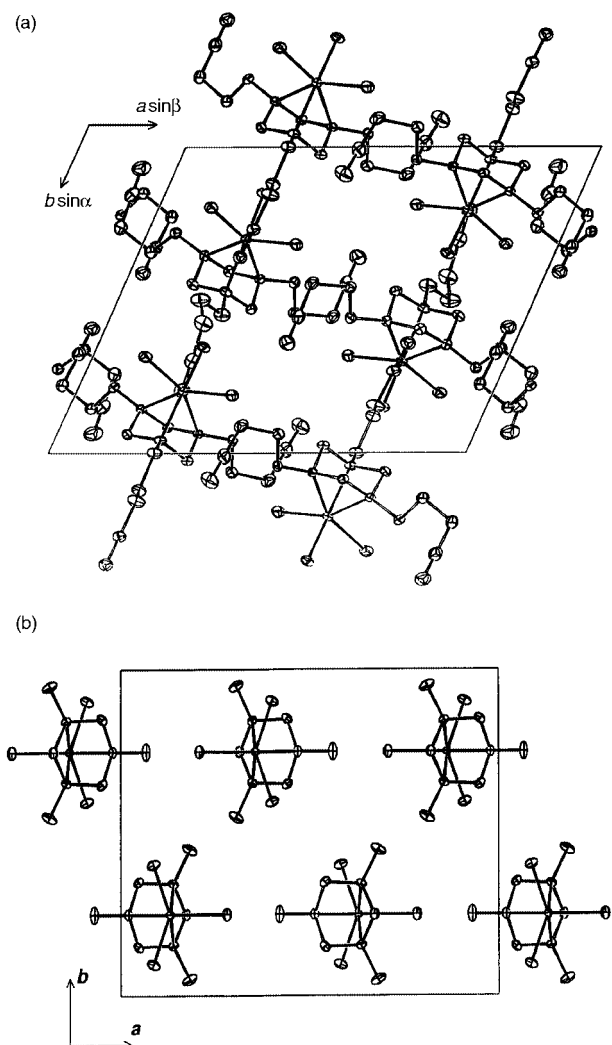
#### Structural characterisation

The results of the room-temperature single crystal X-ray studies of  $[\text{CrBr}_3(\text{tmtach})]$  and  $[\text{CrCl}_3(\text{tptach})]$  are consistent with the formulation of the two complexes as mononuclear (Figs. 1, 2; Tables 1, 2), neither complex being solvated. The complex  $[\text{CrBr}_3(\text{tmtach})]$  crystallises in the orthorhombic space group  $Pnma$ , the molecules lying disposed across crystallographic mirror planes, which contain the Cr atom, one of the bromine atoms, and an opposed C,N pair of ring atoms, the full potential  $3m$  symmetry of the molecule not being realised crystallographically. In this respect the molecule resembles its tricarbonyl analogue,<sup>7</sup> although not isomorphous, the latter similarly is disposed across a crystallographic mirror plane in the orthorhombic space group  $Ibam$ . The only substantial differences between  $[\text{CrBr}_3(\text{tmtach})]$  and  $[\text{Cr}(\text{CO})_3(\text{tmtach})]$  are found, as might be expected, in parameters directly involving the halide atoms, (compare Cr–N for  $[\text{CrBr}_3(\text{tmtach})]$  and  $[\text{Cr}(\text{CO})_3(\text{tmtach})]$  in Table 3). The companion structure,

**Table 1** Non-hydrogen molecular geometry (distances in Å, angles in °) of [CrBr<sub>3</sub>(tmtach)]

Cr–Br(1)	2.4390(6)	N(1)–C(1)	1.459(7)
Cr–Br(2)	2.436(1)	N(1)–C(2)	1.479(4)
		C(2)–N(3)	1.458(5)
Cr–N(1)	2.104(4)	N(3)–C(3)	1.475(6)
Cr–N(3)	2.108(3)	N(3)–C(4)	1.476(4)
Br(1)–Cr–Br(2)	98.58(3)	Cr–N(1)–C(1)	130.0(4)
Br(1)–Cr–N(1)	94.80(3)	Cr–N(1)–C(2)	92.3(2)
Br(1)–Cr–N(3)	94.98(7)	C(1)–N(1)–C(2)	114.8(3)
Br(1)–Cr–Br(1')	99.73(3)	C(2)–N(1)–C(2')	108.9(3)
Br(1)–Cr–N(3')	156.39(8)	N(1)–C(2)–N(3)	101.7(3)
Br(2)–Cr–N(1)	159.2(1)	Cr–N(3)–C(2)	92.7(2)
Br(2)–Cr–N(3)	97.36(8)	Cr–N(3)–C(3)	130.2(2)
N(1)–Cr–N(3)	65.5(1)	Cr–N(3)–C(4)	92.1(2)
N(3)–Cr–N(3')	65.7(1)	C(2)–N(3)–C(3)	113.9(3)
		C(2)–N(3)–C(4)	109.6(3)
		C(3)–N(3)–C(4)	114.7(3)
N(3)–C(4)–N(3')	101.6(3)		

Primed atoms are related by the mirror  $x, \frac{1}{2} - y, z$ . Torsion angles around the ring in bonds 1–2, 2–3, 3–4 are 68.8(3), –68.8(3), 68.4(4)°.



**Fig. 2** Unit cell projections of (a) [CrCl<sub>3</sub>(tptach)] and (b) [CrBr<sub>3</sub>(tmtach)] down the short crystallographic axes (*c* in both cases) showing the actual or quasi-symmetry in the packing of the two complexes.

[CrCl<sub>3</sub>(tptach)], provides a trichloride counterpart, the first so recorded for a tach ligand type; the literature records the structural characterisation of [CrCl<sub>3</sub>(tnbtacn)] (a triazacyclononane array; tnbtacn = 1,4,7-tri-*n*-butyl-1,4,7-triazacyclononane).<sup>15</sup> In [CrCl<sub>3</sub>(tptach)] two independent molecules, pseudosymmetrically related and with similar pendant substituent dispositions, comprise the asymmetric unit of the structure. The

desired functionalisation within the pendants to the ligand is confirmed, the pendant dispositions being quite disparate and seemingly devoid of any significant interactions with neighbouring moieties, either intra- or inter-molecular (exception: Cl(12)⋯H(135) ( $x, 1 + y, z$ ) 2.7 Å). As expected, the Cr–Cl distances are shorter than the Cr–Br distances in the companion compound. Again, the impact on the parameters of the remainder of the molecules is minimal, even, surprisingly, insofar as the interhalogen angles are concerned, these being appreciably splayed above 90° in both compounds as might be expected, given the constraint of the N<sub>3</sub> array. Significant differences are found between the present N<sub>3</sub>CrCl<sub>3</sub> core and that of the [CrCl<sub>3</sub>(tnbtacn)] analogue, the increased spread of the N<sub>3</sub> tridentate tnbtacn being reflected in associated geometries and those of the CrCl<sub>3</sub> array in the manner expected (Table 3).

## Experimental

General procedures were as described previously.<sup>7</sup> Microanalyses were performed by the Microanalytical Unit, Research School of Chemistry, Australian National University, Canberra, A.C.T. The complexes [M(CO)<sub>3</sub>(CH<sub>3</sub>CH<sub>2</sub>CN)<sub>3</sub>] (M = Cr or Mo),<sup>16</sup> [CrCl<sub>3</sub>(thf)<sub>3</sub>],<sup>17</sup> and 5-amino-1-pentyne<sup>18</sup> were prepared according to literature methods.

### Synthesis of 1,3,5-tri(4-pentynyl)-1,3,5-triazacyclohexane (tptach)

Paraformaldehyde (4.2 g, 0.14 mol) was added portionwise to a stirred solution of 5-amino-1-pentyne (6.6 g, 0.08 mol) in ether (150 cm<sup>3</sup>). Stirring was continued overnight. The mixture was filtered and the filtrate dried over MgSO<sub>4</sub> and then concentrated *in vacuo* to afford tptach as a pale yellow oil, in quantitative yield, bp 100–110 °C (0.01–0.05 mmHg) (Found: C, 75.60; H, 9.92; N, 14.60. C<sub>6</sub>H<sub>9</sub>N requires C, 75.74; H, 9.53; N, 14.72%);  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  (NaCl) 3297vs (=C–H stretch), 2947vs, 2804vs, 2116m (C≡C stretch), 1454s, 1365s, 1254s, 1152s, 1006m, 919m and 637s;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>CO] 1.62 (6 H, tt, *J*(H1H2) 7.0, *J*(H2H3) 7.1, 6 × H2), 2.22 (6 H, dt, *J*(H3H5) 2.7 Hz, 6 × H3), 2.30 (3 H, t, 3 × H5), 2.53 (6 H, t, 6 × H1) and 3.3 (6 H, br s, *W*<sub>h/2</sub> 80 Hz, 3 × NCH<sub>2</sub>N);  $\delta_{\text{C}}$  [(CD<sub>3</sub>)<sub>2</sub>CO] 16.4 (C3), 27.4 (C2), 51.7 (C1), 69.8 (C5), 75.1 (NCH<sub>2</sub>N) and 84.8 (C4).

### Synthesis of chromium and molybdenum complexes

**[Cr(CO)<sub>3</sub>(tptach)].** A solution of [Cr(CO)<sub>3</sub>(CH<sub>3</sub>CH<sub>2</sub>CN)<sub>3</sub>] (0.62 g, 2.1 mmol) in acetone (2 cm<sup>3</sup>) was added to a solution of tptach (0.60 g, 2.1 mmol) in acetone (1.5 cm<sup>3</sup>), stirred for 1 h then diluted with ether (20 cm<sup>3</sup>). The resulting precipitate was collected, washed with ether (10 cm<sup>3</sup>) and dried *in vacuo* to yield [Cr(CO)<sub>3</sub>(tptach)] as a yellow-orange powder (0.65 g, 74%), mp 180 °C (decomp.) (Found: C, 60.24; H, 6.75; N, 9.76. C<sub>21</sub>H<sub>27</sub>CrN<sub>3</sub>O<sub>3</sub> requires C, 59.85; H, 6.46; N, 9.97%);  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  (KBr) 2116w (C≡C stretch), 1908, 1771 and 1735 (CO);  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>CO] 1.93 (6 H, m, 6 × H2), 2.34 (6 H, dt, *J*(H2H3) 7.0, *J*(H3H5) 2.66 Hz, 6 × H3), 2.39 (3 H, t, 3 × H5), 2.71 (6 H, m, 6 × H1), 4.14 (3 H, apparent d, splitting 8.4 Hz, 3 × NCH<sub>2</sub>N) and 4.71 (3 H, apparent d, splitting 8.4 Hz, 3 × NCH<sub>2</sub>N);  $\delta_{\text{C}}$  [(CD<sub>3</sub>)<sub>2</sub>CO] 16.5 (C3), 26.2 (C2), 53.8 (C1), 69.8 (C5), 80.9 (NCH<sub>2</sub>N), 83.8 (C4) and 237.4 (CO).

**[Mo(CO)<sub>3</sub>(tptach)].** This compound was prepared in the same way as for [Cr(CO)<sub>3</sub>(tptach)]. Yield 49%; mp 140 °C (decomp.) (Found: C, 53.94; H, 5.87; N, 8.85. C<sub>21</sub>H<sub>27</sub>MoN<sub>3</sub>O<sub>3</sub> requires C, 54.20; H, 5.85; N, 9.03%);  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  (KBr) 2116w (C≡C stretch), 1909, 1776 and 1737 (CO);  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>CO] 1.87 (6 H, m, 6 × H2), 2.36 (6 H, dt, *J*(H2H3) 7.0, *J*(H3H5) 2.6 Hz, 6 × H3), 2.39 (3 H, t, 3 × H5), 2.67 (6 H, m, 6 × H1), 4.20 (3 H, apparent d, splitting 8.8 Hz, 3 × NCH<sub>2</sub>N) and 4.74 (3 H, apparent d, splitting 9.0 Hz, 3 × NCH<sub>2</sub>N);  $\delta_{\text{C}}$  [(CD<sub>3</sub>)<sub>2</sub>CO] 16.4

**Table 2** Selected molecular geometries of [CrCl<sub>3</sub>(tptach)]. The two values in each entry are for molecules 1,2(a) The chromium environments;  $r/\text{\AA}$  is the metal–ligand distance; the other entries are the angles (°) subtended by the atoms at the head of the row and column

	$r$	Cl(2)	Cl(3)	N(1)	N(3)	N(5)
Cl(1)	2.293(2)	98.75(8)	100.66(7)	156.7(1)	95.2(2)	94.7(1)
	2.286(2)	98.69(8)	100.07(7)	157.6(6)	95.7(2)	95.8(1)
Cl(2)	2.267(3)		98.10(8)	96.3(2)	158.1(2)	96.3(2)
	2.277(2)		98.39(7)	95.1(2)	156.0(2)	93.8(2)
Cl(3)	2.292(2)			94.7(1)	95.8(1)	157.0(2)
	2.290(2)			95.2(1)	97.9(1)	158.2(2)
N(1)	2.094(5)				65.7(2)	66.0(2)
	2.094(5)				65.9(2)	65.7(2)
N(3)	2.101(5)					65.6(2)
	2.130(5)					65.5(2)
N(5)	2.099(3)					
	2.106(3)					

(b) Ligand geometries

N(1)–C(2)	1.478(9), 1.477(9)	C(4)–N(5)	1.480(9), 1.466(9)
C(2)–N(3)	1.487(8), 1.477(8)	N(5)–C(6)	1.473(8), 1.478(8)
N(3)–C(4)	1.469(6), 1.481(6)	C(6)–N(1)	1.486(6), 1.482(6)
C(14)–C(15)	1.16(1), 1.16(2)	C(54)–C(55)	1.16(2), 1.15(1)
C(34)–C(35)	1.16(1), 1.19(1)		
Cr–N(1)–C(11)	127.7(3), 127.1(3)	Cr–N(3)–C(31)	125.9(3), 135.3(4)
Cr–N(1)–C(2)	93.3(4), 92.8(4)	Cr–N(3)–C(4)	92.9(4), 91.6(4)
Cr–N(1)–C(6)	92.1(3), 92.7(3)	Cr–N(3)–C(2)	92.7(4), 91.4(4)
C(11)–N(1)–C(2)	115.8(5), 116.2(5)	C(31)–N(3)–C(4)	115.0(4), 109.3(4)
C(11)–N(1)–C(6)	114.1(5), 114.7(5)	C(31)–N(3)–C(2)	116.6(5), 116.6(6)
C(2)–N(1)–C(6)	110.3(4), 109.5(4)	C(2)–N(3)–C(4)	109.6(4), 108.7(5)
Cr–N(5)–C(51)	128.5(4), 127.0(4)	N(1)–C(2)–N(3)	100.2(5), 102.1(5)
Cr–N(5)–C(6)	92.2(2), 92.4(2)	N(3)–C(4)–N(5)	101.0(4), 102.1(4)
Cr–N(5)–C(4)	92.7(3), 93.0(3)	N(5)–C(6)–N(1)	100.9(4), 100.6(5)
C(51)–N(5)–C(6)	114.1(5), 115.1(5)	C(13)–C(14)–C(15)	179.3(6), 179.0(8)
C(51)–N(5)–C(4)	115.7(4), 115.5(4)	C(33)–C(34)–C(35)	178.3(9), 179(1)
C(4)–N(5)–C(6)	110.0(5), 110.2(5)	C(53)–C(54)–C(55)	178.3(6), 178.3(7)

Ring torsion angles (°) in the bonds

N(1)–C(2)	–68.9(5), –69.4(5)	C(4)–N(5)	69.2(4), 69.2(5)
C(2)–N(3)	69.7(5), 68.1(5)	N(5)–C(6)	–68.0(4), –68.8(5)
N(3)–C(4)	–69.9(6), –67.9(6)	C(6)–N(1)	68.6(5), 68.5(6)

**Table 3** Comparative [CrX<sub>3</sub>(tacx)] core data. Average values (distances in Å, angles in °) are given; the data for [Cr(CO)<sub>3</sub>(tmtach)] and [CrCl<sub>3</sub>(tnbtacn)] are taken from references 7 and 15 respectively

	[CrCl <sub>3</sub> (tnbtacn)]	[CrCl <sub>3</sub> (tptach)]	[CrBr <sub>3</sub> (tmtach)]	[Cr(CO) <sub>3</sub> (tmtach)]
Cr–L	2.324(6)	2.28(1)	2.438(2)	1.800(7)
Cr–N	2.149(6)	2.10(1)	2.107(2)	2.17(2)
N–Cr–N	82.4(4)	65.7(2)	65.6(1)	63.3(3)
L–Cr–L	92.4(7)	99(1)	99.0(7)	87(2)
N–Cr–L( <i>trans</i> )	173.0(9)	157.3(9)	156.3(1)	164.13(6)
N–Cr–L	92(1)	96(1)	96(1)	104(1)

(C3), 27.1 (C2), 52.9 (C1), 70.6 (C5), 81.1 (NCH<sub>2</sub>N), 83.8 (C4) and 231.8 (CO).

**[CrCl<sub>3</sub>(tptach)].** A solution of tptach (0.44 g, 1.5 mmol) in thf (40 cm<sup>3</sup>) was dried over 4 Å molecular sieves for 18 h. The solution was filtered and [CrCl<sub>3</sub>(thf)<sub>3</sub>] (0.52 g, 1.4 mmol) added to the filtrate. The resulting solution was stirred for 2 weeks. The mixture was concentrated *in vacuo* and the residue washed with water (100 cm<sup>3</sup>), leaving a purple solid. The solid was extracted with acetone (50 cm<sup>3</sup>). The extract was dried over CaCl<sub>2</sub>, passed through a silica plug, and concentrated *in vacuo* to yield [CrCl<sub>3</sub>(tptach)] as a mauve powder (20 mg, 3%). The powder was recrystallised from acetone by addition of 1:1 hexane–toluene, mp 262 °C (decomp.) (Found: C, 48.15; H, 6.17; N, 9.21. C<sub>18</sub>H<sub>27</sub>Cl<sub>3</sub>CrN<sub>3</sub> requires C, 48.72; H, 6.13; N, 9.47%);  $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$  (KBr) 3280vs, 2940m, 2115w (C≡C stretch),

1642m, 1457m, 1132vs, 1100vs, 934s and 621s;  $m/z$  407.0996 (M – Cl) (requires 407.0987).

**[CrBr<sub>3</sub>(tmtach)].** The complex [Cr(CO)<sub>3</sub>(tmtach)] (0.39 g, 1.5 mmol) was added to a stirred solution of *N*-bromosuccinimide (0.89 g, 5.0 mmol) and tetrabutylammonium bromide (2.8 g, 8.7 mmol) in dichloromethane (20 cm<sup>3</sup>). The solution immediately bubbled and darkened. Stirring was continued for 2 h. The solvent was removed *in vacuo* and the residue diluted with saturated sodium bromide solution (100 cm<sup>3</sup>). The resulting precipitate was collected and washed with water (100 cm<sup>3</sup>), ethyl acetate (150 cm<sup>3</sup>) and methanol (50 cm<sup>3</sup>). The purple solid was extracted with acetone (700 cm<sup>3</sup>). The extract was concentrated to 15 cm<sup>3</sup> and then diluted with light petroleum (bp 64–80 °C) (15 cm<sup>3</sup>). The precipitate was collected and dried *in vacuo* to yield [CrBr<sub>3</sub>–

(tmtach)] as a purple solid (0.16 g, 26%), mp >280 °C (decomp.) (Found : C, 17.07; H, 3.62; N, 10.14. C<sub>6</sub>H<sub>15</sub>Br<sub>3</sub>CrN<sub>3</sub> requires C, 17.12; H, 3.59; N, 9.98%);  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  (KBr) 2997, 2930, 1464s, 1253s, 1115s, 1109s, 1000m, 936m, 918s, 510s and 420.

### Structure determinations

Crystals of [CrCl<sub>3</sub>(tptach)] were grown by the slow evaporation of a saturated acetone solution into DMF. Crystals of [CrBr<sub>3</sub>(tmtach)] were grown from a saturated acetonitrile–nitromethane (1 : 3) solution *via* solvent vapour diffusion into toluene.

For both compounds spheres of diffraction data were measured at room temperature using monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å), yielding  $N_{\text{(total)}}$  reflections, reducing to  $N$  unique ( $R_{\text{int}}$  quoted) after absorption correction,  $N_{\text{o}}$  being considered ‘observed’ and used in the full matrix least squares refinements. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, ( $x, y, z, U_{\text{iso}}\text{H}$ ) being constrained at estimated values. Conventional residuals  $R$ ,  $R_{\text{w}}$  (statistical weights) on  $|F|$  are quoted at convergence. Neutral atom complex scattering factors were employed, the XTAL 3.4 program system<sup>19</sup> being used. Pertinent results are given below and in the Figures, Tables and text.

**[CrCl<sub>3</sub>(tptach)].** C<sub>18</sub>H<sub>27</sub>Cl<sub>3</sub>CrN<sub>3</sub>,  $M = 443.9$ . Single counter diffractometer,  $2\theta$ – $\theta$  scan mode. Triclinic, space group  $P\bar{1}$  ( $C_1^1$ , no. 2) (pseudo-monoclinic  $C$ ),  $a = 15.530(5)$ ,  $b = 13.770(7)$ ,  $c = 12.697(5)$  Å,  $\alpha = 115.93(3)$ ,  $\beta = 101.53(3)$ ,  $\gamma = 105.48(3)^\circ$ ,  $V = 2192$  Å<sup>3</sup>.  $D_{\text{c}}$  ( $Z = 4$ ) = 1.34<sub>5</sub> g cm<sup>-3</sup>;  $F(000) = 924$ .  $\mu_{\text{Mo}}$  = 8.9 cm<sup>-1</sup>; specimen 0.30 × 0.50 × 0.08 mm;  $T_{\text{min, max}} = 0.78, 0.94$  (gaussian correction).  $2\theta_{\text{max}} = 50^\circ$ ;  $N_{\text{t}} = 13900$ ,  $N = 7710$  ( $R_{\text{int}} = 0.033$ ),  $N_{\text{o}}$  ( $I > 2\sigma(I)$ ) = 4519;  $R = 0.048$ ,  $R_{\text{w}} = 0.056$ ;  $n_{\text{v}} = 451$ ,  $|\Delta\rho_{\text{max}}| = 0.49(3)$  e Å<sup>-3</sup>.  $T$  ca. 295 K.

‘Crystal decomposition’, as measured by isotropic deterioration in the standard reflections over time by ca. 10%, was compensated for by appropriate scaling.

**[CrBr<sub>3</sub>(tmtach)].** C<sub>6</sub>H<sub>15</sub>Br<sub>3</sub>CrN<sub>3</sub>,  $M = 420.9$ . Bruker AXS CCD area-detector instrument. Orthorhombic, space group  $Pnma$ , ( $D_{2h}^{16}$ , no. 62),  $a = 15.476(2)$ ,  $b = 12.159(1)$ ,  $c = 7.0261(8)$

Å,  $V = 1322$  Å<sup>3</sup>.  $D_{\text{c}}$  ( $Z = 4$ ) = 2.11<sub>4</sub> g cm<sup>-3</sup>;  $F(000) = 804$ .  $\mu_{\text{Mo}}$  = 99 cm<sup>-1</sup>; specimen 0.35 × 0.30 × 0.20 mm; ‘ $T$ ’<sub>min, max</sub> = 0.40, 0.70 (‘empirical’ correction (‘SADABS’)).  $2\theta_{\text{max}} = 58^\circ$ ;  $N_{\text{t}} = 14359$ ,  $N = 1745$  ( $R_{\text{int}} = 0.030$ ),  $N_{\text{o}}$  ( $F > 4\sigma(F)$ ) = 1449;  $R = 0.031$ ,  $R_{\text{w}} = 0.044$ ;  $n_{\text{v}} = 68$ ,  $|\Delta\rho_{\text{max}}| = 1.27(5)$  e Å<sup>-3</sup>.

CCDC reference number 186/1777.

See <http://www.rsc.org/suppdata/dt/a9/a908349i/> for crystallographic files in .cif format.

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