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FULL PAPER

An investigation of 1,4,7-tri(4-alkynyl)-1,4,7-triazacyclononanes: ligand synthesis and metal co-ordination chemistry †

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Three triazacyclononanes bearing pendant alkynyl groups [1,4,7-tri(4-pentynyl)-1,4,7-triazacyclononane (ptacn), 1,4,7-tri(5-phenyl-4-pentynyl)-1,4,7-triazacyclononane (pptacn) and 1,4,7-tri(4-hexynyl)-1,4,7-triazacyclononane (4htacn)] have been synthesized. Seven complexes, $[Mo(CO)_3(pptacn)]$, $[Rh(cod)(pptacn)][PF_6]$, $[RhCl_3(pptacn)]$, $[CuCl_2(pptacn)]$, $[Ni_2(\mu\text{-}Cl)_3(pptacn)_2]Cl$, $[Rh(CO)_2(4htacn)][PF_6]$ and $[Mo(CO)_3(ptacn)]$, each of which bears three pendant alkynyl groups, have been prepared. Single-crystal structure determinations for $[H(4htacn)][BPh_4]$, $[Mo(CO)_3(pptacn)]$, $[Rh(cod)(pptacn)][PF_6]$ and $[CuCl_2(pptacn)]$ are reported.

Introduction

We recently reported the synthesis of 1,3,5-tri(4-pentynyl)-1,3,5-triazacyclohexane and its $Cr(CO)_3$, $Mo(CO)_3$ and $CrCl_3$ complexes.[1] The instability of the triazacyclohexane ligand and the metal complexes has prevented any substantial study into intramolecular alkyne–metal bonding. We have now turned our attention to the well known triazacyclononanes (tacn), a system which has a more robust azacycle core and well known metal co-ordination chemistry.[2,3] The increased stability of the ligands and their metal complexes should provide a platform for continued study into the intramolecular co-ordination of alkynes to metals, an area which still remains, in the most part, unexplored. Reports of alkynyl functionalised triazacyclononanes are scarce. Latva and co-workers[4,5] have studied the fluorescence of lanthanide ions in the presence of an alkynyl–tacn system, but did not isolate any metal–tacn complexes. Peacock and co-workers have recently published the first isolation and crystallographic study of alkynyl functionalised tacn metal complexes,[6] complexes of Cu^{II}, Ni^{II}, Co^{II}, and Mo^0 being reported, most of which contained a single alkynyl group linked to a tacn nitrogen by a methylene or ethylene spacer unit. Although various metal complexes of simple alkyl substituted tacns have been recorded, including Rh–CO,[7] Rh–cod (cod = cycloocta-1,5-diene),[8] Rh-halide[9] and Group 6 metal carbonyl and halide adducts,[10,11] the study of the co-ordination chemistry of R_3tacns, where R is an extended alkyl substituent, generally remains limited. By contrast, there are many reports of the co-ordination chemistry of R_3tacn where R is methyl or isopropyl.

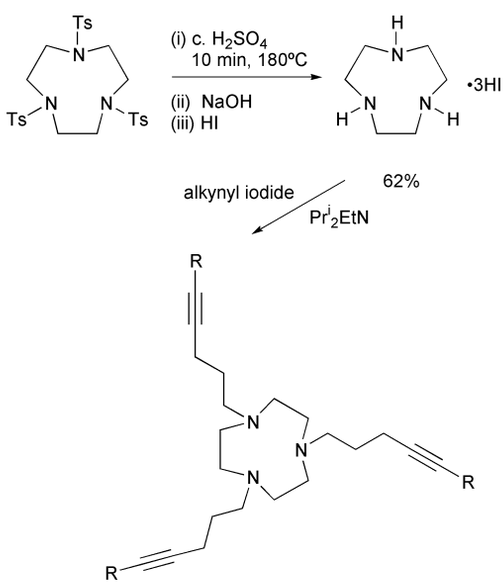
To investigate the possibility of metal–alkyne interactions in alkynyl–tacn complexes, we have explored the use of a three-carbon spacer unit between the alkynyl group and the tacn nitrogens, rather than the shorter units examined by Peacock and co-workers. Here we report the synthesis and some co-ordination chemistry of three trialkynyl tacns, 1,4,7-tri(4-pentynyl)-1,4,7-triazacyclononane (ptacn), 1,4,7-tri(5-phenyl-4-pentynyl)-1,4,7-triazacyclononane (pptacn) and 1,4,7-tri-(4-hexynyl)-1,4,7-triazacyclononane (4htacn).

† Electronic supplementary information (ESI) available: unit cell contents of $[Mo(CO)_3(pptach)]$. See http://www.rsc.org/suppdata/dt/b0/b007324p/

Results and discussion

Synthesis of alkynyl functionalised 1,4,7-triazacyclononanes

The majority of *N*-functionalised tacns are prepared with reactive reagents such as aldehydes, acid chlorides, halogeno-methylcarbonyl compounds and benzyl halides[2,3] with a few examples of alkyl halides[12–15] being used. The easiest synthetic method for the preparation of alkynyl–tacns appeared to be *via* the alkyl halide route. Consequently, the alkynyl tacn ligands were synthesized by the reaction of 1,4,7-triazacyclononane trihydroiodide with the corresponding alkynyl iodide and ethyldiisopropylamine in acetonitrile (Scheme 1). This



Scheme 1 Ts = Toluene-*p*-sulfonyl.

method appears to be general for the high yield preparation of tacns substituted with extended alkyl chains. Initial attempts at the synthesis of the ligands began using tacn·3HCl instead of tacn·3HI but the reactions were slow. Analysis of the reaction

mixtures indicated that reactions involving tacn·3HCl were complicated by conversion of the alkynyl iodides into the less-reactive alkynyl chlorides.

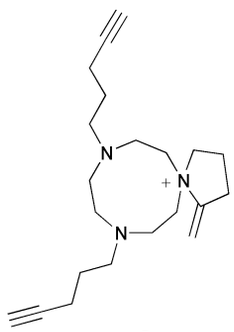
The salt tacn·3HI was prepared by a variation of the method of Fabbrizzi and co-workers.[16] It was isolated, in 62% yield, as a white powder by treatment of free tacn with purified hydriodic acid. It is far more soluble than the chloride analogue. The alkynyl iodides were all easily prepared (see Experimental section).

The phenyl-terminated alkynyl ligand pptacn was prepared in *ca*. 60% yield from tacn·3HI, 5-iodo-1-phenyl-1-pentyne and $(i\text{-Pr})_2$EtN in acetonitrile. If Et_3N was used instead of $(i\text{-Pr})_2$EtN then the yield of pptacn was reduced, as the iodoalkyne reacted with Et_3N to form a quaternary ammonium species, triethyl(5-phenyl-4-pentynyl)ammonium iodide. Purification of pptacn was achieved by flash chromatography (silica with 5% $Et_3N/CHCl_3$). The early fractions in the purification showed traces of 1-phenylpent-4-en-1-yne, an elimination product. The ligand pptacn is readily soluble in most organic solvents. The syntheses of 4htacn and ptacn were analogous to that of pptacn.

The methyl-terminated (*i.e.* 4-hexynyl) ligand 4htacn was purified by rapid silica filtration and isolated in *ca*. 75% yield. The basic nature of the tri-substituted tacns was exemplified by the immediate precipitation of [H(4htacn)][BPh_4] on addition of a methanolic solution of sodium tetraphenylborate to a methanolic solution of 4htacn. In this experiment the proton source was the methanol, with the insoluble nature of the product providing the driving force for the reaction. This protonation phenomenon has been noted previously for the bulky systems 1,4,7-triisopropyl-1,4,7-triazacyclononane and 1,4,7-triisobutyl-1,4,7-triazacyclononane in the presence of a protic solvent (alcohol or water) and a suitably large counter anion (ClO_4^- or $FeCl_4^-$).[11,12] Wieghardt and co-workers reported a large formation constant for the mono-protonated form of 1,4,7-triisopropyl-tacn [pK_a (i-Pr$_3$tacn·H$^+$) > 14], which has been attributed to intramolecular hydrogen bonding. Consequently it has been recommended that attempted syntheses of transition-metal complexes of this ligand should avoid protic species in the reaction (*i.e.* water, alcohols).[11]

The structure of the protonated species [H(4htacn)][BPh_4] was confirmed by an X-ray study, suitable crystals being grown from an EtOAc–MeOH solution. This structure also shows intramolecular hydrogen bonding (see Structural characterisation). The ^{1}H NMR spectrum for solutions of [H(4htacn)][BPh_4] exhibit a downfield singlet for the hydrogen-bonded NH (δ 9.85, acetone-d_6) and a symmetrical multiplet, which we assign as an AA′BB′ pattern, for the ring methylene groups. The downfield chemical shift of the NH signal is consistent with the persistence of strong hydrogen bonding in solution. The apparent symmetry of the ring methylene signals is consistent with a structure in solution where either the NH proton migrates from one ring nitrogen to another rapidly on the NMR timescale, or the proton is simultaneously bound to each nitrogen atom, and where the environments of the *exo* and *endo* ring protons are not undergoing rapid exchange, *i.e.* inversion of the tacn ring is slow on the NMR timescale.

The terminal alkynyl ligand ptacn was isolated in ≈60% yield after purification by rapid silica filtration. In methanol solutions at room temperature, it undergoes a facile intramolecular hydroamination of one of its pendant alkynyl groups, resulting in formation of an azonia-spiro[4.8]tridecane (**I**), synthesis and characterisation of which, including X-ray studies, are reported elsewhere.[17]



I

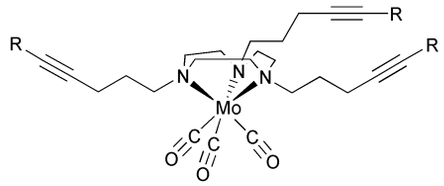
Synthesis of tacn–metal complexes

To study intramolecular alkyne–metal co-ordination in molybdenum and rhodium systems, we aimed first to synthesize complexes in which the metal was bound by the N_3 core of the tacn system, and subsequently investigate reactions of pendant alkynyl groups with the metal centre. Metal–tacn complexes which contained CO, C_2H_4, cod, or Cl as ancillary ligands were targeted, as there are precedents for removal of these ancillary ligands from other metal–tacn systems and related complexes.[9,10,18,19]

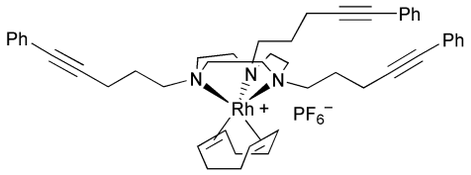
Molybdenum complexes. Pptacn reacted rapidly with [$Mo(CO)_3(CH_3CH_2CN)_3$] in acetone-d_6 to produce [$Mo(CO)_3$(pptacn)] in quantitative yield (by ^{1}H NMR spectroscopy). The reaction solution appeared to be stable and showed no change on standing. On a preparative scale the reaction was performed in acetone and was complete within 1 h. The complex was isolated in high yield (≈73%) as a pale beige powder. The high yield suggested that there were no significant complications arising from alkyne–metal interactions during the reaction. Attempted preparation of [$Mo(CO)_3$(pptacn)] by way of the literature methods for tacn–$Mo(CO)_3$ adducts, using $Mo(CO)_6$ in a high boiling solvent,[11] resulted in intractable black-brown decomposition products.

[$Mo(CO)_3$(pptacn)] showed high solubility in most polar solvents (*e.g.* acetone and CH_2Cl_2) and was insoluble in non-polar solvents (diethyl ether, hexane and benzene). The complex was air stable in the solid state but air-sensitive in solution. The infrared spectrum showed signals consistent with a facially co-ordinated $Mo(CO)_3$ complex.[10,11] The ^{1}H and ^{13}C NMR spectra showed signals typical of a tacn metal complex, the ^{1}H NMR signals for the tacn ring protons (NCH_2CH_2N) changing from a singlet for the "free" ligand to a complex but symmetrical pattern for the metal-bound ligand. The symmetry of this pattern suggests that it corresponds to an AA′BB′ spin system, *i.e.* in each NCH_2CH_2N group the two "inner" protons are chemically equivalent and the two "outer" protons are chemically equivalent. Crystallographic studies indicate that in the solid state the tacn ring adopts a conformation in which the C–H bonds on the tacn ring are staggered so that each proton is different. If such a conformation was maintained in solution the NCH_2CH_2N groups should appear as an ABCD spin system; the observation of an AA′BB′ pattern suggests the tacn ring is fluxional, the two possible staggered conformations interconverting rapidly on the NMR timescale.[20] This dynamic nature is also apparent in the ^{13}C NMR spectrum, which exhibits only one signal for the ring carbons.[20]

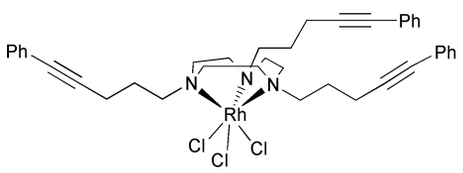
Reaction of ptacn with [$Mo(CO)_3(CH_3CH_2CN)_3$] in acetone afforded [$Mo(CO)_3$(ptacn)] as a beige powder in 65% yield. This complex is much less soluble than the phenyl terminated alkyne analogue [$Mo(CO)_3$(pptacn)]. The infrared, ^{1}H and ^{13}C NMR spectra were consistent with its formulation as *fac*-[$Mo(CO)_3$(ptacn)]. It exhibited slight solubility in acetone, CH_2Cl_2 and CH_3NO_2. The complex could be recrystallised from both acetone and CH_2Cl_2. This crystallisation is in contrast to our attempts with the analogous complex of (1,3,5-tri-(4-pentynyl)-1,3,5-triazacyclohexane), which, while prepared in an identical manner to [$Mo(CO)_3$(ptacn)], showed such instability that no crystals could be grown before the complex decomposed.[1] This result demonstrates the greater stability



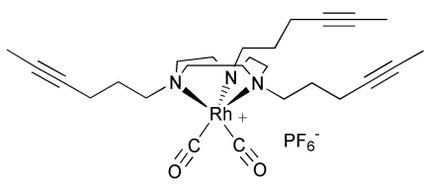
[Mo(CO)$_3$(ptacn)] R = H
[Mo(CO)$_3$(pptacn)] R = Ph



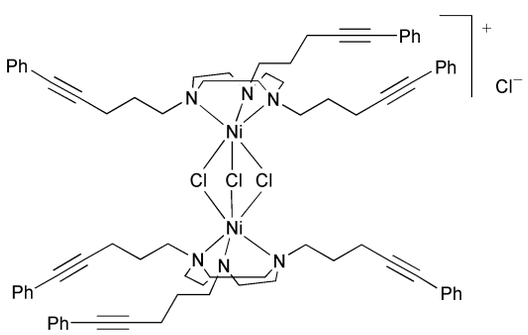
[Rh(cod)(pptacn)]PF$_6$



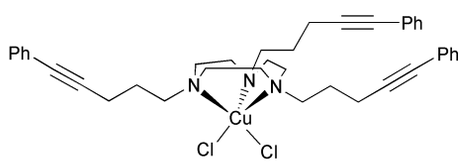
[RhCl$_3$(pptacn)]



[Rh(CO)$_2$(4htacn)]PF$_6$



[Ni$_2$(μ-Cl)$_3$(pptacn)$_2$]Cl



[CuCl$_2$(pptacn)]

of the tacn–metal complexes compared to the less robust triazacyclohexane–metal complexes.

Rhodium complexes. [Rh(cod)(pptacn)][PF$_6$] was prepared by a variation of the literature methods for [Rh(cod)(Me$_3$tacn)][PF$_6$] (Me$_3$tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane)[8] and [Rh(cod)(ttcn)][PF$_6$] (ttcn = 1,4,7-trithiacyclononane).[19] The reaction of pptacn and [Rh$_2$(μ-Cl)$_2$(cod)$_2$] in the presence of KPF$_6$ in acetone yielded [Rh(cod)(pptacn)][PF$_6$], in quantitative yield (by ^{1}H NMR analysis). On a preparative scale the product was isolated as a yellow powder in 67% yield and was recrystallised from acetone–ether solutions. It is readily soluble in acetone, dmso, $CHCl_3$ and CH_2Cl_2, air-stable in the solid state, but decomposes slowly in solutions exposed to air. In the absence of air it shows good thermal stability; a solution of [Rh(cod)(pptacn)][PF$_6$] in acetone showed no appreciable change when heated at 80 °C for 5 h. The ^{1}H and ^{13}C NMR spectra of solutions of [Rh(cod)(pptacn)][PF$_6$] showed signals characteristic of [Rh(cod)(tacn)][PF$_6$] complexes.[8] The ^{1}H NMR spectrum exhibited an AA′BB′ pattern for the tacn ring protons, as well as 3 distinct signals for the cod, co-ordinated through both its alkene groups. The ^{13}C NMR spectrum showed a doublet due to rhodium–carbon coupling (J(Rh–C) 14.4 Hz), for the cod alkene carbons. Solutions in acetone-d_6 slowly decomposed over the course of 2 months.

An "NMR tube" reaction of 4htacn with [Rh$_2$(μ-Cl)$_2$(cod)$_2$] and KPF$_6$ in acetone-d_6 resulted in the quantitative formation of [Rh(cod)(4htacn)][PF$_6$]. A similar reaction with ptacn, however, resulted in a solution that exhibited large, broad signals in the ^{1}H NMR spectrum, as well as signals consistent with free cod, and on standing the sample became gelatinous. These results suggested that a polymerisation reaction had occurred in the ptacn experiment. The polymerisation did not, however, involve acetone-d_6; when the solvent was removed from the gelatinous sample the mass of the residue corresponded to the combined masses of the reagents. When either 1-hexyne or 1,8-nonadiyne was treated with [Rh$_2$(μ-Cl)$_2$(cod)$_2$] under similar conditions no reaction occurred. It is possible that ptacn reacted, through one or more of its nitrogens, with [Rh$_2$(μ-Cl)$_2$(cod)$_2$] to generate a species that subsequently reacted with the terminal alkynes. The reaction of terminal alkynes with rhodium complexes is well documented and often results in Rh–acetylide or alkyne oligomerisation products.[21,22]

A literature method for the preparation of [RhCl$_3$(tacn)] complexes involves mixing alcoholic solutions of $RhCl_3 \cdot 3H_2O$ and the tacn ligand, with the product being isolated as a yellow precipitate.[9,23] Flood and co-workers have reported the synthesis of [RhCl$_3$(R$_3$tacn)] (R = methyl, benzyl or neohexyl) and, whereas the methyl and benzyl complexes were found to be soluble in dmso, the neohexyl complex was insoluble in all common organic solvents, including dmso. Their attempts to prepare [RhCl$_3$(np$_3$tacn)] (np$_3$tacn = 1,4,7-tri(neopentyl)-1,4,7-triazacyclononane) failed, no reason being suggested.[9]

The reaction of pptacn with $RhCl_3 \cdot 3H_2O$ in ethanol resulted in immediate precipitation of a very insoluble brown solid. Its infrared spectrum exhibited broad signals, rather than the sharp signals characteristic of pptacn which are seen in the spectra of other pptacn metal complexes, which suggests the presence of polymeric species. Analysis of the filtrate from the reaction by ^{1}H NMR spectroscopy showed broadened and downfield-shifted signals for the methylene groups adjacent to the ring nitrogens of pptacn, suggesting the presence of protonated pptacn species. These results may be a consequence of metal–alkyne interactions, but in aprotic solvents (see below) [RhCl$_3$(CH$_3$CN)$_3$] forms a simple mononuclear adduct with pptacn. Perhaps a combination of metal–alkyne interactions and complications arising from the basicity of the tacn core and the presence of the protic solvent (ethanol), similar to those

encountered previously[11] and in the reaction of 4htacn with methanol (see above), result in the polymeric products in the $RhCl_3 \cdot 3H_2O$ case.

The reaction of pptacn with $[RhCl_3(CH_3CN)_3]$ in CH_3CN at room temperature rapidly afforded $[RhCl_3(pptacn)]$ as a yellow, micro-crystalline product in *ca*. 65% yield. While the solvent here was "aprotic", it was not rigorously dry. Small amounts of adventitious water did not affect the reaction, but the crystalline product did contain one molecule of water per molecule of complex (verified by ^1H NMR and microanalysis). The crystals were air stable and only sparingly soluble in cold dmso. The ^1H and ^{13}C NMR spectra of fresh dmso-d_6 solutions of the crystals showed signals consistent with pptacn bound to a metal centre. The mass spectrum (FAB) of a fresh solution of $[RhCl_3(pptacn)]$ in dmso showed strong peaks attributed to $\{[RhCl_3(pptacn)] \cdot dmso\}^+$ and $[RhCl_2(pptacn)]^+$ and a weaker peak attributed to $[RhCl_2(dmso)(pptacn)]^+$. $[RhCl_3(pptacn)]$ appeared to undergo slow solvolysis over the course of 2 weeks in dmso solutions, as indicated by changes in their NMR and mass spectra.

The ^1H and ^{13}C NMR spectra of a two week old solution of $[RhCl_3(pptacn)]$ in dmso-d_6 showed two sets of signals, one attributed to $[RhCl_3(pptacn)]$ and the other to $[RhCl_2(dmso\text{-}d_6)(pptacn)]Cl$. The mass spectrum (FAB) of this solution showed a strong signal attributed to the solvolysis product $[RhCl_2(dmso\text{-}d_6)(pptacn)]^+$ [*m*/*z* 812.2530 (requires 812.2561)]. The ^1H NMR spectra of solutions of the complexes showed the expected behaviours when the relative amounts of dmso-d_6 or chloride were changed; NMR spectra of more dilute solutions indicated a higher concentration of $[RhCl_2(dmso\text{-}d_6)(pptacn)]Cl$ compared to $[RhCl_3(pptacn)]$, while addition of KCl to a sample, followed by gentle warming, resulted in spectra showing an increase in the concentration of $[RhCl_3(pptacn)]$ compared to $[RhCl_2(dmso\text{-}d_6)(pptacn)]Cl$. Other examples of solvolysis in $RhCl_3$–tacn systems are known. During this work, Südfeld and Sheldrick reported the solvolysis of $[RhCl_3(Me_3tacn)]$ in dmso in the presence of $Ag(CF_3SO_3)$.[24] They found that only one chloride could be displaced by dmso even when an excess of Ag^+ was present.

The reaction of ptacn with $[RhCl_3(CH_3CN)_3]$ resulted in a complex mixture of species which could not satisfactorily be characterised. On prolonged standing of the mixture many of the species precipitated. The major product remaining in solution was tentatively identified as $[RhCl_3(ptacn)]$ on the basis of its ^1H NMR spectrum. It may be that in ptacn the terminal alkynes and ring nitrogens compete for the metal centre: when the alkynes bind to the metal first, other reactions subsequently occur and lead to many products, but when the tacn ring nitrogens bind first a more stable complex is formed.

The reaction of 4htacn with $[Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4]$ and KPF_6 in acetone-d_6 resulted in a dark brown solution. The ^1H NMR spectrum of the sample showed many signals but none that could be attributed to a product of formulation $[Rh(C_2H_4)_2(4htacn)][PF_6]$. The analogous reaction with pptacn gave similar results. The poor results in these experiments may be due to alkyne–alkene competition for the rhodium centre.

When 4htacn was treated with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ and KPF_6 in methanol-d_4 or acetone-d_6, $[Rh(CO)_2(4htacn)][PF_6]$ was formed. The ^1H and ^{13}C NMR spectra of the product showed resonances attributed to 4htacn bound to Rh only *via* its ring nitrogens. The ^{13}C NMR spectrum also showed a CO signal (δ_C 189.2, d, J(RhC) = 72 Hz) indicative of CO groups bound to a single Rh, *i.e.* the complex is mononuclear. In previous studies of the reaction of Me_3tacn with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in methanol both mononuclear and dinuclear products were reported.[7] Increased steric hindrance associated with the larger substituents in 4htacn relative to Me_3tacn may be responsible for the absence of dinuclear products in the present work. On a preparative scale, crude $[Rh(CO)_2(4htacn)][PF_6]$ was isolated as a dark brown-green powder which recrystallised as very thin bright yellow crystals from benzene–hexane. The complex is, however, unstable in solution; it has proven difficult to purify on a preparative scale, and crystals suitable for X-ray studies have not been obtained.

Nickel and copper complexes. The reaction of pptacn with $CuCl_2 \cdot 2H_2O$ or $NiCl_2 \cdot 6H_2O$ in ethanol yielded respectively the mononuclear species $[CuCl_2(pptacn)]$ and a product tentatively assigned as the dinuclear species $[Ni_2(\mu\text{-}Cl)_3(pptacn)_2]Cl$. There were no apparent complications arising from metal–alkyne interactions or the formation of $(pptacn)H^+$ in these experiments.

X-Ray studies (see below) confirmed the structure of $[CuCl_2(pptacn)]$ in the solid state, and the mass spectrum (FAB) for a CH_2Cl_2 solution of the complex showed a peak due to $[CuCl(pptacn)]^+$ but no peaks that could be attributed to any dinuclear species. Recrystallisation of $[Ni_2(\mu\text{-}Cl)_3(pptacn)_2]Cl$ proved difficult and yielded very fine light green needles, unsuitable for X-ray work. The structure of this complex was proposed on the basis of the mass spectrum (electrospray) of its solution in CH_3CN, which showed only a strong signal attributed to $[Ni_2(\mu\text{-}Cl)_3(pptacn)_2]^+$. In principle, an alternative possible structure is $[Ni_2Cl_2(\mu\text{-}Cl)_2(pptacn)_2]$, which contains a pair of edge-sharing octahedra. Previous studies[2,25] have shown that, for dinuclear metal halide adducts of 1,4,7-trimethyl-1,4,7-triazacyclononane, structures containing edge-sharing octahedra exhibit unfavourable steric interactions, so that structures containing face-sharing octahedra (as in $[Ni_2(\mu\text{-}Cl)_3(pptacn)_2]Cl$) tend to be formed.

Structure determinations

The results of the single crystal structure determinations for $[H(4htacn)][BPh_4]$, $[Mo(CO)_3(pptacn)]$, $[Rh(cod)(pptacn)][PF_6]$ and $[CuCl_2(pptacn)]$, executed at 'low'-temperature, are consistent with the stoichiometries, connectivities and stereochemistries indicated. In all cases one formula unit devoid of crystallographic symmetry comprises the asymmetric unit; the protonation pattern is unambiguous, and there is no reason to believe the bulk compound to be other than a racemate despite the fact that in two cases chiral space groups are adopted. In all of the species the torsion angles adopt a common pattern around the symmetrically substituted nine-membered ring of essentially threefold symmetry, regardless of whether the ring is co-ordinated or not. The substituent dispositions at the three nitrogens are likewise similar ('equatorial') about each ring and throughout the array, varying but slightly in pitch depending on co-ordination status, the immediate array being very similar throughout, *e.g.* taking the N_3 plane as datum, deviations δ_C(2,3; 5,6; 8,9; 11,41,71) are: 1.077(3), 0.608(3); 0.983(3), 0.506(3); 1.039(3), 0.561(3); 0.944(3), 0.734(4), 0.690(3) Å in $[H(4tacn)]^+$ and 1.072(8), 0.587(8); 1.061(8), 0.588(7); 1.046(7), 0.561(8); 0.491(9), 0.524(9), 0.533(9) Å in $[Mo(CO)_3(pptacn)]$, perhaps the most conspicuous difference being a 'flattening' of the pendant dispositions in the co-ordinated ligand *cf.* the other. Within the ring, the torsion angle pattern is broadly in conformity with that of the 'twist–boat–chair' ('TBC') form, the subject of previous molecular mechanics studies.[26]

$[H(4tacn)][BPh_4]$. This is a less usual example of the tacn ring in monoprotonated form. The structure (Fig. 1(a)) shows the protonic hydrogen H(1), with close contacts to N(4, 7) (distances: 2.12(2), 2.21(2) Å), the symmetry of the torsions suggesting that it does not impart undue perturbation to the conformation, and with a conformation similar to that in its tri-methyl substituted analogue,[27] where, although the ring has quasi-3 symmetry, torsions in the C–C bonds are 11(2), 18(1), 7(2)° and those either side −103(1), −108(1), −113(1); 91(1), 95(1), 91(1)°. The pendant rods, that at site 4 disordered, play a significant, if unremarkable, role in crystal packing. Anion

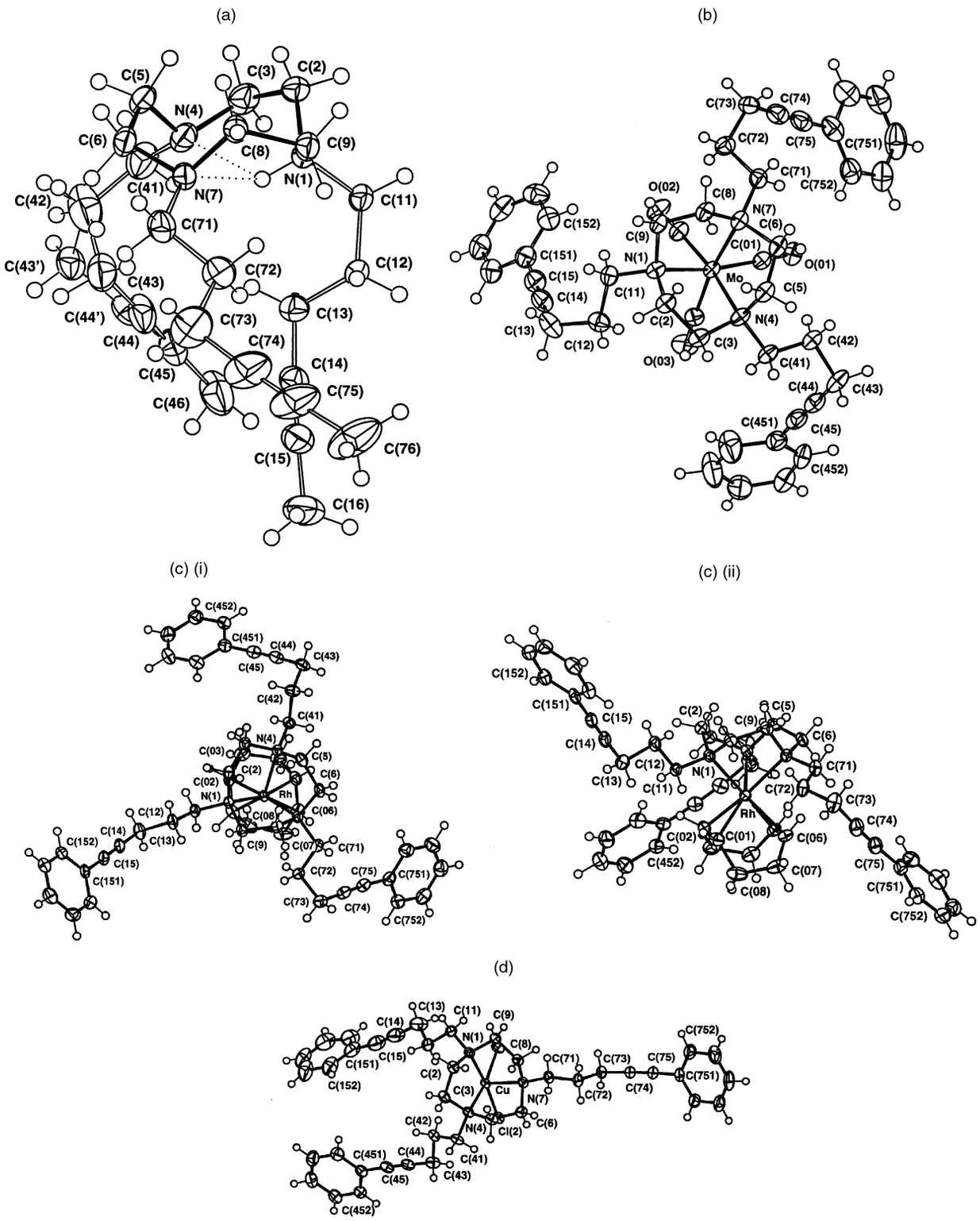


Fig. 1 Molecular projections of: (a) The $[H(4htacn)]^+$ cation (the minor component of disorder has single line bonds); (b) $[Mo(CO)_3(pptacn)]$; (c) (i) and (ii) the $[Rh(cod)(pptacn)]^+$ cation; and (d) $[CuCl_2(pptacn)]$.

geometries are normal, seemingly without untoward interactions with the cation pendants.

$[Mo(CO_3)(pptacn)]\cdot\frac{1}{2}(CH_3)_2CO$. Although devoid of crystallographic symmetry, this molecule, inclusive of substituents, has putative threefold symmetry (Fig. 1(b)). The molecular axis is oriented closely parallel to *b*, with interesting implications for packing consequent upon Mo lying at (0.74755(1), −0.02057(2), 0 (constraint)) (Fig. 2, deposited as ESI). The metal atom environment is presented in Table 1, ⟨Mo–N⟩ 2.351(9), ⟨M–C⟩ 1.931(6) Å, *cf.* the tris(*i*-propyl)-substituted analogue ⟨Mo–N⟩ 2.369(7), ⟨Mo–C⟩ 1.918(3) Å ($T = 298$ K),[11] which has a similar ring conformation to the present (C–C torsions 50.5(4), 49.8(4), 50.8(3), N–C −129.9(3), −128.7(8), −130.8(3), C–N 64.3(3), 64.9(3), 63.2(3)°), while in the tris-(benzyl), 17-electron, cationic counterpart (225 K, *3* symmetry) Mo–N is 2.281(6) and Mo–C 1.95(1) Å.[10] In the latter the ring conformation is similar to that of the trimethyl substituted protonated ligand, conforming to *3* symmetry, but with no mention of ligand disorder, having a torsion in the C–C ring bond of 2(1)°, with those in the bonds to either side of the nitrogen 98(1), −100(1)°, with ring carbon atom deviations from the N_3 plane 0.81(1), 0.81(2) and the pendant atom 0.66(2) Å.

Table 1 Metal atom environments. *r*/Å is the metal–ligand atom distance; other entries in the matrices are the angles (°) subtended at the metal by the relevant atoms at the head of the row and column

	$[Mo(CO)_3(pptacn)]$					
Atom	*r*	N(4)	N(7)	C(01)	C(02)	C(03)
N(1)	2.344(5)	76.3(2)	76.5(2)	169.6(2)	94.7(2)	103.8(2)
N(4)	2.344(4)		76.1(2)	103.0(2)	170.8(2)	94.7(2)
N(7)	2.364(4)			93.2(2)	104.1(2)	170.6(2)
C(01)	1.924(5)				86.3(2)	86.6(2)
C(02)	1.938(5)					83.5(2)
C(03)	1.930(5)					

Mo–C–O angles (carbonyls 1–3) are: 178.4(4), 177.5(4), 177.9(5)°.

	$[Rh(cod)(pptacn)]^+$						
Atom	*r*	N(4)	N(7)	C(01)	C(02)	C(05)	C(06)
N(1)	2.232(4)	79.7(1)	79.9(1)	95.6(2)	93.7(2)	167.0(2)	155.7(2)
N(4)	2.415(4)		75.6(1)	143.9(2)	104.5(2)	90.0(2)	119.0(2)
N(7)	2.313(4)			139.3(2)	173.4(2)	105.3(2)	89.6(2)
C(01)	2.114(5)				39.5(2)	88.2(2)	78.3(2)
C(02)	2.075(5)					81.3(2)	96.0(2)
C(05)	2.139(5)						37.2(2)
C(06)	2.173(5)						

	$[CuCl_2(pptacn)]$				
Atom	*r*	N(4)	N(7)	Cl(1)	Cl(2)
N(1)	2.115(1)	83.07(5)	83.00(5)	90.36(4)	173.77(4)
N(4)	2.090(1)		85.08(5)	171.00(4)	93.55(4)
N(7)	2.228(1)			100.27(3)	101.97(4)
Cl(1)	2.2847(5)				92.41(2)
Cl(2)	2.2805(5)				

$[Rh(cod)(pptacn)][PF_6]$. The cation in this complex is intrinsically unsymmetrical, the potential *3* symmetry of the {Rh(tacn)} moiety incompatible with that of the {Rh(cod)}, resulting in a diverse scatter of Rh–N and Rh–C distances; a similar array has been described for the tris(methyl)-substituted analogue[8] in which Rh–N (2.339(2), 2.335(2), 2.198(2) Å), Rh–C (2.083(3), 2.076(3), 2.158(3), 2.169(3) Å) have a number of more conspicuously pairwise groupings, provoking the description[8] of the rhodium environment as 'trigonal bipyramidal (*TBPY*)', the short Rh–N distance and the midpoint of the double bond supporting the two long Rh–C distances defining the *TBPY* axis, to our mind somewhat uncomfortably, since the other two nitrogen atoms support an equatorial angle diminished to 76.77(9)°. In the present complex, if there is to be a similar ascription, the axial array must be N(1), again the shortest Rh–N, and the midpoint of C(05)–C(06), again the longest C(cod) distances, with N(1)–Rh–(centroid) 174.$_2$°. However, N(1)–Rh–C(05,06) here are much less symmetrical (167.0(2), 155.7(2)°) than their counterparts in the tris(methyl) analogue (162.4(1), 160.3(1)°), with N(7)–Rh–C(02) also approaching linearity (173.4(2)°) and it is evident that the array of the tris(methyl) derivative is much more symmetrical, pseudo-*m* (but with ligand torsions pseudo-*3*), degrading further to that of the present cation, shown in projection down its 'axis', by a twist of the two ligands relative to each other, Fig. 1(c).

$[CuCl_2(pptacn)]$. In principle, at least, the array of this complex is potentially rather similar. It has a metal environment, which, apart from perturbations imposed by the unconforming torsions of the tridentate, is a reasonable approximation to *m* symmetry, with N(7) the apex of a square pyramid, the closure of N(7)–Cu–N(1,4) by the macrocycle allowing enlargement of N(7)–Cu–Cl(1,2). The geometry is rather similar to that found in the *N*-(5-pent-2-ynyl)-1,4,7-triazacyclononane adduct,[6] in which a pair of large N–Cu–Cl *trans* angles (167.6(2), 172.6(2)°) also describe the base of a square pyramid with the substituent at the apical nitrogen (Cu–N 2.256(4), *cf*. 2.228(1) Å (the present)); the other *cis*-basal Cu–unsubstituted N distances in that compound (2.026(5), 2.045(4) Å) are rather shorter than in the present (2.090(1), 2.115(1) Å).

Ring torsion angles for all the structures are given in Table 2.

Table 2 Ring torsion angles (°). Atoms are designated by number only, N italicised

	$[H(4htacn)]^+$	$[Mo(CO)_3$-(pptacn)]	$[Rh(cod)$ (pptacn)$]^+$	$[CuCl_2$ (pptacn)]
1–2–3–*4*	44.0(2)	52.2(6)	−49.5(5)	45.3(2)
2–3–*4*–5	66.7(2)	64.5(5)	−65.4(5)	69.4(2)
3–*4*–5–6	−132.3(2)	−132.8(4)	130.8(4)	−133.6(1)
4–5–6–7	50.5(2)	51.0(6)	−51.6(5)	50.7(2)
5–6–*7*–8	65.0(2)	64.1(6)	−61.8(5)	63.9(2)
6–*7*–8–9	−128.3(2)	−131.3(5)	134.0(4)	−129.3(1)
7–8–9–*1*	47.6(2)	51.7(6)	−50.2(5)	49.1(2)
8–9–*1*–2	74.3(2)	63.5(6)	−65.3(5)	68.1(2)
9–*1*–2–3	−139.1(2)	−132.7(5)	127.5(4)	−134.4(1)
8–9–*1*–11	−158.4(1)	−177.1(4)	175.1(4)	−169.1(5)
3–2–*1*–11	92.3(2)	110.1(5)	−114.5(4)	103.9(2)
2–3–*4*–41	−166.4(2)	−176.1(4)	169.3(4)	−171.6(1)
6–5–*4*–41	102.2(2)	110.4(5)	−104.3(4)	107.4(2)
5–6–*7*–71	−168.3(2)	−174.9(4)	−178.3(4)	−163.5(1)
9–8–*7*–71	105.7(2)	110.4(5)	−109.1(4)	98.2(2)

Reactions involving pendant alkynes

Our initial studies of reactions of complexes with pendant alkynes have focussed on Mo and Rh. For $[Mo(CO)_3(pptacn)]$ in various solutions (CH_2Cl_2, acetone, thf, CH_3NO_2) we

attempted to labilise the CO groups by oxidation of the metal centre with ferrocenium hexafluorophosphate or $AgBF_4$.[10] In each case, examination of the product by infrared spectroscopy showed CO stretching frequencies ($\tilde{\nu}_{CO}$ 2015, 1875(br) cm^{-1}) consistent with three facially co-ordinated CO groups attached to Mo^{I}.[10] On photolysis of solutions of the oxidised complexes a gas (presumably CO) was evolved, and CO bands were of reduced intensity or absent in the infrared spectra of the photolysis products. Unfortunately, we have been unable to identify the photolysis products or obtain evidence for any metal–alkyne interactions. The products were paramagnetic and therefore not amenable to characterisation by NMR; they could not be crystallised, and C≡C stretching bands in the infrared spectra of $[Mo(CO)_3(pptacn)]$ and the oxidation and photolysis products were too weak to provide useful information.

When $[Rh(cod)(pptacn)][PF_6]$ was heated (at reflux, in propionitrile solution) or irradiated (visible light, in acetonitrile solution) analysis by ^1H NMR spectroscopy indicated that the pptacn remained bound to the metal and retained apparent C_3 symmetry but the cod ligand had been displaced, presumably by solvent molecules. There was no evidence for metal–alkyne interactions in either case.

$[Rh(CO)_2(4htacn)][PF_6]$ appears moderately stable in acetone, methanol, benzene and toluene solutions for short periods of time (<1 week). On prolonged standing (>1 week) the ^1H and ^{13}C NMR spectra of the samples begin to change, becoming very complex. The changes could be hastened by heating (80 °C) or irradiation (UV light, through a Pyrex vessel) of a sample with provision for removal of evolved CO. The ^{13}C NMR spectra of such samples typically show no signals in the CO region but several doublets in the region δ 135–80, each with splittings of 5–10 Hz which we tentatively attribute to Rh–C coupling. These signals may be due to Rh-bound alkyne groups,[28] but the complexity of the ^1H and ^{13}C NMR spectra (*e.g.* some ^{13}C NMR spectra show more than 50 signals) prevents definitive identification of the complexes present.

Conclusion

We have prepared various metal complexes of tacns bearing pendant alkynes. Compared to 1,3,5-triazacyclohexanes and their metal complexes the alkynyl–tacns and their metal complexes show far greater stability, even at elevated temperatures. The more robust tacn system allows a broader survey of metal co-ordination than the more sensitive triazacyclohexane system. Nevertheless, attempts to achieve intramolecular co-ordination of the pendant alkynes to the metal centres in a well defined manner have so far been unsuccessful, and many of our attempts to investigate these systems have been thwarted by difficulties in characterising products by spectroscopic means.

Experimental

General procedures were as described previously.[29] Microanalyses were performed by the Microanalytical Unit, Research School of Chemistry, Australian National University, Canberra, Australia. 1,4,7-Tri(*p*-tolylsulfonyl)-1,4,7-triazacyclononane,[16] 5-iodo-1-pentyne,[30] $[RhCl_3(CH_3CN)_3]$,[31] $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$[32] and $[Mo(CO)_3(CH_3CH_2CN)_3]$[33] were prepared according to literature methods. 5-Chloro-1-pentyne was purchased from Aldrich. Aqueous hydroiodic acid was purified by refluxing over red phosphorus, under nitrogen, followed by filtration through a sintered glass funnel containing solid carbon dioxide.[34]

Synthesis of alkynyl functionalised 1,4,7-triazacyclononanes

1,4,7-Triazacyclononane trihydroiodide. 1,4,7-Tri(*p*-tolylsulfonyl)-1,4,7-triazacyclononane (20.8 g, 35 mmol) was added portionwise to concentrated sulfuric acid (65 cm^3) heated at 180 °C. The mixture was stirred, with continued heating, for 10 minutes and then allowed to cool. It was diluted with ethanol (150 cm^3) then poured into diethyl ether (350 cm^3). The solid precipitated was collected and dissolved in water (110 cm^3), and the resulting solution treated with charcoal, heated and filtered. The filtrate was concentrated *in vacuo* to 25 cm^3 and then made basic with sodium hydroxide solution (15 M, 30 cm^3). The mixture was filtered and the filtrate continuously extracted with $CHCl_3$ for 4 days. The organic extract was dried (Na_2SO_4) and concentrated *in vacuo*. The residue was dissolved in ethanol (25 cm^3), filtered, and the filtrate cooled (ice-bath). Aqueous hydroiodic acid (55% w/w, 30 cm^3, 0.22 mol) and then ether (40 cm^3) were added to the ethanolic solution. The resulting precipitate was collected, washed with ethanol (40 cm^3) and ether (80 cm^3) and then dried *in vacuo* to yield 1,4,7-triazacyclononane trihydroiodide as a white powder (11.1 g, 62%), mp 248–250 °C (decomp.) (Found: C, 14.63; H, 3.39; N, 8.39. C_2H_6IN requires C, 14.05; H, 3.54; N, 8.39%); δ_H (D_2O) 3.18 (12H, s, 3 × NCH_2CH_2N); δ_C (D_2O) 42.7 (NCH_2CH_2N).

5-Chloro-1-phenyl-1-pentyne. Phenylacetylene (20.5 cm^3, 0.183 mol) was added to a cooled (−70 °C) solution of *n*-butyllithium (2.5 M in hexanes, 72 cm^3, 0.18 mol) in thf (120 cm^3). The mixture was stirred at −70 °C for 15 min and then 1-bromo-3-chloropropane (20 cm^3, 0.20 mol) added. The resulting mixture was stirred at −70 °C for 30 min and then allowed to warm to room temperature with continued stirring overnight. It was then refluxed for 3 h, cooled and concentrated *in vacuo*. The residue was diluted with water (100 cm^3) and extracted with ether (2 × 150 cm^3). The ether extract was washed with water (80 cm^3) and brine (40 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled (Kugelrohr) to afford 5-chloro-1-phenyl-1-pentyne as a colourless oil (13.4 g, 42%), bp 100 °C (1 mmHg). δ_H ($CDCl_3$) 2.05 (2 H, tt, *J*(H3H4) 6.8, *J*(H4H5) 6.4 Hz, 2 × H4), 2.60 (2 H, t, 2 × H3), 3.71 (2 H, t, 2 × H5), 7.26–7.30 (3 H, m, aryl H) and 7.37–7.41 (2 H, m, aryl H); δ_C ($CDCl_3$) 16.8 (C3), 31.4 (C4), 43.7 (C5), 81.5 (C1), 88.0 (C2), 123.5 (C, aryl), 127.7 (CH, aryl), 128.2 (CH, aryl) and 131.5 (CH, aryl). The ^1H NMR spectrum is consistent with that reported.[35]

5-Iodo-1-phenyl-1-pentyne. A mixture of 5-chloro-1-phenyl-1-pentyne (5.3 g, 30 mmol), sodium iodide (18.9 g, 126 mmol) and acetone (30 cm^3) was heated at reflux for 20 h. The mixture was filtered and the solid residue washed with acetone (20 cm^3). The filtrate was concentrated *in vacuo*, diluted with water (40 cm^3) and then extracted with ether (2 × 100 cm^3). The ether extract was washed with aqueous sodium thiosulfate solution (10%, 50 cm^3), dried ($MgSO_4$) and concentrated *in vacuo* to give 5-iodo-1-phenyl-1-pentyne as a colourless oil (7.0 g, 87%). δ_H ($CDCl_3$) 2.07 (2 H, tt, *J*(H3H4) 6.7, *J*(H4H5) 6.8 Hz, 2 × H4), 2.54 (2 H, t, 2 × H3), 3.35 (2 H, t, 2 × H5), 7.26–7.29 (3 H, m, aryl H) and 7.36–7.40 (2 H, m, aryl H); δ_C ($CDCl_3$) 5.4 (C5), 20.4 (C3), 32.1 (C4), 81.6 (C1), 87.5 (C2), 123.5 (C, aryl), 127.8 (CH, aryl), 128.2 (CH, aryl) and 131.5 (CH, aryl).

6-Iodo-2-hexyne. *n*-Butyllithium (2.5 M in hexanes, 19.5 cm^3, 49 mmol) was added to a cooled (−78 °C) solution of 5-chloro-1-pentyne (5.0 cm^3, 47 mmol) in thf (20 cm^3). The solution was stirred for 5 min, with cooling, and for 5 min without cooling. The solution was then cooled to −78 °C and methyl iodide (3.3 cm^3, 53 mmol) added. The resulting solution was stirred for 5 h during which time it was allowed to come to room temperature. Water (1.5 cm^3) was added and the thf distilled off at atmospheric pressure. The residue was extracted with pentane (100 cm^3). The pentane extract was washed with water (30 cm^3), dried ($MgSO_4$) and concentrated *in vacuo* to give a mixture of 6-iodo-2-hexyne and 6-chloro-2-hexyne. Sodium iodide (25 g, 167 mmol) and acetone (40 cm^3) were added and the resulting mixture was heated at reflux for 2 days. The acetone was removed

by distillation and the residue diluted with water (150 cm^3) and extracted with pentane (150 cm^3). The pentane extract was washed with water (30 cm^3) and aqueous sodium thiosulfate solution (10%, 20 cm^3), dried ($MgSO_4$) and concentrated *in vacuo* to leave a yellow oil, distillation of which afforded 6-iodo-2-hexyne as a colourless oil (5.9 g, 63%), bp 90–98 °C (32 mmHg). δ_H (C_6D_6) 1.46 (3 H, t, *J*(H1H4) 2.6, 3 × H1), 1.53 (2 H, m, 2 × H5), 1.97 (2 H, m, 2 × H4) and 2.83 (2 H, t, *J*(H5H6) 6.8 Hz, 2 × H6); δ_C (C_6D_6) 3.2 (C1), 5.4 (C6), 19.8 (C4), 32.7 (C5), 76.7 (C2) and 77.2 (C3). The ^1H NMR spectrum for a $CDCl_3$ solution was consistent with the literature,[36] but the NMR spectrum for a C_6D_6 solution is a better indicator of sample purity.

1,4,7-Tri(5-phenyl-4-pentynyl)-1,4,7-triazacyclononane (pptacn). A mixture of ethyldiisopropylamine (13.5 cm^3, 78 mmol) in acetonitrile (25 cm^3) was added to a mixture of 5-iodo-1-phenyl-1-pentyne (7.26 g, 26.9 mmol) and 1,4,7-triazacyclononane trihydroiodide (4.22 g, 8.2 mmol) in acetonitrile (40 cm^3). The resulting solution was stirred for 2 days at ambient temperature and then refluxed for 3 days. It was concentrated *in vacuo* and then diluted with sodium hydroxide solution (5 M, 50 cm^3) and extracted with CH_2Cl_2 (200 cm^3). The organic extract was washed with water (50 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (silica, 5% $Et_3N/CHCl_3$) to yield 1,4,7-tri(5-phenyl-4-pentynyl)-1,4,7-triazacyclononane as a light orange oil (3.0 g, 67%) (Found: C, 84.09; H, 7.89; N, 7.44. $C_{13}H_{15}N$ requires C, 84.28; H, 8.16; N, 7.56%). δ_H (C_6D_6) 1.64 (6 H, tt, *J*(H1H2) 6.8, *J*(H2H3) 7.1 Hz, 6 × H2), 2.42 (6 H, t, 6 × H3), 2.51 (6 H, t, 6 × H1), 2.63 (12 H, s, 3 × NCH_2-CH_2N), 6.94–7.01 (9 H, m, aryl H) and 7.51–7.53 (6 H, m, aryl H); δ_C (C_6D_6) 17.6 (C3), 27.8 (C2), 56.7 (NCH_2CH_2N), 58.0 (C1), 81.5 (C5), 90.8 (C4), 124.9 (C, aryl), 127.7 (CH, aryl), 128.5 (CH, aryl) and 131.9 (CH, aryl); *m/z* (EI) 556.3673 (M + 1) (requires 556.3692).

1,4,7-Tri(4-hexynyl)-1,4,7-triazacyclononane (4htacn). Ethyldiisopropylamine (4.1 cm^3, 24 mmol) was added to a stirred mixture of 6-iodo-2-hexyne (2.71 g, 13.0 mmol) and 1,4,7-triazacyclononane trihydroiodide (2.02 g, 3.9 mmol) in acetonitrile (30 cm^3). The resulting solution was stirred for 4 days at ambient temperature and then refluxed for 16 h. It was concentrated *in vacuo* and the residue diluted with aqueous sodium hydroxide solution (3 M, 40 cm^3) and then extracted with CH_2Cl_2 (2 × 100 cm^3). The organic extract was washed with water (40 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by rapid silica filtration (5% Et_3N/ether) to yield 1,4,7-tri(4-hexynyl)-1,4,7-triazacyclononane as a pale yellow oil (1.1 g, 76%) (Found: C, 78.04; H, 10.33; N, 11.10. $C_8H_{13}N$ requires C, 77.99; H, 10.64; N, 11.37%). δ_H ($CDCl_3$) 1.58 (6 H, m, 6 × H2), 1.75 (6 H, t, *J*(H3H6) 2.5, 6 × H6), 2.14 (6 H, m, 6 × H3), 2.50 (6 H, t, *J*(H1H2) 7.2 Hz, 6 × H1) and 2.69 (12 H, s, 3 × NCH_2CH_2N); δ_C ($CDCl_3$) 3.48 (C6), 16.7 (C3), 27.6 (C2), 56.0 (NCH_2CH_2N), 57.9 (C1), 75.5 (C5) and 79.2 (C4).

1,4,7-Tri(4-pentynyl)-1,4,7-triazacyclononane (ptacn). Ethyldiisopropylamine (4.1 cm^3, 24 mmol) was added to a stirred mixture of 5-iodo-1-pentyne (2.4 g, 12 mmol) and 1,4,7-triazacyclononane trihydroiodide (2.0 g, 3.9 mmol) in acetonitrile (30 cm^3). The resulting solution was stirred for 2 days at ambient temperature and then refluxed for 20 h. It was concentrated *in vacuo* and the residue diluted with aqueous sodium hydroxide solution (3 M, 40 cm^3) and extracted with CH_2Cl_2 (2 × 100 cm^3). The organic extract was washed with water (40 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by rapid silica filtration (5% Et_3N/47.5% ether/47.5% CH_2Cl_2) to yield 1,4,7-tri(4-pentynyl)-1,4,7-triazacyclononane as a pale yellow oil (0.74 g, 58%) [Found: C, 76.04; H, 10.61; N, 12.63. $C_{24}H_{39}N_3 \cdot \frac{1}{4}H_2O$ (H_2O content estimated by NMR analysis) requires C, 75.97; H, 10.17; N, 12.66%]. δ_H [$(CD_3)_2CO$] 1.62 (6 H, tt, *J*(H1H2) 6.8, *J*(H2H3) 7.1, 6 × H2), 2.26 (6 H, dt, *J*(H3H5) 2.7 Hz, 6 × H3), 2.30 (3 H, t, 3 × H5), 2.56 (6 H, t, 6 × H1) and 2.70 (12 H, s, 3 × NCH_2-CH_2N); δ_C [$(CD_3)_2CO$] 16.5 (C3), 28.1 (C2), 57.2 (NCH_2-CH_2N), 58.2 (C1), 69.8 (C5) and 85.0 (C4).

[H(4htacn)][BPh_4]. A solution of $NaBPh_4$ (24 mg, 70 μmol) in methanol (2 cm^3) was added to a solution of 4htacn (18.5 mg, 50 μmol) in methanol (4 cm^3). The resulting mixture was allowed to stand overnight, and the precipitate collected, washed with methanol (3 cm^3), and dried *in vacuo* to afford H(4htacn)·BPh_4 as fluffy colourless crystals in quantitative yield, mp 120–122 °C (decomp.) (Found: C, 83.69; H, 8.17; N, 6.04. $C_{48}H_{60}BN_3$ requires C, 83.54; H, 8.77; N, 6.09%). δ_H [$(CD_3)_2CO$] 1.75 (9 H, t, *J*(H3H6) 2.6 Hz, 9 × H6), 1.79 (6 H, m, 6 × H2), 2.20 (6 H, m, 6 × H3), 2.94–3.03 (12 H, m, 3 × NCH_2CH_2N), 3.04 (6 H, m, 6 × H1), 6.78 (4 H, m, aryl), 6.92 (8 H, m, aryl), 7.33 (8 H, m, aryl) and 9.85 (1 H, s, NH); δ_C [$(CD_3)_2CO$] 3.2 (C6), 16.8 (C2), 26.4 (C3), 50.1 (NCH_2-CH_2N), 55.2 (C1), 77.1 (C5), 78.3 (C4), 122.2 (aryl), 126.0 (q, *J*(CB) 2.8, aryl), 137.0 (aryl) and 164.9 (q, *J*(CB) 49.4 Hz, aryl).

Synthesis of tacn–metal complexes

[$Mo(CO)_3$(pptacn)]. A solution of [$Mo(CO)_3(CH_3CH_2CN)_3$] (0.179 g, 0.52 mmol) in acetone (2 cm^3) was added to a solution of pptacn (0.289 g, 0.52 mmol) in acetone (2 cm^3). The solution was stirred for 1 h, during which time a precipitate formed. The mixture was diluted with ether (6 cm^3) and the precipitate collected, washed with ether (10 cm^3) and dried *in vacuo*, to yield [$Mo(CO)_3$(pptacn)] as a pale beige powder (0.281 g, 73%) (Found: C, 68.69; H, 6.48; N, 5.75. $C_{42}H_{45}MoN_3O_3$ requires C, 68.56; H, 6.16; N, 5.71%). $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1895 and 1754br (CO); δ_H [$(CD_3)_2CO$] 2.17 (6 H, m, 6 × H2), 2.50 (6 H, t, *J*(H2H3) 6.9 Hz, 6 × H3), 2.94–3.12 (12 H, m, 3 × NCH_2-CH_2N), 3.40 (6 H, m, 6 × H1), 7.29–7.32 (9 H, m, aryl) and 7.41–7.44 (6 H, m, aryl); δ_C [$(CD_3)_2CO$] 17.8 (C3), 25.3 (C2), 55.1 (NCH_2CH_2N), 64.9 (C1), 81.9 (C5), 90.0 (C4), 124.8 (C, aryl), 128.5 (aryl), 129.2 (aryl), 132.3 (aryl) and 230.3 (CO).

[$Mo(CO)_3$(ptacn)]. A solution of ptacn (0.156 g, 0.48 mmol) in acetone (5 cm^3) was added to a solution of [$Mo(CO)_3$(CH_3-$CH_2CN)_3$] (0.165 g, 0.48 mmol) in acetone (5 cm^3). A precipitate soon formed and the mixture was stirred for 3 h. It was diluted with ether (10 cm^3) and the precipitate collected, washed with ether (5 cm^3) and dried *in vacuo*, to give [$Mo(CO)_3$(ptacn)] as a beige powder (0.158 g, 65%) (Found: C, 55.93; H, 6.41; N, 8.06. $C_{24}H_{33}MoN_3O_3$ requires C, 56.80; H, 6.55; N, 8.28%). $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1890 and 1743br (CO); δ_H [$(CD_3)_2CO$] 2.08 (6 H, m, 6 × H2), 2.25 (6 H, dt, *J*(H2H3) 7.2, *J*(H3H5) 2.7 Hz, 6 × H3), 2.37 (3 H, t, 3 × H5), 2.88–2.97 and 3.01–3.08 (12 H, m, 3 × NCH_2CH_2N) and 3.28 (6 H, m, 6 × H1); δ_C [$(CD_3)_2CO$] 16.9 (C3), 25.2 (C2), 55.0 (NCH_2CH_2N), 64.8 (C1), 70.4 (C5), 84.1 (C4) and 230.0 (CO).

[Rh(cod)(pptacn)][PF_6]. A solution of pptacn (0.163 g, 0.29 mmol), [$Rh_2(\mu$-$Cl)_2(cod)_2$] (72 mg, 0.15 mmol) and KPF_6 (56 mg, 0.30 mmol) in acetone (20 cm^3) was stirred for 2 h. The solution was filtered and the filtrate concentrated *in vacuo*. The residue was triturated in benzene (5 cm^3) until a fine suspension formed. The mixture was diluted with ether (10 cm^3) and the precipitate collected, washed with ether (10 cm^3) and dried *in vacuo* to leave [Rh(cod)(pptacn)][PF_6] as a yellow powder (178 mg, 67%) which was pure according to spectroscopy. Recrystallisation from acetone–ether solutions yielded analytically pure yellow crystals (Found: C, 61.35; H, 5.77; N, 4.50. $C_{47}H_{57}F_6N_3PRh$ requires C, 61.91; H, 6.30; N, 4.61%). δ_H [$(CD_3)_2CO$] 1.58 (4 H, m, cod C*H*H), 2.31 (6 H, m, 6 × H2),

2.53 (4 H, m, cod CH*H*), 2.61 (6 H, t, *J*(H2H3) 6.9 Hz, 6 × H3), 2.93–3.11 (12 H, m, 3 × NCH_2CH_2N), 3.34 (6 H, m, 6 × H1), 3.68 (4 H, br s, cod CH) and 7.31–7.40 (15 H, m, aryl); δ_C [$(CD_3)_2CO$] 17.7 (C3), 24.8 (C2), 31.0 (cod CH_2), 55.7 (NCH_2CH_2N), 61.1 (C1), 74.8 (d, *J*(Rh–C) 14.4 Hz, cod CH), 82.1 (C5), 89.6 (C4), 124.5 (C, aryl), 128.8 (aryl), 129.3 (aryl) and 132.2 (aryl).

[$RhCl_3$(pptacn)]. A solution of pptacn (0.114 g, 0.205 mmol) in acetonitrile (4 cm^3) was added to a solution of [$RhCl_3$-$(CH_3CN)_3$] (67 mg, 0.20 mmol) in acetonitrile (10 cm^3). The resulting solution was stirred rapidly for 10 s and then allowed to stand for 4 days. The yellow crystals that formed were collected, washed with benzene (4 cm^3) and dried *in vacuo* to yield [$RhCl_3$(pptacn)] as a yellow microcrystalline solid (99 mg, 64%) (Found: C, 59.74; H, 5.49; N, 5.41. $C_{39}H_{45}Cl_3N_3Rh{\cdot}H_2O$ requires C, 59.82; H, 6.05; N, 5.37%). δ_H [$(CD_3)_2SO$] 1.92 (6 H, m, 6 × H2), 2.45 (6 H, t, *J*(H2H3) 6.7 Hz, 6 × H3), 2.93–3.00 and 3.28–3.35 (12 H, m, 3 × NCH_2CH_2N), 3.75 (6 H, m, 6 × H1), 7.30–7.35 (9 H, m, aryl) and 7.40–7.45 (6 H, m, aryl); δ_C [$(CD_3)_2SO$] 16.8 (C3), 21.4 (C2), 56.4 (NCH_2CH_2N), 59.5 (C1), 81.2 (C5), 89.7 (C4), 123.1 (C, aryl), 128.0 (aryl), 128.5 (aryl) and 131.3 (aryl); *m*/*z* (FAB) 844.1894 (M + dmso) (requires 844.1922) and 728.2049 (M − Cl) (requires 728.2046).

[$Rh(CO)_2$(4htacn)][PF_6]. A solution of 4htacn (0.141 g, 0.38 mmol) in acetone (5 cm^3) was added to a solution of [Rh_2(μ-$Cl)_2(CO)_4$] (68.3 mg, 0.17 mmol) in acetone (5 cm^3). A solution of KPF_6 (78 mg, 0.42 mmol) in acetone (5 cm^3) was added and the mixture stirred for 3 h, then filtered and diluted with ether (10 cm^3). The resulting precipitate was collected, washed with ether (5 cm^3) and dried *in vacuo*, to leave a dark off-green powder (160 mg, 56%) (Found: C, 41.95; H, 5.30; N, 5.45. $C_{26}H_{39}F_6N_3O_2PRh{\cdot}KCl$ requires C, 41.75; H, 5.26; N, 5.62%). $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 2061 and 1982 (CO); δ_H [$(CD_3)_2CO$] 1.71 (9 H, t, *J*(H4H6) 2.4 Hz, 9 × H6), 2.21 (6 H, m, 6 × H2), 2.25 (6 H, m, 6 × H3), 3.15–3.22 (12H, m, 3 × NCH_2CH_2N) and 3.38 (6 H, m, 6 × H1); δ_C [$(CD_3)_2CO$] 3.7 (C6), 16.8 (C3), 28.5 (C2), 57.8 (NCH_2CH_2N), 65.9 (C1), 77.0 and 78.2 (C4 and C5) and 189.2 (d, *J*(RhC) 72 Hz, CO); *m*/*z* (FAB) 528.2069 (M − PF_6) (requires 528.2097) and 500.2147 (M − PF_6 − CO) (requires 500.2148). Recrystallisation from benzene–hexane yielded bright yellow, very thin plate-like crystals.

[$CuCl_2$(pptacn)]. A solution of $CuCl_2{\cdot}2H_2O$ (8.6 mg, 50 μmol) in ethanol (1 cm^3) was added to a solution of pptacn (30 mg, 55 μmol) in ethanol (1 cm^3) and stirred for 1 week. The green precipitate that formed was collected, washed with ethanol (2 cm^3) and ether (5 cm^3) and dried *in vacuo* to afford a green powder (15 mg, 43%) (Found: C, 68.16; H, 6.33; N, 5.92. $C_{39}H_{45}Cl_2CuN_3$ requires C, 67.86; H, 6.57; N, 6.09%); *m*/*z* (FAB) 653.2590 (M − Cl) (requires 653.2598).

[Ni_2(μ-Cl)$_3$(pptacn)$_2$]Cl. A solution of $NiCl_2{\cdot}6H_2O$ (10 mg, 43 μmol) in ethanol (1 cm^3) was added to a solution of pptacn (27 mg, 49 μmol) in ethanol (1 cm^3) and stirred for 1 week. The resulting mixture was concentrated *in vacuo* and then triturated with ether (5 cm^3). The solid was collected and dried to yield [Ni_2(μ-Cl)$_3$(pptacn)$_2$]Cl as a light green powder (21 mg, 71%). Recrystallisation from CH_2Cl_2 gave green needles (Found: C, 67.84; H, 6.44; N, 5.98. $C_{39}H_{45}Cl_2N_3Ni$ requires C, 68.34; H, 6.62; N, 6.13%). *m*/*z* (FAB) 1331.49978 (M − Cl) (requires 1331.49995).

Structure determinations

Crystals of [H(4htacn)][BPh_4] were grown from ethyl acetate–methanol, of [$Mo(CO)_3$(pptacn)] by slow cooling of an acetone solution and of [Rh(cod)(pptacn)][PF_6] by slow evaporation of an acetone solution of the complex. Recrystallisation of [$CuCl_2$(pptacn)] from CH_3NO_2–toluene solutions yielded large dark green crystals suitable for an X-ray study.

Full-spheres of 'low-temperature' CCD area-detector diffractometer data ($2\theta_{max} = 58°$, ω scans; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; *T ca.* 153 K) were measured yielding $N_{t(otal)}$ reflections, these merging to *N* unique (R_{int} quoted) after 'empirical'/multiscan absorption correction, N_o with $F > 4\sigma(F)$ being considered 'observed' and used in the full matrix least squares refinement, anisotropic thermal parameter forms for the non-hydrogen atoms (x, y, z, $U_{iso})_H$ being treated as indicated. Conventional residuals *R*, R_w (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$ are quoted at convergence. Neutral atom complex scattering factors were employed within the XTAL 3.4 program system.[37] Individual features, difficulties, idiosyncrasies are noted below. In Fig. 1 50% displacement ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

Crystal/refinement data. *[H(4htacn)][BPh$_4$].* $C_{48}H_{60}BN_3$, $M = 689.8$, monoclinic, space group $P2_1/n$ (C_{2h}^5, no. 14, variant), $a = 11.763(1)$, $b = 26.994(3)$, $c = 12.907(1)$ Å, $\beta = 90.296(2)°$, $V = 4098$ Å^3, D_c ($Z = 4$) $= 1.11_8$ g cm^{-3}, $\mu_{Mo} = 0.64$ cm^{-1}, specimen 0.38 × 0.35 × 0.14 mm, 'T'$_{min,max} = 0.76$, 0.93, $N_t = 40295$, $N = 10355$ ($R_{int} = 0.032$), $N_o = 7171$, $R = 0.048$, $R_w = 0.058$, $|\Delta\rho_{max}| = 0.31(3)$ e Å^{-3}.

C(43,44) were modelled as disordered over two sets of sites, occupancies refining to 0.657(5) and complement; associated disordered hydrogen atom parameters were constrained at estimated values, other (x, y, z, $U_{iso})_H$ refined.

[Mo(CO)$_3$(pptacn)]·(CH$_3$)$_2$CO. $C_{45}H_{51}MoN_3O_4$, $M = 793.9$, orthorhombic, space group *Iba*2 (C_{2v}^{21}, no. 45), $a = 25.283(5)$, $b = 14.986(3)$, $c = 21.337(4)$ Å, $V = 8084(3)$ Å^3, D_c ($Z = 8$) $= 1.30_4$ g cm^{-3}, $\mu_{Mo} = 3.7$ cm^{-1}, specimen: 0.45 × 0.30 × 0.15 mm, 'T'$_{min,max} = 0.82$, 0.90, $N_t = 46797$, $N = 5249$ ($R_{int} = 0.048$), $N_o = 4249$, $R = 0.036$, $R_w = 0.045$, $|\Delta\rho_{max}| = 1.10(4)$ e Å^{-3}. (x, y, z, $U_{iso})_H$ constrained at estimates throughout.

'Friedel pairs' were retained distinct, here (and in the next determination), x_{abs} refining to −0.02(5). The acetone solvent comprises two moieties, one disposed on a crystallographic *2* axis, the other disordered about it.

[Rh(cod)(pptacn)][PF$_6$]. $C_{47}H_{57}F_6N_3PRh$, $M = 911.9$, orthorhombic, space group $P2_12_12_1$ (D_2^4, no. 19), $a = 11.485(1)$, $b = 12.312(2)$, $c = 30.350(4)$ Å, $V = 4291$ Å^3, D_c ($Z = 4$) $= 1.41_1$ g cm^{-3}, $\mu_{Mo} = 5.0$ cm^{-1}, specimen 0.25 × 0.15 × 0.04 mm, 'T'$_{min,max} = 0.82$, 0.93, $N_t = 50587$, $N = 6089$ ($R_{int} = 0.051$), $N_o = 5265$, $R = 0.037$, $R_w = 0.040$, $|\Delta\rho_{max}| = 0.82(7)$ e Å^{-3}, $x_{abs} = 0.02(3)$. (x, y, z, $U_{iso})_H$ constrained throughout.

The fluorine atoms of the anion were modelled as disordered over two sets of sites, occupancies refining to 0.85(1) and complement.

[CuCl$_2$(pptacn)]. $C_{39}H_{45}Cl_2CuN_3$, $M = 690.3$, monoclinic, space group $P2_1/n$, $a = 16.974(2)$, $b = 12.331(2)$, $c = 17.456(2)$ Å, $\beta = 101.945(2)°$, $V = 3575$ Å^3, D_c ($Z = 4$) $= 1.28_2$ g cm^{-3}, $\mu_{Mo} = 7.9$ cm^{-1}, specimen 0.50 × 0.45 × 0.30 mm, 'T'$_{min,max} = 0.66$, 0.80, $N_t = 34673$, $N = 8951$ ($R_{int} = 0.022$), $N_o = 7508$, $R = 0.028$, $R_w = 0.039$, $|\Delta\rho_{max}| = 0.44(3)$ e Å^{-3}, (x, y, z, $U_{iso})_H$ refined throughout.

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See http://www.rsc.org/suppdata/dt/b0/b007324p/ for crystallographic files in .cif format.

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