

# A Stable Copper(I)–Triazacyclononane Complex with an Intramolecularly Coordinated Alkyne Group

Murray V. Baker,<sup>\*,1</sup> David H. Brown, Neil Somers, and Allan H. White

Department of Chemistry, The University of Western Australia, Crawley, WA 6009, Australia

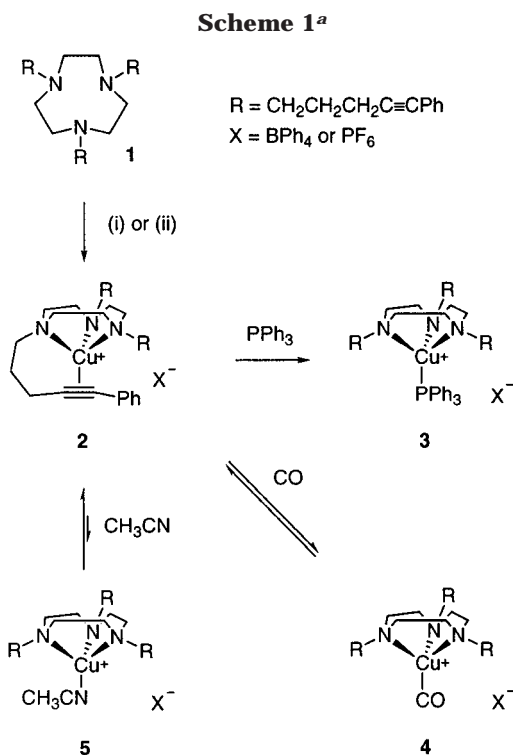
Received November 21, 2000

A 1,4,7-triazacyclononane copper(I) complex with an intramolecularly coordinated pendant alkyne has been synthesized and characterized spectroscopically and by X-ray studies. This complex is air-stable indefinitely in the solid state and stable in acetone solutions in air for several days.

## Introduction

1,4,7-Triazacyclononane metal complexes with intramolecularly coordinated pendant functional groups (especially those with O, N, S, and P donors) have received much attention.<sup>2,3</sup> In contrast, complexes of 1,4,7-triazacyclononanes containing intramolecularly coordinated carbon–carbon multiple bonds are rare. Despite recent reports of metal complexes of alkynyl-functionalized 1,4,7-triazacyclononanes,<sup>4,5</sup> there appear to be no reports of intramolecularly coordinated pendant alkynes in such systems. There has been one report of a triazacyclononane complex containing an intramolecularly coordinated alkene,<sup>6</sup> but this complex was extremely air sensitive and only characterized by infrared spectroscopy. In the broader area of facially coordinating ligands (arenes, cyclopentadienyls, N tripods, etc.) bearing pendant functional groups, the only reports of complexes containing an intramolecularly coordinated pendant alkyne appear to be the ( $\eta^8$ -alkynylarene)-dicarbonylchromium complexes of Krivykh and co-workers.<sup>7–9</sup>

We have synthesized a family of triazacycles with pendant alkynyl groups and explored their reactions with metals,<sup>5,10</sup> with a view toward intramolecular coordination and subsequent coupling of pendant alkynes to form organometallic cage complexes. In our previous studies, we were unable to isolate any complex containing an intramolecularly coordinated alkyne, apparently because the alkynes either competed poorly with other ligands for the metal center or underwent subsequent reactions that led to complex mixtures of products. In



<sup>a</sup> Reagents: (i) CuI, CH<sub>3</sub>OH, NaBPh<sub>4</sub>; (ii) [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub>, THF.

this paper, we report on the coordination of a 1,4,7-trialkynyl-1,4,7-triazacyclononane to copper(I), which results in the first example of a stable, well-defined TACN complex with an intramolecularly coordinated alkynyl group.

## Results and Discussion

The reaction of 1,4,7-tri(5-phenyl-4-pentynyl)-1,4,7-triazacyclononane **1** with CuI in methanol, followed by the addition of NaBPh<sub>4</sub>, yielded the Cu(I) salt **2**·BPh<sub>4</sub> (Scheme 1) as a colorless solid in high yield (86%). Alternatively, **2** could be obtained as the hexafluorophosphate salt **2**·PF<sub>6</sub> by the reaction of **1** with [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> in THF. The structure of the cation **2** was deduced by spectroscopic techniques and subsequently confirmed by an X-ray study of the BPh<sub>4</sub><sup>−</sup> salt. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **2**·BPh<sub>4</sub> in acetone-*d*<sub>6</sub> showed

(1) To whom correspondence should be addressed. Fax: +61 8 9380 1005. E-mail: mvb@chem.uwa.edu.au.

(2) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329.

(3) Wainwright, K. P. *Coord. Chem. Rev.* **1997**, *166*, 35.

(4) Ellis, D.; Farrugia, L. J.; Peacock, R. D. *Polyhedron* **1999**, *18*, 1229.

(5) Baker, M. V.; Brown, D. H.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2000**, 4607.

(6) Farrugia, L. J.; Lovatt, P. A.; Peacock, R. D. *Inorg. Chim. Acta* **1996**, *246*, 343.

(7) Krivykh, V. V.; Il'minskaya, E. S.; Rybinskaya, M. I. *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1981**, *30*, 1563.

(8) Rybinskaya, M. I.; Krivykh, V. V.; Gusev, O. V.; Il'minskaya, E. S. *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1981**, *30*, 2371.

(9) Taits, E. S.; Petrovskii, P. V.; Krivykh, V. V. *Russ. Chem. Bull.* **1999**, *48*, 1157.

(10) Baker, M. V.; Brown, D. H.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2000**, 763.

**Table 1. Selected Cation Parameters**

atoms	parameter	atoms	parameter
Distances (Å)			
Cu–N(1)	2.041(1), 2.041(1)	Cu–C(14)	1.950(1), 1.955(2)
Cu–N(4)	2.248(1), 2.195(1)	Cu–C(15)	1.996(1), 2.002(2)
Cu–N(7)	2.087(1), 2.124(1)	C(14)–C(15)	1.236(2), 1.234(2)
Angles (deg)			
N(1)–Cu–N(4)	84.88(4), 85.80(5)	N(4)–Cu–C(14)	117.29(5), 130.33(5)
N(1)–Cu–N(7)	88.71(5), 86.85(5)	N(4)–Cu–C(15)	115.17(5), 117.67(5)
N(1)–Cu–C(14)	102.10(6), 103.75(5)	N(7)–Cu–C(14)	157.51(5), 144.24(5)
N(1)–Cu–C(15)	138.25(6), 140.07(5)	N(7)–Cu–C(15)	128.04(6), 125.13(5)
N(4)–Cu–N(7)	82.97(4), 83.83(4)	C(14)–Cu–C(15)	36.49(7), 36.33(6)
Cu–N(1)–C(2)	109.42(9), 108.51(9)	Cu–N(4)–C(5)	106.97(8), 107.39(8)
Cu–N(1)–C(9)	100.8(1), 102.87(7)	Cu–N(7)–C(6)	105.77(8), 103.85(9)
Cu–N(4)–C(3)	100.20(8), 98.48(7)	Cu–N(7)–C(8)	104.58(9), 105.66(8)
C(13)–C(14)–C(15)	163.6(1), 167.0(2)	C(14)–C(15)–C(151)	156.9(1), 157.6(2)
Torsion Angles <sup>b</sup> (deg)			
2-1-9-8	68.1(2), 68.3(2)	9-1-2-3	-130.3(1), -134.0(1)
Cu-1-9-8	-48.1(1), -47.5(1)	Cu-1-2-3	-19.6(2), -21.7(1)
1-9-8-7	47.0(2), 46.3(2)	1-2-3-4	47.5(2), 52.1(2)
9-8-7-Cu	-17.8(1), -18.7(1)	2-3-4-Cu	-45.4(1), -49.8(1)
9-8-7-6	-131.3(1), -130.7(1)	2-3-4-5	68.1(1), 63.3(2)
8-7-6-5	65.9(2), 66.1(2)	3-4-5-6	-132.8(1), -134.1(1)
Cu-7-6-5	-46.9(1), -47.0(2)	Cu-4-5-6	-23.5(2), -23.9(2)
11-1-2-3	105.7(2), 103.4(1)	11-1-9-8	-167.6(1), -169.4(1)
4-5-6-7	48.7(2), 49.8(2)	Cu-1-11-12	49.7(2), -37.7(2)
15-Cu-4-41	4.9(1), 2.2(1)	15-Cu-7-71	28.3(1), 24.7(1)
1-11-12-13	-78.0(2), 76.1(2)	11-12-13-14	56.7(2), -69.0(2)
12-13-14-15	174.1(5), -148.1(6)		

<sup>a</sup> The two values in each entry are for unprimed and primed cations, respectively. <sup>b</sup> C, N denoted by number only, N italicized.

features expected for a complex with one bound and two free alkynes. The <sup>13</sup>C NMR spectrum contained four signals in the alkyne region ( $\delta$  81.9, 86.1, 89.4, 94.4). Two of these signals had chemical shifts similar to those of the alkyne carbons of free **1** ( $\delta$  81.4, 91.1 for **1** in acetone-*d*<sub>6</sub>) and are thus attributed to the carbons of the pendant alkyne groups, while the other two signals, which were of lower intensity, are assigned to the carbons of the coordinated alkyne group. The <sup>1</sup>H NMR spectrum showed signals at  $\delta$  2.28 and 2.91 (relative areas 4H and 2H, respectively), which are attributed to the methylene protons adjacent to the two free alkynes and the single bound alkyne, respectively. The infrared spectrum of **2**·BPh<sub>4</sub> contained a weak signal at 2229 cm<sup>-1</sup>, which, being similar in position to the signal due to the C≡C stretching mode for **1** (2227 cm<sup>-1</sup>), is attributed to the free alkyne groups in **2**. A slightly more intense signal at 2022 cm<sup>-1</sup> is attributed to C≡C stretching of the coordinated alkyne group. The decrease in stretching frequency (ca. 200 cm<sup>-1</sup>) on coordination of the alkyne to the Cu(I) center in **2** is within the range reported previously for other alkynes on coordination to Cu(I) centers.<sup>11</sup>

Crystals of **2**·BPh<sub>4</sub> suitable for X-ray studies were grown from acetone/light petroleum solutions. The results of the low-temperature single-crystal X-ray study are consistent with the stoichiometry and connectivity as given above. Two independent molecules, devoid of crystallographic symmetry, comprise the asymmetric unit of the structure. Within each molecule the copper atom is coordinated by the three nitrogen atoms of the triazacyclononane moiety, together with an  $\eta^2$ -alkyne group from one of the pendants. While in broad terms the copper–ligand atom distances fall into the ranges expected, there are surprising divergences in the pa-

rameters of the coordination geometry between the two molecules, and from the putative noncrystallographic *m*-symmetries of the core environments (*m* through Cu, N(1), C(14,15)). In terms of distances there are differences in Cu–N(4) and Cu–N(7) both within each molecule and between the two molecules (Table 1), with very large associated differences in derivative angles, presumably a concomitant of different ring conformations, between the two molecules (Figure 1) and between the two quasi-*m*-related halves of each molecule. Comparing the two molecules, the conformations of the triazacyclononane components about the two metal atoms are very similar (see torsion angles in Table 1), despite the considerable differences in geometries of the CuN<sub>3</sub> arrays.

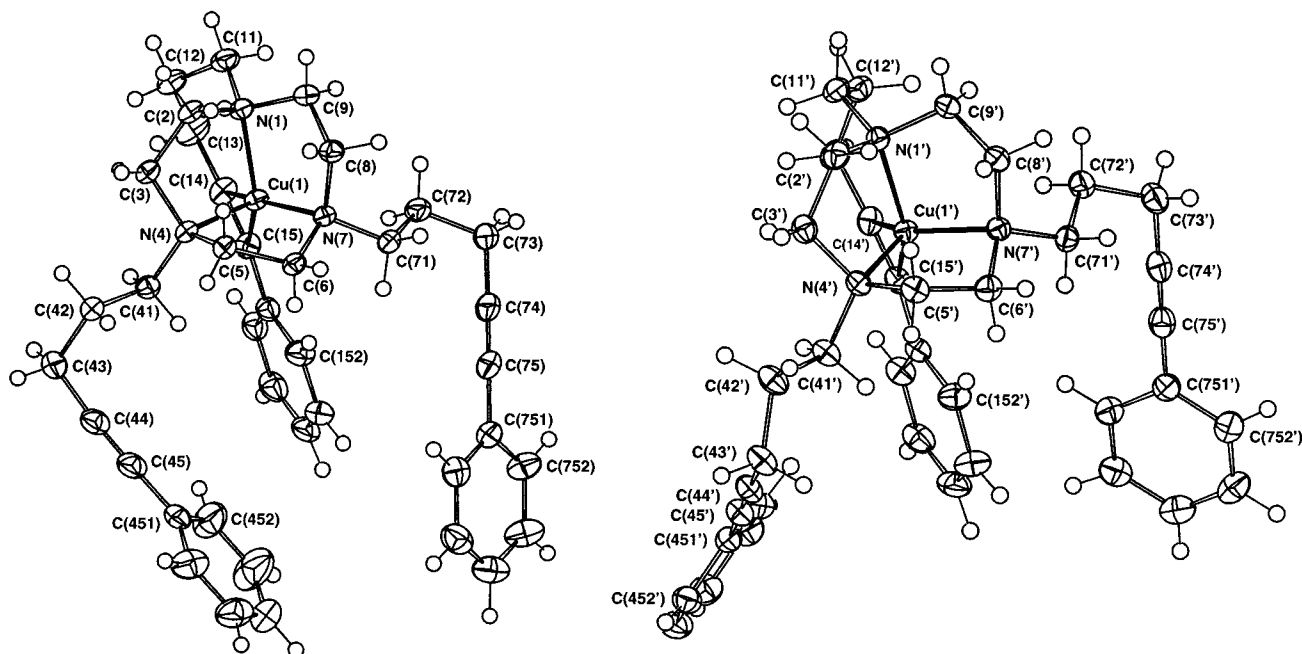
Related systems with N<sub>3</sub>-donors of appropriate symmetry and simplicity with an (N<sub>3</sub>-donor)Cu<sup>I</sup>( $\eta^2$ -C<sub>2</sub>) coordination environment are rather few (Table 2). Diethylenetriamine (H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>, dien) is a close analogue of the present triazacyclononane, lacking the ring closure provided by the last (CH<sub>2</sub>)<sub>2</sub> moiety; two complexes are recorded of it, both with alkenes rather than alkynes, viz. hex-1-ene<sup>12</sup> and norbornadiene.<sup>13</sup> A further complex [{HB(pz)<sub>3</sub>}Cu(C<sub>2</sub>H<sub>4</sub>)] (pz = pyrazolyl, C<sub>2</sub>H<sub>4</sub> = ethylene)<sup>14</sup> is also relevant. In all of these, a “central” nitrogen atom may be discerned, either by virtue of lack of closure of the ligand or the putative symmetry of the situation. In all cases, presumably because of the absence of a tether linking the coordinated alkene to the N<sub>3</sub> core, the C=C bond lies parallel to the line joining the outer nitrogen donors, rather than perpendicular to this line as for the C≡C bond in **2**. The

(12) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *Inorg. Chem.* **1979**, *18*, 3535.

(13) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **1978**, *100*, 4918.

(14) Thompson, J. S.; Harlow, R. L.; Whitney, F. J. *J. Am. Chem. Soc.* **1983**, *105*, 3522.

(11) Munakata, M.; Kitagawa, S.; Kawada, I.; Maekawa, M.; Shimo, H. *J. Chem. Soc., Dalton Trans.* **1992**, 2225.



**Figure 1.** Projections of the two independent molecules (unprimed, primed), showing 50% probability amplitude displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Note the different conformations of the coordinated rings (cf. Table 1).

**Table 2. Comparative Geometries for (N<sub>3</sub>-Donor)Cu(η<sup>2</sup>-C<sub>2</sub>) Systems**

complex	<b>2</b> <sup>a</sup>	[(dien)Cu(C <sub>6</sub> H <sub>12</sub> )] <sup>+</sup> <sup>b</sup>	[(dien)Cu(C <sub>7</sub> H <sub>10</sub> )] <sup>+</sup> <sup>c</sup>	{[HB(pz) <sub>3</sub> ]Cu(C <sub>2</sub> H <sub>4</sub> )] <sup>d</sup>
		Distances (Å)		
Cu–N(central)	2.041(1), 2.041(1)	2.25(1), 2.21(2)	2.252(7)	2.160(4)
Cu–N(outer)	2.248(1), 2.195(1)	2.11(1), 2.13(2)	2.008(6)	2.017(3)
Cu–C	2.087(1), 2.124(1)	2.09(1), 2.14(1)	2.109(8)	2.041(3)
	1.950(1), 1.955(2)	2.10(2), 2.03(2)	2.19(1)	2.023(5)
Cu–C <sub>2</sub> (midpt)	1.996(1), 2.002(2)	2.13(2), 2.10(2)	2.19(1)	2.004(6)
C–C	1.874(1), 1.880(1)	2.01(2), 1.98(2)	2.08(1)	1.90(1)
	1.236(2), 1.234(2)	1.30(3), 1.18(3)	1.38(2)	1.329(9)
		Angles (deg)		
N(central)–Cu–N(outer)	84.88(4), 85.80(5)	83.2(7), 84.1(8)	83.3(3)	89.8(1)
	88.71(5), 86.85(5)	83.5(6), 83.1(7)	81.5(4)	89.7(1)
N(outer)–Cu–N(outer)	82.97(4), 83.83(4)	108.0(7), 105.2(8)	105.6(3)	92.4(1)
C <sub>2</sub> (midpt)–Cu–N(central)	120.4(1), 122.1(4)	121.1(9), 130.8(11)	108.2(4)	115.6(1)
C <sub>2</sub> (midpt)–Cu–N(outer)	117.7(1), 125.7(4)	127.4(9), 130.1(11)	125.6(4)	129.9(1)
	144.0(1), 136.8(3)	119.7(9), 112.4(10)	128.4(4)	127.6(1)

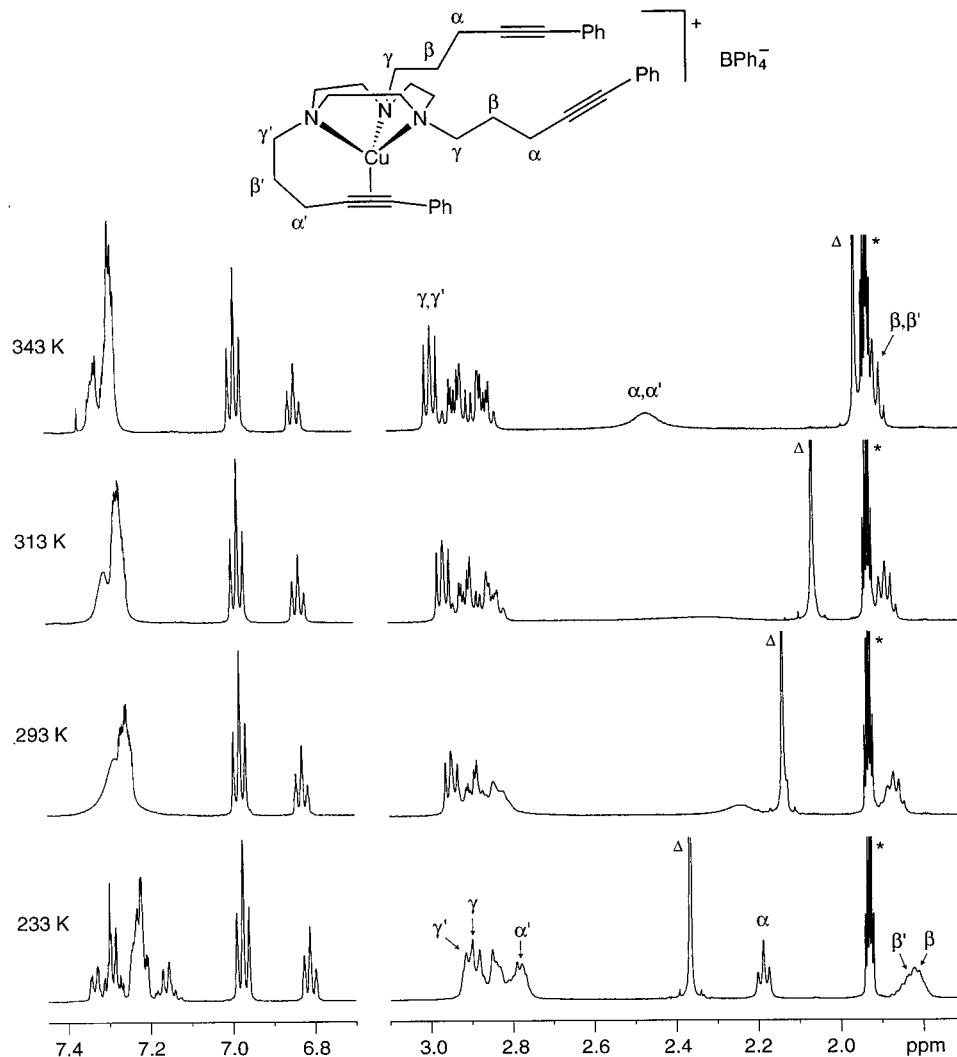
<sup>a</sup> Two molecules of different conformation. <sup>b</sup> Reference 12. Two molecules of different conformation. C<sub>6</sub>H<sub>12</sub> = hex-1-ene. <sup>c</sup> Reference 13. <sup>d</sup> Reference 14. The “central” nitrogen here is the “different” one (N(31) in ref 14), the C=C bond of the ethylene lying parallel to N(11)⋯N(21).

presence of the tether in **2** may also explain why in this complex the Cu–N(central) bond is the shortest Cu–N bond, by a considerable margin, whereas the Cu–N(outer) bond is the longest Cu–N bond in each alkene complex. The N(outer)–Cu–N(outer) angles in the three alkene complexes vary diversely, those of the dien complexes greatly enlarged compared to those in the [HB(pz)<sub>3</sub>]<sup>–</sup> complex and **2**. To what extent these differences may be a consequence of electronic factors associated with the type of η<sup>2</sup>-C<sub>2</sub> donor and its orientation, cf. the pendant constraint in **2**, is unclear, but it is noteworthy that in **2**, regardless of which molecule, the N–Cu–C angles are very divergent, suggestive of some tension between the disposition of the C≡C moiety and its tether.

The coordinated alkyne in **2** can be displaced. Addition of PPh<sub>3</sub> to solutions containing **2**·BPh<sub>4</sub> or **2**·PF<sub>6</sub> resulted in quantitative displacement of the bound alkyne and formation of a product identified as **3** on the basis of its NMR spectra. The <sup>1</sup>H and <sup>13</sup>C NMR spectra

were consistent with a complex with C<sub>3</sub> symmetry (i.e., three equivalent phenylpentynyl groups), while the <sup>31</sup>P NMR spectrum of the product showed a resonance at δ 6.8, which is close to that observed for the cation in [(<sup>i</sup>Pr<sub>3</sub>TACN)Cu(PPh<sub>3</sub>)]PF<sub>6</sub> (δ 5.27 in dichloromethane-*d*<sub>2</sub>).<sup>15</sup> When an 8 mM solution of **2**·PF<sub>6</sub> in acetone-*d*<sub>6</sub> solution was purged with CO and maintained under an atmosphere of CO, an equilibrium mixture containing **2** and a product tentatively assigned as the CO adduct **4** was formed (Scheme 1). The adduct **4** was identified by new signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the solution, and the ratio of **2** to **4** was ca. 1.4:1, respectively (by <sup>1</sup>H NMR). When the sample was purged with N<sub>2</sub>, **4** was converted to **2**, but when the CO atmosphere was restored, the equilibrium between **2** and **4** was reestablished. Other Cu(I) TACN complexes are known to bind CO reversibly.<sup>16</sup>

(15) Halfen, J. A.; Mahapatra, S.; Wilkinson, E. C.; Gengenbach, A. J.; Young, V. G., Jr.; Que, L., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1996**, *118*, 763.



**Figure 2.**  $^1\text{H}$  NMR spectra (500.1 MHz, acetonitrile- $d_3$ ) for solutions of  $2 \cdot \text{BPh}_4$  at the temperatures indicated. Signals marked  $\Delta$  are due to adventitious moisture and the signal marked \* is the solvent signal.

The  $^1\text{H}$  NMR spectra of acetonitrile- $d_3$  solutions containing  $2 \cdot \text{BPh}_4$  at ambient temperatures were broadened, apparently due to exchange of free and coordinated alkyne groups. Variable-temperature NMR studies (Figure 2) show that, at 233 K, this process is essentially frozen out. The most dramatic change between spectra recorded at 233 and 343 K is that at the higher temperature the six protons ( $\alpha$  and  $\alpha'$ ) adjacent to the alkyne groups appear as a singlet (albeit still somewhat broad) resonance near  $\delta$  2.47, whereas at 233 K, the four protons ( $\alpha$ ) adjacent to the free alkyne groups resonate as a triplet at  $\delta$  2.19 and the two protons ( $\alpha'$ ) adjacent to the coordinated alkyne group resonate near  $\delta$  2.8. The coalescence temperature for the signals due to these protons is ca. 320 K. Assuming that the difference in resonant frequencies of the  $\alpha$  and  $\alpha'$  protons at this temperature is the same as at 233 K (305 Hz), we estimate<sup>17</sup> the rate constant for the exchange process as  $610 \text{ s}^{-1}$  at 320 K.

We presume the acetonitrile solvate **5** to be an intermediate in the exchange process responsible for the temperature dependence of the NMR spectra. The fact that the chemical shift of the  $\alpha/\alpha'$  protons at high

temperature is close to the population-weighted average of the chemical shifts observed for the  $\alpha$  and  $\alpha'$  protons at low temperature ( $\delta$  2.39) suggests that if **5** is formed it is not present in significant amounts at any given instant. If the changes of the NMR spectra with temperature were simply a consequence of acetonitrile displacing the coordinated alkyne then we would expect the signal due to the  $\alpha/\alpha'$  protons to appear near  $\delta$  2.19 in the high-temperature spectra.

Triacyclononane-Cu(I) complexes are generally extremely sensitive to air and water,<sup>15,18</sup> TACN-Cu(I) adducts of alkynes particularly so.  $[\text{Cu}(\eta^2\text{-PhC}\equiv\text{CPh})(\eta^3\text{-R}_3\text{TACN})]\text{BPh}_4$  (R = H or Me), formed by the reaction of  $\text{R}_3\text{TACN}$  with CuI, diphenylacetylene, and  $\text{NaBPh}_4$  in methanol, decomposed in solution before a  $^{13}\text{C}$  NMR spectrum could be recorded.<sup>19</sup> In contrast, the

(17) The commonly used expression for estimation of rate constants at coalescence is  $k_c = 2.22\Delta\nu$ , where  $\Delta\nu$  is the difference between the resonant frequencies of the exchanging protons. The expression applies when the exchange involves equally populated sites. In this study, the  $\alpha$  and  $\alpha'$  protons have relative populations 0.67 and 0.33, respectively, and as a result the expression for the rate constant becomes  $k_c = 2.01\Delta\nu$ . See: Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; pp 81–82.

(18) Berreau, L. M.; Halfen, J. A.; Young, V. G., Jr.; Tolman, W. B. *Inorg. Chem.* **1998**, *37*, 1091.

(19) Chaudhuri, P.; Oder, K. *J. Organomet. Chem.* **1989**, *367*, 249.

(16) Berreau, L. M.; Halfen, J. A.; Young, V. G., Jr.; Tolman, W. B. *Inorg. Chim. Acta* **2000**, *297*, 115.

Cu(I) complex **2**, as its PF<sub>6</sub><sup>−</sup> or BPh<sub>4</sub><sup>−</sup> salt, is remarkably stable. Crystals of **2**·BPh<sub>4</sub> exposed to the laboratory atmosphere showed no signs of decomposition after several months in the laboratory atmosphere at ambient temperature. Solutions of **2**·BPh<sub>4</sub> in acetone-*d*<sub>6</sub> or **2**·PF<sub>6</sub> in methanol-*d*<sub>4</sub> prepared in the laboratory atmosphere showed no changes in color or <sup>1</sup>H NMR spectra even after exposure to oxygen over several hours. Over the course of several weeks, however, the solutions developed a green color, and their <sup>1</sup>H NMR spectra indicated the presence of unidentified products.

The resistance of **2** to aerial oxidation is reflected in the behavior of the complex in cyclic voltammetry experiments (ca. 1 mM solutions of **2** in 0.1 M (Bu<sub>4</sub>N)–(PF<sub>6</sub>) in acetonitrile, scan rate 200 mV/s). In these experiments, **2** showed no redox activity over the range −0.5 to +0.8 V (vs Ag/AgCl). Previously studies<sup>15,16</sup> of (R<sub>3</sub>TACN)Cu(I)L systems (L = heterocyclic N-donor or CH<sub>3</sub>CN) found that the complexes exhibited quasi-reversible one-electron redox transformations with *E*<sub>1/2</sub> values in the range −0.1 to +0.36 V vs SCE (i.e., ca. −0.05 to +0.41 V vs Ag/AgCl). In experiments cycled over the range −1.0 to +1.5 V, solutions of **2** showed an oxidation wave centered near +1.1 V (vs Ag/AgCl) and an associated reduction wave centered near +0.4 V. The large separation between the waves suggests a complicated redox behavior. We tentatively interpret these results in terms of four steps: (i) a single-electron oxidation of **2** to the Cu(II) form; (ii) displacement of the coordinated alkyne leading to formation of [(R<sub>3</sub>TACN)Cu(CH<sub>3</sub>CN)]<sup>2+</sup> (R = 5-phenyl-4-pentynyl); (iii) single-electron reduction of [(R<sub>3</sub>TACN)Cu(CH<sub>3</sub>CN)]<sup>2+</sup> (R = 5-phenyl-4-pentynyl) to form the acetonitrile solvate **5**; and (iv) subsequent displacement of coordinated acetonitrile by an alkyne group to regenerate **2**. We note that the potential of the reduction wave is very close to the *E*<sub>1/2</sub> value (+0.36 vs SCE, ca. +0.41 V vs Ag/AgCl) reported<sup>15</sup> for [(Pr<sub>3</sub>TACN)Cu(CH<sub>3</sub>CN)]<sup>+</sup>. Whatever the processes responsible for the observed cyclic voltammograms, the absence of any redox behavior over the range −0.5 to +0.8 V demonstrates that the Cu(I) state is remarkably stable in **2** compared to related TACN–Cu(I) complexes. This stability may be due in part to the “soft” nature of the alkyne group,<sup>16</sup> but the notable instability of [Cu(η<sup>2</sup>-PhC≡CPh)(η<sup>3</sup>-R<sub>3</sub>TACN)]·BPh<sub>4</sub> (R=H or Me),<sup>19</sup> complexes with intermolecularly coordinated alkynes, suggests that the chelate effect is also a significant factor in the stability of **2**.

## Experimental Section

**Materials.** 1,4,7-Tri(5-phenyl-4-pentynyl)-1,4,7-triazacyclononane **1** was synthesized by reaction of 1,4,7-triazacyclononane trihydroiodide with 5-iodo-1-phenyl-1-pentyne in acetonitrile.<sup>5</sup> Methanol was dried and distilled prior to use. Reactions were performed in a N<sub>2</sub>-atmosphere drybox. NMR spectra were recorded using a Bruker ARX 500 spectrometer (500.1 MHz for <sup>1</sup>H, 125.8 MHz for <sup>13</sup>C, 202.5 MHz for <sup>31</sup>P) and were referenced with respect to solvent signals (<sup>1</sup>H, <sup>13</sup>C) or external 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). DEPT, COSY, and decoupling experiments were used in assignment of <sup>1</sup>H and <sup>13</sup>C NMR spectra. Mass spectra were obtained by Dr A. Reeder using a VG Autospec mass spectrometer, using fast atom bombardment (FAB) with a cesium ion source and *m*-nitrobenzyl alcohol as the matrix. Microanalysis was performed by the Microanalytical Laboratory, Research School of Chemistry,

Australian National University, Canberra. Cyclic voltammograms were recorded with a MacLab potentiostat controlled by a Macintosh LC computer equipped with AD Instruments Echem Software, using platinum working and counter electrodes and a silver/silver chloride reference electrode. Each solution was purged with argon and studied at ambient temperatures.

**Synthesis of 2·BPh<sub>4</sub>.** A solution of **1** (106 mg, 0.191 mmol) in methanol (2 mL) was added to a suspension of CuI (33 mg, 0.17 mmol) in methanol (8 mL), and the mixture was stirred for 3 h. A solution of NaBPh<sub>4</sub> (84 mg, 0.25 mmol) in CH<sub>3</sub>OH (2 mL) was then added, and a white precipitate formed immediately. The precipitate was collected, washed with methanol (3 mL), and dried in vacuo to yield **2**·BPh<sub>4</sub> as a white powder (139 mg, 86%) that was spectroscopically pure. A sample of analytical purity was obtained by recrystallization from acetone/ether. Anal. Calcd for C<sub>63</sub>H<sub>65</sub>BCuN<sub>3</sub>·2(CH<sub>3</sub>)<sub>2</sub>CO: C, 78.57; H, 7.36; N, 3.98. Found: C, 78.92; H, 7.31; N, 4.08. HR-MS (FAB): *m/z* 618.2934 [(M – BPh<sub>4</sub>)<sup>+</sup>, exact mass calcd for C<sub>39</sub>H<sub>45</sub>CuN<sub>3</sub> 618.2909]. IR data (KBr, cm<sup>−1</sup>): 2229 (free C≡C); 2022 (coordinated C≡C). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 295 K): δ 1.98 (6H, m, 3 × CH<sub>2</sub>CH<sub>2</sub>C≡C), 2.28 (4H, m, 2 × CH<sub>2</sub>C≡C), 2.91 (2H, m, 1 × CH<sub>2</sub>C≡C), 2.95–3.11 (18H, m, 3 × NCH<sub>2</sub>CH<sub>2</sub>N and 3 × CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C≡C), 6.78 (4H, m, 4 × H<sub>BPh</sub>), 6.92 (8H, m, 8 × H<sub>BPh</sub>), 7.23–7.36 (21H, m, 8 × H<sub>BPh</sub> and 13 × H<sub>CPh</sub>) and 7.48 (2H, m, 2 × H<sub>CPh</sub>); (acetonitrile-*d*<sub>3</sub>, 233 K): δ 1.84 (6H, m, 3 × CH<sub>2</sub>CH<sub>2</sub>C≡C), 2.19 (4H, t, *J*<sub>HH</sub> = 6.8 Hz, 2 × CH<sub>2</sub>C≡C), 2.75–2.95 (20H, m, 3 × NCH<sub>2</sub>CH<sub>2</sub>N, 3 × CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C≡C and 1 × CH<sub>2</sub>C≡C), 6.81 (4H, m, 4 × H<sub>BPh</sub>), 6.98 (8H, m, 8 × H<sub>BPh</sub>), 7.12–7.35 (23H, m, 8 × H<sub>BPh</sub> and 15 × H<sub>CPh</sub>); (acetonitrile-*d*<sub>3</sub>, 343 K): δ 1.91 (6H, quintet, *J*<sub>HH</sub> = 7.0 Hz, 3 × CH<sub>2</sub>CH<sub>2</sub>C≡C), 2.47 (6H, br, *W*<sub>1/2</sub> 31 Hz, 3 × CH<sub>2</sub>C≡C), 2.83–2.97 (12H, AA'BB' pattern, 3 × NCH<sub>2</sub>CH<sub>2</sub>N), 2.99 (6H, apparent t, splitting 7.2 Hz, 3 × CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C≡C), 6.84 (4H, m, 4 × H<sub>BPh</sub>), 6.99 (8H, m, 8 × H<sub>BPh</sub>), 7.26–7.36 (23H, m, 8 × H<sub>BPh</sub> and 15 × H<sub>CPh</sub>). <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>, 295 K): δ 17.6 (2 × CH<sub>2</sub>C≡C), 19.6 (1 × CH<sub>2</sub>C≡C), 26.6 (2 × CH<sub>2</sub>CH<sub>2</sub>C≡C), 26.8 (1 × CH<sub>2</sub>CH<sub>2</sub>C≡C), 53.6, 54.1, 56.8 and 60.6 (2 × CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C≡C and 3 × NCH<sub>2</sub>CH<sub>2</sub>N), 61.9 (1 × CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C≡C), 81.9 (2 × C≡CPh), 86.1 (1 × C≡CPh), 89.4 (2 × C≡CPh), 94.4 (1 × C≡CPh), 122.2 (4 × CH<sub>BPh</sub>), 124.6 (2 × C<sub>Ph</sub>), 125.2 (1 × C<sub>Ph</sub>), 126.0 (8 × CH<sub>BPh</sub>), 128.7 (2 × CH<sub>Ph</sub>), 129.21 (4 × CH<sub>Ph</sub>), 129.23 (1 × CH<sub>Ph</sub>), 129.8 (2 × CH<sub>Ph</sub>), 131.4 (2 × CH<sub>Ph</sub>), 132.2 (4 × CH<sub>Ph</sub>), 137.0 (8 × CH<sub>BPh</sub>) and 164.9 (4 × C<sub>BPh</sub>).

**Structure Determination for 2·BPh<sub>4</sub>.** A full sphere of CCD area-detector diffractometer data was measured (Bruker AXS instrument; ω-scans, 2θ<sub>max</sub> = 68°; monochromatic Mo Kα radiation, λ = 0.71073 Å; *T* ca. 153 K) yielding 75 226 reflections, these merging to 38 319 (*R*<sub>int</sub> = 0.026) after “empirical”/multiscan absorption correction (*μ*<sub>Mo</sub> = 4.7 cm<sup>−1</sup>; specimen: 0.45 × 0.35 × 0.15 mm; *T*<sub>min,max</sub> = 0.69, 0.80), 25986 with *F* > 4σ(*F*) being considered “observed” and used in the full-matrix least-squares refinement, refining anisotropic thermal parameter forms for the non-hydrogen atoms, together with (*x*, *y*, *z*, *U*<sub>iso</sub>)<sub>H</sub>. Final conventional residuals on |*F*| at convergence were *R* (= Σ(|Δ|*F*)/Σ|*F*<sub>o</sub>|) = 0.039, *R*<sub>w</sub> = (Σ(*w*Δ<sup>2</sup>)/Σ|*F*<sub>o</sub>|<sup>2</sup>)<sup>1/2</sup> (*w* = (*σ*<sup>2</sup>(*F*) + 0.0004*F*<sup>2</sup>)<sup>−1</sup>) = 0.042. Neutral atom complex scattering factors were employed within the Xtal 3.7 program system.<sup>20</sup> Pertinent results are given below and in Tables 1 and 2 and Figure 1.

**Crystal data:** C<sub>63</sub>H<sub>65</sub>BCuN<sub>3</sub>, *M* = 938.6; triclinic, space group *P*1̄(*C*<sub>1</sub><sup>i</sup>, No. 2), *a* = 13.0957(7) Å, *b* = 19.682(1) Å, *c* = 20.655(1) Å, α = 74.829(1)°, β = 81.526(1)°, γ = 89.799(1)°, *V* = 5079 Å<sup>3</sup>, *D*<sub>c</sub> (*Z* = 4) = 1.227 g cm<sup>−3</sup>. Δρ<sub>max</sub> = 0.8(1) e Å<sup>−3</sup>.

**Spectral Characterization of 3·BPh<sub>4</sub>.** Triphenylphosphine (2.0 mg, 7.6 μmol) was added to a solution of **2**·BPh<sub>4</sub> (6.7 mg, 7.1 μmol) in acetonitrile-*d*<sub>3</sub> (1.0 mL). The product, formed in quantitative yield (by <sup>1</sup>H NMR), was identified as

(20) Hall, S. R.; du Boulay, D. J.; Olthof-Hazekamp, R., Eds. *The Xtal 3.7 System*; The University of Western Australia: Nedlands, 2000.

**3**·BPh<sub>4</sub> on the basis of its NMR spectral data. <sup>1</sup>H NMR (acetonitrile-*d*<sub>6</sub>, 295 K): δ 1.76 (6H, m, 3 × CH<sub>2</sub>C≡C), 1.80 (6H, m, 3 × CH<sub>2</sub>CH<sub>2</sub>C≡C), 2.72 (6H, m, 3 × CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-C≡C), 2.79–2.92 (12H, AA'BB' pattern, 3 × NCH<sub>2</sub>CH<sub>2</sub>N), 6.83 (4H, m, 4 × H<sub>BPh</sub>), 6.98 (8H, m, 8 × H<sub>BPh</sub>), 7.23–7.33 (29H, m, 8 × H<sub>BPh</sub> and 21 × H<sub>Ph</sub>) and 7.35–7.46 (9H, m, 9 × H<sub>Ph</sub>). <sup>13</sup>C NMR (acetonitrile-*d*<sub>6</sub>, 295 K): δ 17.2 (3 × CH<sub>2</sub>C≡C), 28.3 (3 × CH<sub>2</sub>CH<sub>2</sub>C≡C), 54.9 (3 × NCH<sub>2</sub>CH<sub>2</sub>N), 61.8 (3 × CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>C≡C), 81.6 (3 × C≡CPh), 89.7 (3 × C≡CPh), 122.7 (4 × CH<sub>BPh</sub>), 124.5 (3 × C<sub>Ph</sub>), 126.5 (8 × CH<sub>BPh</sub>), 128.8 (3 × CH<sub>Ph</sub>), 129.4 (6 × CH<sub>Ph</sub>), 130.3 (d, *J*<sub>PC</sub> = 10 Hz, 6 × CH<sub>PPH</sub>), 131.5 (d, *J*<sub>PC</sub> = 2 Hz, 3 × CH<sub>PPH</sub>), 132.2 (6 × CH<sub>Ph</sub>), 132.9 (d, *J*<sub>PC</sub> = 37 Hz, 3 × C<sub>PPH</sub>), 134.0 (d, *J*<sub>PC</sub> = 14 Hz, 6 × CH<sub>PPH</sub>), 136.7 (8 × CH<sub>BPh</sub>) and 164.7 (4 × C<sub>BPh</sub>). <sup>31</sup>P NMR (acetonitrile-*d*<sub>6</sub>, 295 K): δ 6.8.

**Spectral Characterization of 4**·PF<sub>6</sub>. Carbon monoxide was bubbled through a solution of **2**·PF<sub>6</sub> (6 mg) in acetone-*d*<sub>6</sub> (1 mL) in an NMR tube fitted with a rubber septum. The resulting sample was maintained under an atmosphere of CO and was found (by integration of <sup>1</sup>H NMR peaks) to contain the cation **2** and the CO adduct **4** in a ratio of 1.4:1, respectively. The adduct **4** was identified on the basis of its signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the sample. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 295 K): δ 2.14 (6H, m, 3 × CH<sub>2</sub>CH<sub>2</sub>C≡C), 2.54

(6H, t, *J* = 6.8 Hz, 3 × CH<sub>2</sub>C≡C), 3.04–3.20 (12H, m, 3 × NCH<sub>2</sub>CH<sub>2</sub>N; partly obscured by resonances due to **2**), 3.28 (6H, m, 3 × CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C≡C), 7.25–7.38 (15H, m, 15 × H<sub>Ph</sub>; partly obscured by resonances due to **2**). <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>, 295 K): δ 17.6 (3 × CH<sub>2</sub>C≡C), 28.6 (3 × CH<sub>2</sub>CH<sub>2</sub>C≡C), 55.1 (3 × NCH<sub>2</sub>CH<sub>2</sub>N), 61.6 (3 × CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C≡C), 81.9 (3 × C≡CPh), 89.6 (3 × C≡CPh), 124.5 (3 × C<sub>Ph</sub>), 128.8 (3 × CH<sub>Ph</sub>), 129.3 (6 × CH<sub>Ph</sub>), 132.2 (6 × CH<sub>Ph</sub>) and 185.0 (CO).

**Acknowledgment.** We thank the Australian Research Council for Small Grant funding and for an Australian Postgraduate Research Award (to D.H.B.). We thank the Crystallography Center of The University of Western Australia for a Ted Maslen Scholarship (to N.S.).

**Supporting Information Available:** Full details of crystallographic study of **2**·BPh<sub>4</sub>, including a figure showing the unit cell array and tables giving all crystallographic data, atomic positional parameters, bond distances and angles, and anisotropic thermal parameters. This information is available free of charge via the Internet at <http://pubs.acs.org>.

OM000999Z