Novel *triangulo* Copper(I) Complexes Containing μ_3-η^1-Alkynyl, μ_3-Chloride, and μ-η^1-Isocyanide Ligands: X-ray Crystal Structure of $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)(\mu\text{-}\eta^1\text{-}C{\equiv}NC_6H_4CH_3\text{-}4)(\mu\text{-dppm})_3][BF_4]_2{\cdot}3CH_2Cl_2$

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Received March 17, 1997[⊗]

Trinuclear copper(I) isocyanide complexes $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR^1)(\mu\text{-}\eta^1\text{-}C{\equiv}NR^2)(\mu\text{-dppm})_3][BF_4]_2$ (dppm = bis(diphenylphosphino)methane; $R^1 = C_6H_5$, $R^2 = CH_2C_6H_5$ (**1**), C_6H_{11} (**2**), 4-$CH_3C_6H_4$ (**3**); R^1 = 4-$CH_3C_6H_4$, $R^2 = CH_2C_6H_5$ (**4**), C_6H_{11} (**5**), 4-$CH_3C_6H_4$ (**6**)) have been prepared by reaction of the complexes $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR^1)(\mu\text{-dppm})_3][BF_4]_2$ with isocyanides in CH_2Cl_2 at room temperature. Similarly, the treatment of the complex $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-dppm})_3][BF_4]$ with isocyanides in CH_2Cl_2 and in the presence of $AgBF_4$ affords the complexes $[Cu_3(\mu_3\text{-}Cl)(\mu\text{-}\eta^1\text{-}C{\equiv}NR)(\mu\text{-dppm})_3][BF_4]_2$ (R = $CH_2C_6H_5$ (**7**), C_6H_{11} (**8**), 4-$CH_3C_6H_4$ (**9**)). Crystal structure of the complex **6** has been determined by X-ray diffraction methods. The cationic complex consists of a scalene triangle arrangement of the copper atoms bridged by three dppm ligands, with the *p*-tolyl isocyanide ligand bridging the shortest edge and the *p*-tolylethynyl ligand showing an asymmetric μ_3-η^1 bridging mode. The isocyanide group shows an unusual linearity (C−N−C = 171.13(9)°). ^1H and $^{31}P\{^1H\}$ NMR data are also reported. Variable-temperature $^{31}P\{^1H\}$ NMR studies reveal a dynamic behavior of the isocyanide ligand in solution on the basis of a μ-η^1 to μ_3-η^1 isocyanide exchange process.

Introduction

It is well-known that trinuclear complexes containing group 10 or 11 metals can be stabilized by three bridging bis(diphenylphosphino)methane (dppm) ligands and at least one triply bridging ligand.[1] The triangular framework $[M_3(\mu\text{-dppm})_3]$ appears to be appropriate support for different μ_3-bridging ligands, for instance (i) carbonyl and halide groups in $[M_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (M = Pt,[2a] Pd,[2b,c]), $[Pt_3(\mu_3\text{-CO})L(\mu\text{-dppm})_3]^{n+}$ (L = SCN, CN, n = 1; L =CO, PR_3, $P(OR)_3$, n = 2),[2d−g] $[Pd_3(\mu_3\text{-}X)(\mu_3\text{-CO})(\mu\text{-dppm})_3]^+$ (X = CF_3CO_2, Cl, Br, I),[1c,2b,3] $[Ni_3(\mu_3\text{-}X)(\mu_3\text{-}L)(\mu\text{-dppm})_3]^{n+}$ (L = I, Br, CO; X =I, Br, n = 0,1),[4,5] and $[Ag_3(\mu_3\text{-}X)_2(\mu\text{-dppm})_3]^+$ (X = Cl, Br),[6] (ii) alkynyl groups in $[Ni_3(\mu_3\text{-}C{\equiv}CPh)_2(\mu\text{-dppm})_3]^+$,[7] and (iii) isocyanide groups in $[Ni_3(\mu_3\text{-CNMe})(\mu_3\text{-I})(\mu\text{-dppm})_3]^+$,[8] $[Ni_3(\mu_3\text{-CNR})(\mu_3\text{-}X)(\mu\text{-dppm})_3]^{n+}$ (X = I, Br, n = 0, 1),[5b] $[Pd_3(\mu_3\text{-}CNC_6H_3Me_2\text{-}2,6)_n(\mu\text{-dppm})_3]^{2+}$ (n = 1, 2)[9] and $[\{Pd_3(\mu\text{-dppm})_3\}_2\{\mu\text{-}(\mu_3\text{-}CNC_6Me_4NC)\}]^{4+}$.[9] A wide variety of triply bridging units, some of them very unusual (e.g. Tl(acac), ReO_3, and PF_3), can also be incorporated into the triangular framework.[10]

Recently we have also reported[11,12] the synthesis and structural characterization of a series of cationic trinuclear copper(I) complexes containing the moiety $[Cu_3(\mu\text{-dppm})_3]$ stabilized by μ_3-η^1-acetylide and μ_3-chloride groups, $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(\mu\text{-dppm})_3]^{2+}$, $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)_2(\mu\text{-dppm})_3]^+$, and $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3]^+$ (R = Ph, Bu^t, CH_2OCH_3),[11] as well as by alkoxide and thiolate groups, $[Cu_3(\mu_3\text{-OR})(\mu_3\text{-Cl})(\mu\text{-dppm})_3]^+$ (R = 2,4,6-$Bu^t{}_3C_6H_2$, 2,6-$Bu^t{}_2C_6H_3$, 2,6-$Bu^t{}_2$-4-$CH_3C_6H_2$, 4-$CH_3C_6H_4$) and $[Cu_3(\mu_3\text{-XR})_2(\mu\text{-dppm})_3]^+$ (R = 4-$CH_3C_6H_4$; X = O, S).[12] Moreover, the complexes $[Cu_3(\mu_3\text{-Cl})_2(\mu\text{-dppm})_3]^+$ and $[Cu_3(\mu\text{-OH})(\mu\text{-dppm})_3]^{2+}$ have also been described.[13a,b]

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

(1) (a) Burrows, A. D.; Mingos, D. M. P. *Coord. Chem. Rev.* **1996**, *154*, 19. (b) *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; M = Ni (Vol. 4.1), M = Pd (Vol. 4.4), M = Pt (Vol. 4.7), M = Cu, Ag (Vol. 3.2). (c) Puddephatt, R. J.; Manojlovic-Muir, L.; Muir, K. W. *Polyhedron* **1990**, *9*, 2767.

(2) (a) Ferguson, G.; Lloyd, B. R.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 344. (b) Lloyd, B. R.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1993**, *12*, 1231. (c) Manojlovic-Muir, L.; Muir, K. W.; Lloyd, B. R.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1336. (d) Ferguson, G.; Lloyd, B. R.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Inorg. Chem.* **1986**, *25*, 4190. (e) Jennings, M. C.; Puddephatt, R. J.; Manojlovic-Muir, L.; Muir, K. W.; Mwariri, B. N. *Organometallics* **1992**, *11*, 4164. (f) Lloyd, B. R.; Bradford, A. M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 424. (g) Bradford, A. M.; Douglas, G.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1990**, *9*, 409.

(3) Manojlovic-Muir, L.; Muir, K. W.; Lloyd, B. R.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1985**, 536.

(4) Manojlovic-Muir, L.; Muir, K. W.; Mirza, H. A.; Puddephatt, R. J. *Organometallics* **1992**, *11*, 3440.

(5) (a) Morgenstern, D. A.; Wittrig, R. E.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1993**, *115*, 6470. (b) Morgenstern, D. A.; Ferrence, G. M.; Washington, J.; Henderson, J. I.; Rosenhein, L.; Heise, J. D.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1996**, *118*, 2198.

(6) (a) Aly, A. A. M.; Neugebauer, D.; Orama, O.; Schubert, U.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 125. (b) Franzoni, D.; Pelizzi, G.; Predieri, G.; Tarasconi, P.; Vitali, F.; Pelizzi, C. *J. Chem. Soc., Dalton Trans.* **1989**, 247.

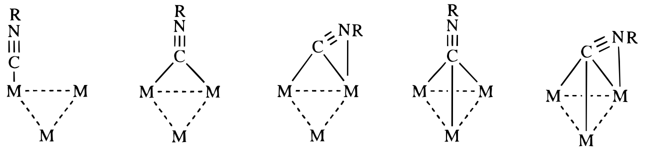
(7) Maekawa, M.; Munakata, M.; Kuroda-Sowa, T.; Hachiya, K. *Inorg. Chim. Acta* **1995**, *233*, 1.

(8) Ratliff, K. S.; Fanwick, P. E.; Kubiak, C. P. *Polyhedron* **1990**, *9*, 1487.

(9) Rashidi, M.; Kristof, E.; Vittal, J. J.; Puddephatt, R. J. *Inorg. Chem.* **1994**, *33*, 1497.

S0276-7333(97)00213-6 CCC: $14.00

Chart 1



A (η^1) **B** (μ_2- η^1) **C** (μ_2- η^2) **D** (μ_3- η^1) **E** (μ_3- η^2)

Since isocyanides are also suitable bridging ligands, we believed it to be of interest to explore their bonding ability in the $[Cu_3(\mu\text{-dppm})_3]$ framework. At the present, to the best of our knowledge, only mono- and dinuclear copper(I) complexes containing terminal isocyanide ligands have been described.[14]

Although isocyanides can bind to trinuclear clusters by adopting any of the limiting structures shown in Chart 1, in the triangular framework $[M_3(\mu\text{-dppm})_3]$ the isocyanide ligand only adopts the triply bridging (**D**; M = Ni, Pd) [5b,8,9] and terminal (**A**; M = Pt[15]) bonding modes.

This paper reports the reaction of isocyanides with the coordinatively unsaturated trinuclear complexes $[Cu_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}CR)(\mu\text{-dppm})_3][BF_4]_2$, as well as with $[Cu_3(\mu_3\text{-Cl})_2(\mu\text{-dppm})_3][BF_4]$. The synthesis of complexes $[Cu_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}CR^1)(\mu\text{-}\eta^1\text{-C}{\equiv}NR^2)(\mu\text{-dppm})_3][BF_4]_2$ (**1**−**6**) and $[Cu_3(\mu_3\text{-Cl})(\mu\text{-}\eta^1\text{-C}{\equiv}NR)(\mu\text{-dppm})_3][BF_4]_2$ (**7**−**9**) and the X-ray structure of $[Cu_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}CC_6H_4CH_3\text{-}4)(\mu\text{-}\eta^1\text{-C}{\equiv}NC_6H_4CH_3\text{-}4)(\mu\text{-dppm})_3][BF_4]_2$ (**6**) are described. These complexes represent the first examples of copper(I) complexes with isocyanide bridging ligands.

Results and Discussion

Synthesis and Characterization of $[Cu_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}CR^1)(\mu\text{-}\eta^1\text{-C}{\equiv}NR^2)(\mu\text{-dppm})_3][BF_4]_2$ (1−6) and $[Cu_3(\mu_3\text{-Cl})(\mu\text{-}\eta^1\text{-C}{\equiv}NR)(\mu\text{-dppm})_3][BF_4]_2$ (7−9). The treatment of a solution of $[Cu_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}CC_6H_5)(\mu\text{-dppm})_3][BF_4]_2$ in dichloromethane with CNR^2 (molar ratio 1:1.3) at room temperature leads to the formation of the trinuclear complexes $[Cu_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}CC_6H_5)(\mu\text{-}\eta^1\text{-C}{\equiv}NR^2)(\mu\text{-dppm})_3][BF_4]_2$ (R^2 = $CH_2C_6H_5$ (**1**), C_6H_{11} (**2**), 4-$CH_3C_6H_4$ (**3**)), which are isolated from the reaction mixture as insoluble tetrafluoroborate salts in good yields (70−80%). The analogous complexes $[Cu_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}CC_6H_4CH_3\text{-}4)(\mu\text{-}\eta^1\text{-C}{\equiv}NR^2)(\mu\text{-dppm})_3][BF_4]_2$ (R^2 = $CH_2C_6H_5$ (**4**), C_6H_{11} (**5**), 4-$CH_3C_6H_4$ (**6**)) have been prepared under similar reaction conditions (eq 1).

$$[Cu_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}CR^1)(\mu\text{-dppm})_3][BF_4]_2 + CNR^2 \rightarrow [Cu_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}CR^1)(\mu\text{-}\eta^1\text{-C}{\equiv}NR^2)(\mu\text{-dppm})_3][BF_4]_2 \quad \mathbf{1{-}6} \tag{1}$$

$$R^1 = C_6H_5,\ R^2 = CH_2C_6H_5\ (\mathbf{1}),\ C_6H_{11}\ (\mathbf{2}),\ 4\text{-}CH_3C_6H_4\ (\mathbf{3});\ R^1 = 4\text{-}CH_3C_6H_4,\ R^2 = CH_2C_6H_5\ (\mathbf{4}),\ C_6H_{11}\ (\mathbf{5}),\ 4\text{-}CH_3C_6H_4\ (\mathbf{6})$$

On the other hand, the complexes $[Cu_3(\mu_3\text{-Cl})(\mu\text{-}\eta^1\text{-C}{\equiv}NR)(\mu\text{-dppm})_3][BF_4]_2$ (R = $CH_2C_6H_5$ (**7**), C_6H_{11} (**8**), 4-$CH_3C_6H_4$ (**9**) are synthesized in good yield (*ca.* 75%) by the reaction of $[Cu_3(\mu_3\text{-Cl})_2(\mu\text{-dppm})_3][BF_4]$ in CH_2Cl_2 with the corresponding isocyanide C≡NR (molar ratio 1/3) in the presence of $AgBF_4$ (eq 2).

$$[Cu_3(\mu_3\text{-Cl})_2(\mu\text{-dppm})_3][BF_4] + CNR \xrightarrow[-AgCl]{AgBF_4} [Cu_3(\mu_3\text{-Cl})(\mu\text{-}\eta^1\text{-C}{\equiv}NR)(\mu\text{-dppm})_3][BF_4]_2 \quad \mathbf{7{-}9} \tag{2}$$

$$R = CH_2C_6H_5\ (\mathbf{7}),\ C_6H_{11}\ (\mathbf{8}),\ 4\text{-}CH_3C_6H_4\ (\mathbf{9})$$

All attempts to remove the remaining bridging chloride by treatment of complexes **7**−**9** with an equimolar amount of $AgBF_4$ and excess isocyanide have failed, giving instead unidentified copper(I) species. Similarly, removal of the halide in other transition-metal clusters has been reported to give degradation products; for instance the treatment of $[Ni_3(\mu_3\text{-CNMe})(\mu_3\text{-I})(CNMe)_2(\mu\text{-dppm})_2]I$ with 2 equiv of AgO_3SCF_3 leads to $[Ni_2(CNMe)_3(dppm)_2]^{2+}$.[16]

Complexes **1**−**9** are air stable in the solid state and have been characterized by elemental analyses, conductance measurements, and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Selected spectroscopic data are given in Table 1. In addition the structure of the complex **6** has been determined by X-ray diffraction methods (see below). Conductivity data (in Me_2CO) show that the complexes **1**−**9** are 1:2 electrolytes. The IR spectra (KBr) exhibit the expected absorptions for the BF_4^- anion as well as those characteristic for the dppm and ν(C≡N) ligands (see Table 1). IR spectra of complexes **1**−**7** and **9** show two ν(C≡N) bands in the range of 2105−2200 cm^{-1} probably due to solid-state splitting,[9] since only one band appears in CH_2Cl_2 solution. The

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(10) [Hg]: (a) Schoettel, G.; Vittal, J. J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 6400. (b) Hao, L.; Xiao, J.; Vittal, J. J.; Puddephatt, R. J.; Manojlovic-Muir, L.; Muir, K. W.; Torabi, A. A. *Inorg. Chem.* **1996**, *35*, 658. [AuPR$_3$]: Reference 10a. (c) Payne, N. C.; Ramachandran, R.; Schoettel, G.; Vittal, J. J.; Puddephatt, R. J. *Inorg. Chem.* **1991**, *30*, 4048. [ReO$_3$]: Reference 10b. [Tl(acac)]: Reference 10b. (d) Rashidi, M.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 7111. [H]: Reference 10d. (e) Lloyd, B. R.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 7785. (f) Ramachandran, R.; Payne, N. C.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1989**, 128. [E (E = S, Se)] and [ER (E = S, Se)]: Reference 2d. (g) Hadj-Bagheri, N.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1269. (h) Jennings, M. C.; Payne, N. C.; Puddephatt, R. J. *Inorg. Chem.* **1987**, *26*, 3776. (i) Jennings, M. C.; Puddephatt, R. J. *Inorg. Chem.* **1988**, *27*, 4280. (j) Douglas, G.; Jennings, M. C.; Manojlovic-Muir, L. Puddephatt, R. J. *Inorg. Chem.* **1988**, *27*, 4516. (k) Bradford, A. M.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **1989**, *8*, 2367. [AgCl]: Reference 10i. [SnX$_3$] and [SnMe$_2$(O$_2$PF$_2$)]: (l) Douglas, G.; Jennings, M. C.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1989**, 159 and references therein. [PF$_3$]: (m) Balch, A. L.; Davis, B. J.; Olmstead, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 8592.

(11) (a) Díez, J.; Gamasa, M. P.; Gimeno, J.; Aguirre, A.; García-Granda, S. *Organometallics* **1991**, *10*, 380. (b) Díez, J.; Gamasa, M. P.; Gimeno, J.; Lastra, E.; Aguirre, A.; García-Granda, S. *Organometallics* **1993**, *12*, 2213. (c) These complexes show a photoluminiscent behavior: Yam, V. W.-W.; Lee, W.-K.; Cheung, K.-K.; Crystall, B.; Phillips, D. *J. Chem. Soc., Dalton Trans.* **1996**, 3283.

(12) Díez, J.; Gamasa, M. P.; Gimeno, J. *Polyhedron* **1995**, *14*, 741.

(13) (a) Bresciani, N.; Marsich, G.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta* **1974**, *10*, L5. (b) Ho, D. M.; Bau, R. *Inorg. Chem.* **1983**, *22*, 4079.

(14) Toth, A.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1988**, 1599 and references therein. Kruck, T.; Terfloth, C. *Chem. Ber.* **1993**, *126*, 1101. Ardizzoia, G. A.; Cenini, S.; La Monica, G.; Masciocchi, N.; Moret, M. *Inorg. Chem.* **1994**, *33*, 1458 and references therein. Bell, A.; Walton, R. A.; Edwards, D. A.; Poulter, M. A. *Inorg. Chim. Acta* **1985**, *104*, 171. Albertin, G.; Baldan, D.; Bordignon, E. *J. Organomet. Chem.* **1989**, *377*, 145. Lenders, B.; Kläui, W. *Chem. Ber.* **1990**, *123*, 2233.

(15) Bradford, A. M.; Kristof, E.; Rashidi, M.; Yang, D. S.; Payne, N. C.; Puddephatt, R. J. *Inorg. Chem.* **1994**, *33*, 2355 and references therein.

(16) DeLaet, D. L.; Del Rosario, R.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1987**, *109*, 754.

Table 1. IR and $^{31}P\{^1H\}$ and ^1H NMR[a] Data for the Isocyanide Complexes

complex	IR[b] $\nu(C{\equiv}N)$	$^{31}P\{^1H\}$	^1H C≡NR	C≡CR	P_2CH_2	others
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_5)(\mu\text{-}\eta^1\text{-}C{\equiv}NCH_2C_6H_5)(\mu\text{-dppm})_3][BF_4]_2$ (**1**)	2187 sh, 2162 s	−5.32	4.50 (s, 2H, $CH_2C_6H_5$)		3.13 (m, 3H, P_2CH_a), 3.58 (m, 3H, P_2CH_b)	6.24−7.40 (M, 70H, C_6H_5, $CH_2C_6H_5$, Ph_2)
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_5)(\mu\text{-}\eta^1\text{-}C{\equiv}NC_6H_{11})(\mu\text{-dppm})_3][BF_4]_2$ (**2**)	2178 sh, 2153 s	−5.40	0.90−2.00 (m, 11H, C_6H_{11})		3.33 (m, 3H, P_2CH_a), 3.69 (m, 3H, P_2CH_b)	6.37−7.50 (m, 65H, C_6H_5, PPh_2)
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_5)(\mu\text{-}\eta^1\text{-}C{\equiv}NC_6H_4CH_3\text{-}4)(\mu\text{-dppm})_3][BF_4]_2$ (**3**)	2156 s, 2105 m	−4.31	2.42 (s, 3H, $C_6H_4CH_3$)		3.41 (m, 3H, P_2CH_a), 3.75 (m, 3H, P_2CH_b)	6.60−7.40 (m, 69H, C_6H_5, $C_6H_4CH_3$, PPh_2)
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)(\mu\text{-}\eta^1\text{-}C{\equiv}NCH_2C_6H_5)(\mu\text{-dppe})_3][BF_4]_2$ (**4**)	2200 sh, 2163 s	−5.40	4.53 (s, 2H, $CH_2C_6H_5$)	2.33 (s, 3H, $C_6H_4CH_3$)	3.11 (m, 3H, P_2CH_a), 3.61 (m, 3H, P_2CH_b)	6.14−7.50 (m, 69H, $CH_2C_6H_5$, $C_6H_4CH_3$, PPh_2)
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)(\mu\text{-}\eta^1\text{-}C{\equiv}NC_6H_{11})(\mu\text{-dppm})_3][BF_4]_2$ (**5**)	2186 m, 2155 s	−5.50	1.10−2.10 (m, 11H, C_6H_{11})	2.40 (s, 3H, $C_6H_4CH_3$)	3.28 (m, 3H, P_2CH_a), 3.55 (m, 3H, P_2CH_b)	6.27−7.50 (m, 64H, $C_6H_4CH_3$, PPh_2)
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)(\mu\text{-}\eta^1\text{-}C{\equiv}NC_6H_4CH_3\text{-}4)(\mu\text{-dppm})_3][BF_4]_2$ (**6**)	2157 s, 2106 m	−4.42	2.42 (s, 3H, $C_6H_4CH_3$)	2.46 (s, 3H, $C_6H_4CH_3$)	3.38 (m, 3H, P_2CH_a), 3.62 (m, 3H, P_2CH_b)	6.51−7.40 (m, 68H, $C_6H_4CH_3$, $C_6H_4CH_3$, PPh_2)
$[Cu_3(\mu_3\text{-}Cl)(\mu\text{-}\eta^1\text{-}C{\equiv}NCH_2C_6H_5)(\mu\text{-dppm})_3][BF_4]_2$ (**7**)	2186 s, 2160 sh	−14.20	4.79 (s, 2H, $CH_2C_6H_5$)		3.27 (m, 6H, P_2CH_2)	6.90−7.50 (m, 65H, $CH_2C_6H_5$, PPh_2)
$[Cu_3(\mu_3\text{-}Cl)(\mu\text{-}\eta^1\text{-}C{\equiv}NC_6H_{11})(\mu\text{-dppm})_3][BF_4]_2$ (**8**)	2179 s	−14.02	1.30−2.10 (m, 11H, C_6H_{11})		3.25 (m, 6H, P_2CH_2)	6.80-7.40 (m, 60H, PPh_2)
$[Cu_3(\mu_3\text{-}Cl)(\mu\text{-}\eta^1\text{-}C{\equiv}NC_6H_4CH_3\text{-}4)(\mu\text{-dppm})_3][BF_4]_2$ (**9**)	2168 s, 2147 m	−14.04	2.41 (s, 3H, $C_6H_4CH_3$)		3.27 (m, 6H, P_2CH_2)	6.80−7.60 (m, 64H, $C_6H_4CH_3$, PPh_2)

[a] Spectra recorded in $CDCl_3$; δ in ppm. [b] ν(B−F) values are in the range 1055−1062 cm^{-1}.

Table 2. Crystallographic Data for Complex 6

formula	$C_{95}H_{86}B_2F_8P_6Cu_3Cl_6N$
fw	2004.5
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	18.276(2)
b, Å	22.182(3)
c, Å	22.754(7)
β, deg	95.18(2)
V, Å^3	9187(3)
Z	4
d_{calcd}, g cm^{-3}	1.45
F_{000}	4096
μ(Mo Kα), cm^{-1}	10.30
cryst size, mm	0.33 × 0.26 × 0.26
temp, K	200
2θ range, deg	46
data collected	$-20 \le h \le 19$, $0 \le k \le 24$, $0 \le l \le 24$
no. of collcd rflns	13 555
no. of unique rflns	12 743
no. of obsd rflns	5581 ($I > 3\sigma(I)$)
R^a	0.065
weight	unit weight
no. of variables	980
$\Delta(\rho)$, e Å^{-3}	0.87

[a] $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

Table 3. Selected Bond and Interatomic Distances (Å) and Bond Angles (deg) for Complex 6

Distances					
Cu(1)−Cu(2)	2.497(2)	Cu(1)−Cu(3)	2.800(2)	Cu(2)−Cu(3)	3.294(2)
Cu(1)−P(5)	2.315(4)	Cu(1)−P(8)	2.246(4)	Cu(2)−P(4)	2.244(4)
Cu(2)−P(6)	2.301(4)	Cu(3)−P(7)	2.249(4)	Cu(3)−P(9)	2.266(4)
Cu(1)−C(13)	2.06(1)	Cu(1)−C(22)	2.06(1)	Cu(2)−C(13)	2.17(1)
Cu(2)−C(22)	2.14(1)	Cu(3)−C(13)	2.04(1)	C(13)−C(14)	1.24(2)
C922)−N(23)	1.17(2)				

Angles			
C(14)−C(13)−Cu(1)	144(1)	C(14)−C(13)−Cu(2)	122(1)
C(14)−C(13)−Cu(3)	118(1)	C(15)−C(14)−C(13)	177(1)
N(23)−C(22)−Cu(1)	142(1)	N(23)−C(22)−Cu(2)	144(1)
C(24)−N(23)−C(22)	171(1)		

$\nu(C{\equiv}N)$ stretching frecuencies are slightly shifted to higher energy compared to the free ligands, showing negligible back-bonding from the copper to π^* orbitals of the isocyanide[17] according to the linearity observed in the X-ray structure (see below). IR spectra of other copper(I) complexes containing terminal isocyanide ligands show similar $\nu(C{\equiv}N)$ shifting.[14] In contrast, IR spectra of complexes **1**−**6** do not show the expected ν-(C≡C) absorption.[11b]

The structure of complex **6** has been determined by X-ray diffraction (Tables 2 and 3 and Experimental Section). ORTEP drawings of **6** are shown in Figure 1. X-ray-quality crystals have been obtained by slow diffusion of hexane into a dichloromethane solution of **6**. The crystallographic study shows that **6** crystallizes, as the CH_2Cl_2 solvate, in a monoclinic cell containing 4 unique discrete molecules and 12 molecules of dichloromethane.

The cationic complex consists of a scalene triangle of copper atoms, with the dppm ligands bridging each edge to form a roughly planar $[Cu_3P_6]^{3+}$ core. Two of the edges of the triangle are significantly shorter than the third one, with copper−copper distances of 2.495(2) Å (Cu(1)−Cu(2)), 2.800(1) Å (Cu(1)−Cu(3)), and 3.295(4) Å (Cu(2)−Cu(3)), all of them being consistent with

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[17] The CN stretching frequencies of μ_2-bridging bent isocyanide coordinated to two metals are in the range, from 1880 to 1580 cm^{-1}: Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 194.

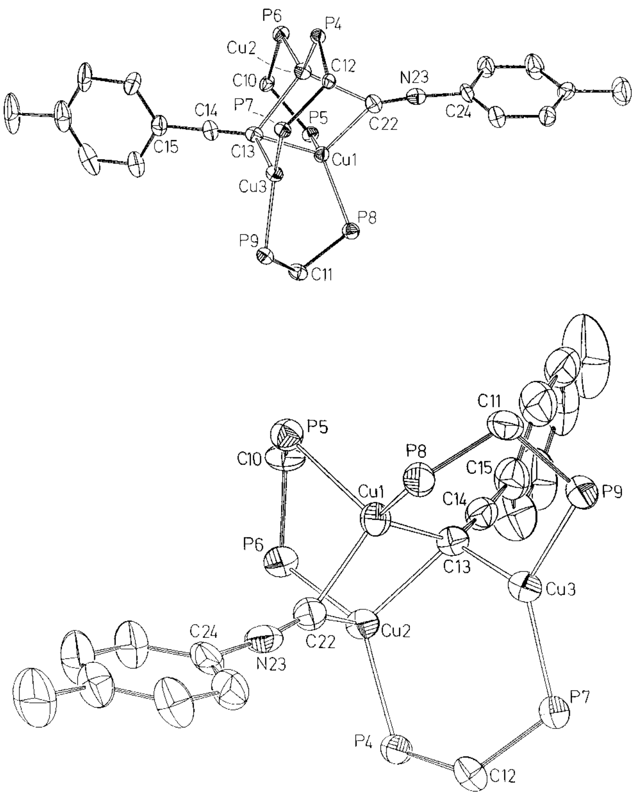

Figure 1. ORTEP views of the structure of the cationic part of the complex **6**, $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)(\mu\text{-}\eta^1\text{-}C{\equiv}NC_6H_4CH_3\text{-}4)(\mu\text{-dppm})_3]^{2+}$. For clarity, phenyl groups of the bis(diphenylphosphino)methane ligands are omitted.

nonbonding interactions.[18] The deviations of the P atoms from the Cu_3 plane (P(4), 1.324(3) Å; P(7), 1.111(3) Å; P(5), −1.307(3) Å; P(6), −1.435(3) Å; P(8), 0.842(3) Å; P(9), −0.443(3) Å) are higher than those found in the complexes $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)_n(\mu\text{-dppm})_3]^{(3-n)+}$ (n =1, 2) and $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3]^+$.[11] The triangle is capped by a *p*-tolylethynyl ligand in an asymmetric μ_3-η^1 bridging mode with Cu-C distances in the range 2.04(1)−2.17(1) Å; the bond angles between the alkynyl group and the copper atoms (Cu−C(13)−C(14)) are significantly different from each other, lying in the range of 118(1)−144(1)°. The isocyanide ligand is only bridging the Cu(1) and Cu(2) atoms and remains approximately linear (C(22)−N(23)−C(24) = 171(1)°). It is worth noting that most of the complexes containing μ_2-bridging isocyanide groups show substancial bending at the nitrogen atom.[19] The C≡N distance 1.17(2) Å is also shorter by *ca.* 0.06 Å than the average for μ_2 bridging structures, which is probably due to the linearity.

Table 4 collects for comparison the Cu−C distances and Cu−C−C bond angles of complex **6** and of several copper(I) alkynyl complexes with the $[Cu_3(\mu\text{-dppm})_3]$ framework which have been prepared by us.[11] The alkynyl ligand shows an asymmetric μ_3-η^1 bridging mode in all complexes. The linearity of the *p*-tolyl ethynyl group (C(13)−C(14)−C(15) = 177(1)°) and the C≡C bond distance (1.24(2) Å) are characteristic of typical metal-acetylide σ-bonding, showing coordination similar to that found for the alkynyl complexes of Table 4. It is interesting to note that two Cu−Cu bond lengths are comparable to those of the monocapped alkynyl complex $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_5)(\mu\text{-dppm})_3][BF_4]_2$, while the shortest distance, 2.495(2) Å (*vs* 2.904(3) Å), involves the four-coordinate copper atoms Cu(1) and Cu(2), which are bridged by the isocyanide group.

NMR Studies. At room temperature $^{31}P\{^1H\}$ NMR spectra of complexes **1**−**6** show a single resonance (δ *ca.* −5 ppm; Table 1), indicating that all phosphorus atoms in each molecule are formally equivalent. These chemical shifts are in the range of those exhibited by similar trinuclear copper(I) complexes,[11,12] However, according to the X-ray structure (Figure 1), the spectra should show a more complicated pattern. Variable-temperature $^{31}P\{^1H\}$ NMR studies reveal a dynamic behavior of the isocyanide ligand in solution. Thus, the spectrum of complex **3** at 295 K in CD_2Cl_2 exhibits a single resonance (δ −4.58 ppm), which gradually splits into two singlets as the temperature decreases (at −193 K, δ −4.30, −7.21 (broad) ppm). These resonances are consistent with the presence of the two sets of two and four nuclei as shown by the structure in the solid state (see the X-ray results). The formal equivalence of the six phosphorus atoms at room temperature probably implies a fast equilibrium between the μ-η^1 and μ_3-η^1 coordination of the isocyanide group, as shown in Figure 2. Fluxionality of isocyanide ligands has been observed in dimeric and cluster complexes,[20] such as $[Ni_4(CNBu^t)_7]$,[20b] $[Co_2(CNBu^t)_8]$,[20c] $[Pt_3(CNBu^t)_6]$,[20d] and $[Fe_2(CNEt)_9]$.[20e] Dynamic behavior has also been reported in the complexes $[Pt_3(\mu_3\text{-}CO)(CNR)(\mu\text{-dppm})_3]^{2+}$ and $[Pt_3(CNR)_2(\mu\text{-dppm})_3]^{2+}$ on the basis of a terminal μ_3-η^1 isocyanide exchange process.[15]

At room temperature ^1H NMR spectra of complexes **1**−**6** exhibit signals due to aromatic and methylene (P_2-CH_2) protons of dppm, along with those assigned to the alkynyl and isocyanide ligands. The resonances of the inequivalent methylene protons appear as two unresolved multiplets that resemble the ABX_2 or AA′XX′ spin systems. This pattern is typical for unsymmetrical bicapped $[Cu_3(\mu_3\text{-dppm})_3]$ frameworks, such as those contained in the μ_3-η^1-alkynyl complexes $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(\mu\text{-dppm})_3][BF_4]_2$ and $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3][BF_4]$ (R = Ph, Bu^t, CH_2OCH_3)[11] as well as in the μ_3-alkoxide complexes $[Cu_3(\mu_3\text{-}OR)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3][BF_4]$ (R = 2,4,6-$Bu^t{}_3C_6H_2$, 2,6-$Bu^t{}_2$-4-$CH_3C_6H_2$).[12] These spectroscopic data are also in accordance with the observed fluxional behavior.

The NMR data of **7**−**9** do not allow the coordination mode of the isocyanide ligands to be ascertained, and all attempts to grow suitable crystals for X-ray structural determination have been unsuccessful. The $^{31}P\{^1H\}$

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(18) Cotton, F. A.; Feng, X.; Matusz, M.; Bli, R. *J. Am. Chem. Soc.* **1988**, *110*, 7077 and references therein.

(19) Other unusual, almost linear C−N−C bond angles are also found in the following: $[Pd_2Cl_2(\mu\text{-}CNC_6H_3Me_2\text{-}2,6)_2(py)_2]$: Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1986**, *25*, 3327. $[Pd_4(\mu\text{-}OAc)_4(\mu\text{-}CNBu^t)_4]$: Tanase, T.; Nomura, Y.; Fukushima, T.; Yamamoto, Y.; Kobayashi, K. *Inorg. Chem.* **1993**, *32*, 4578. $[Pd_5(\mu\text{-}SO_2)(\mu\text{-}CNC_6H_3Me_2\text{-}2,6)_2(CNC_6H_3Me_2\text{-}2,6)_5]$: Burrows, A. D.; Fleischer, H.; Mingos, D. M. P. *J. Organomet. Chem.* **1992**, *433*, 311. $[Pd_2(\eta^5\text{-}C_5HPh_4)_2(\mu\text{-}CNC_6H_2Me_3\text{-}2,4,6)_2]$, $[Pd_2(\eta^5\text{-}C_5Ph_5)_2(\mu\text{-}CNC_6H_3Me_2\text{-}2,6)_2]$, $[Pd_2(\mu\text{-}CNC_6H_2Me_3\text{-}2,4,6)_2\{HB(pz)_3\}_2]$: Tanase, T.; Fukushima, T.; Nomura, Y.; Yamamoto, Y.; Kobayashi, K. *Inorg. Chem.* **1994**, 33, 32.

(20) (a) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209. (b) Day, V. W.; Day, R. O.; Kristoff, J. S.; Hirsekorn, F. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 2571. (c) Carroll, W. E.; Green, M.; Galas, A. M. R.; Murray, M.; Turney, T. W.; Welch, A. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 80. (d) Green, M.; Howard, J. A. K.; Murray, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1509. (e) Bassett, J. M.; Barker, G. K.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Wolsey, W. C. *J. Chem. Soc., Dalton Trans.* **1981**, 219.

Table 4. Selected Atomic and Bond Distances (Å) and Bond Angles (deg) for Copper(I) Alkynyl Complexes

complex	Cu···Cu	Cu−C[a]	Cu−C−C[a]	ref
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_5)(\mu\text{-dppm})_3][BF_4]_2$	2.813(2), 2.904(3), 3.274(3)	1.96(1)−2.08(1)	100(1)−138(1)	11
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_5)_2(\mu\text{-dppm})_3][BF_4]$	2.570(3), 2.598(3), 2.615(3)	2.06(2)−2.34(2)	126(2)−146(2)	11
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_5)(\mu_3\text{-Cl})(\mu\text{-dppm})_3][BF_4]$	2.803(3), 2.785(3), 2.871(3)	1.98(2)−2.34(2)	107(1)−151(1)	11
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)(\mu\text{-}\eta^1\text{-}C{\equiv}NC_6H_4CH_3\text{-}4)(\mu\text{-dppm})_3][BF_4]_2$	2.800(1), 2.495(2), 3.295(4)	2.04(1)−2.17(1)	118(1)−144(1)	*b*

[a] Range of values. [b] This paper.

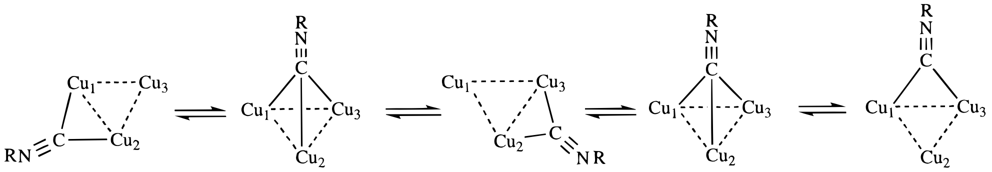

Figure 2.

NMR spectra in CD_2Cl_2 at room temperature show a single resonance (*ca.* δ −14 ppm) that broadens on cooling down to −193 K. These data seem suggest a μ-η^1-CNR coordination mode in analogy to that found in complexes **1**−**6**. It must be pointed out that a μ_3-η^1 coordination of the isocyanide, similar to that of the alkynyl or the chloride ligands, cannot be entirely ruled out.

Conclusions

A new family of novel *triangulo* copper(I) complexes containing μ-η^1-isocyanide and μ_3-η^1-alkynyl or μ_3-chloride ligands is described in this paper. As far as we are aware, this type of complex represents the first example of copper(I) complexes with isocyanide bridging ligands. These complexes are structurally related to the clusters $[M_3(\mu_3\text{-}\eta^1\text{-L})(\mu\text{-dppm})_3]^{n+}$ (M = Ni, Pd, Pt) with different μ_3-η^1 triply bridging ligands. A particularly interesting difference between complexes of group 10 metals and those of copper(I) is observed when these trinuclear isocyanide ligands are involved. In the case of copper(I) the isocyanide ligand adopts the μ-η^1-bonding mode, while a μ_3-η^1-bonding mode is found for nickel and palladium and only terminal isocyanides are formed with platinum. On the other hand, these copper(I) isocyanide complexes are new examples of the easy fluxionality of the isocyanide ligands, behavior already reported for related platinum complexes.

Experimental Section

The reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. Infrared spectra were recorded (4000−400 cm^{-1}) on a Perkin-Elmer 1720-X FT spectrometer using KBr pellets. The C, H, and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. Conductivities of acetone solutions in ca. 5×10^{-4} mol dm^{-3} were measured with a Jenway PCM3 conductimeter. NMR spectra were recorded on a Bruker AC300 at 300 MHz (^{1}H) or 121.5 MHz (^{31}P) using $SiMe_4$ or 85% H_3PO_4 as standard. The complexes $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_5)(\mu\text{-dppm})_3][BF_4]_2$ and $[Cu_3(\mu\text{-Cl})_2(\mu\text{-dppm})_3][BF_4]$ as well as the new complex $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)(\mu\text{-dppm})_3][BF_4]_2$ were prepared as previously described.[11b,12] Infrared and NMR spectral data for all new isocyanide complexes are collected in Table 1. The attempted recrystallizations of these derivatives under several sets of conditions led in all cases to decomposition. Complexes **7** and **9** could not be obtained in analytical purity, since they always contain small amounts of the free isocyanide.

Synthesis of $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR^1)(\mu\text{-}\eta^1\text{-}CNR^2)(\mu\text{-dppm})_3][BF_4]_2$ ($R^1 = C_6H_5$, $R^2 = CH_2C_6H_5$ (1), C_6H_{11} (2), 4-$CH_3C_6H_4$ (3); R^1 = 4-$CH_3C_6H_4$, $R^2 = CH_2C_6H_5$ (4), C_6H_{11} (5), 4-$CH_3C_6H_4$ (6)). To a solution of $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR^1)(\mu\text{-dppm})_3][BF_4]_2$ (0.2 mmol) in dichloromethane (40 mL) was added at room temperature the corresponding isocyanide $C{\equiv}NR^2$ (0.26 mmol). The mixture was stirred at room temperature for 5 h and evaporated to dryness, giving a cream colored solid, which was washed with diethyl ether (3 × 20 mL) and vacuum-dried. The NMR and IR (ν(C≡N), ν(B−F)) spectroscopic data are collected in Table 1. Yield (%), conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), and analytical data are as follows. **1**: 80; 186. Anal. Calcd for $C_{91}H_{78}B_2Cu_3F_8NP_6$: C, 62.97; H, 4.53; N, 0.81. Found: C, 62.43; H, 4.59; N, 0.86. **2**: 80; 177. Anal. Calcd for $C_{90}H_{82}B_2Cu_3F_8NP_6$: C, 62.57; H, 4.78; N, 0.81. Found: C, 62.42; H, 4.95; N, 0.98. **3**: 73; 190. Anal. Calcd for $C_{91}H_{78}B_2Cu_3F_8NP_6$: C, 62.97; H, 4.53; N, 0.81. Found: C, 62.45 H, 4.74; N, 0.90. **4**: 76; 177. Anal. Calcd for $C_{92}H_{80}B_2Cu_3F_8NP_6$: C, 63.12; H, 4.66; N, 0.80. Found: C, 62.77; H, 4.76; N, 0.88. **5**: 70; 190. Anal. Calcd for $C_{91}H_{84}B_2Cu_3F_8NP_6$: C, 62.75; H, 4.86; N, 0.80. Found: C, 62.34; H, 5.11; N, 0.92. **6**: 75; 200. Anal. Calcd for $C_{92}H_{80}B_2Cu_3F_8NP_6$: C, 63.12; H, 4.66; N, 0.80. Found: C, 63.74; H, 4.66; N, 0.90.

Synthesis of $[Cu_3(\mu_3\text{-Cl})(\mu\text{-}\eta^1\text{-CNR})(\mu\text{-dppm})_3][BF_4]_2$ (R = $CH_2C_6H_5$ (7), C_6H_{11} (8), 4-$CH_3C_6H_4$ (9)). A mixture of the complex $[Cu_3(\mu_3\text{-Cl})_2(\mu\text{-dppm})_3][BF_4]$ (0.3 g, 0.2 mmol), $AgBF_4$ (0.039 g, 0.2 mmol), and the isocyanide C≡NR (0.6 mmol) in dichloromethane (50 mL) was stirred in the dark for about 5 h, and the resulting suspension was then filtered off. The remaining solution was evaporated to dryness, giving a white solid, which was washed with diethyl ether (3 × 20 mL) and vacuum-dried.

Yield (%), conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), and analytical data are as follows. **7**: 75; 163. Anal. Calcd for $C_{83}H_{73}B_2ClCu_3F_8NP_6$: C, 59.70; H, 4.41. Found: C, 59.55; H, 4.39. **8**: 76; 178. Anal. Calcd for $C_{82}H_{77}B_2ClCu_3F_8NP_6$: C, 59.26; H, 4.67; N, 0.84. Found: C, 58.34; H, 4.77; N, 0.81. **9**: 74; 181. Anal. Calcd for $C_{83}H_{73}B_2ClCu_3F_8NP_6$: C, 59.70; H, 4.41. Found: C, 59.34; H, 4.41.

X-ray Diffraction Study. Data collection, crystal, and refinement parameters are collected in Table 2. Diffraction measurements were made on an Enraf-Nonius CAD4 diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The unit cell parameters were obtained from a least-squares fit of 25 reflections (10° < θ < 15°). Data were collected with the ω-2θ scan technique and a variable scan rate with a maximum scan time of 60 s/reflection. This maximum scan time was reduced to 30 s/reflection after reflection number 5789 (h = −3, k =4, l = 4) due to decaying. Three standard reflections were monitored every 3600 s. In the reduction of data, profile analysis,[21,22] drift, and Lorentz and polarization corrections were performed; an empirical absorption correction (DIFABS) was applied.[23] The final drift correction factors were between 1.00 and 2.25. The structure was solved by using SHELXS86,[24] expanded by using DIRDIF[25] and refined by least squares using a local version of the program SHELX76.[26] All non-hydrogen atoms were anisotropically refined, except those of the dichloromethane and tetrafluoroborate groups. All hydrogen atoms were located at ideal positions and were refined riding on their parent atoms. Geometrical calculations were made with PARST.[27] All calculations were performed at the Centro de Cálculo Científico of the University of Oviedo.

Acknowledgment. This work was supported by the Dirección General de Investigación Científica y Técnica (Project PB93-0325).

Supporting Information Available: Tables giving all bond lengths and angles, positional and thermal parameters, torsion angles, and least-squares planes for **6** (21 pages). Ordering information is given on any current masthead page.

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[21] Lehman, M. S.; Larsen, F. A. *Acta Crystallogr., Sect. A* **1974**, *30*, 580.

[22] Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1978**, *11*, 114.

[23] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

[24] Sheldrick, G. M., Kruger, C., Goddard, R., Eds. *Crystallographic Computing*; Clarendon Press: Oxford, U.K., 1985; p 175.

[25] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF Program System; Technical Report of the Crystallographic Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

[26] Sheldrick, G. M. SHELX76: Program for Crystal Structure Determination; University of Cambridge, Cambridge, U.K., 1976. van der Maelen, J. F. Ph.D. Thesis, Universidad de Oviedo, 1991.

[27] Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.