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Articles

cis,cis,cis-1,5,9-Cyclododecatriene−Metal Complexes

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The ligand properties of *cis,cis,cis*-1,5,9-cyclododecatriene (c,c,c-cdt) have been explored. For the known (c,c,c-cdt)Ni (**1b**) and (c,c,c-cdt)(AgNO$_3$)$_3$ (**5**) complexes and the new [(c,c,c-cdt)Cu(MeOH)]BF$_4$ (**6b**), [(c,c,c-cdt)Cu][Al{OC(CF$_3$)$_3$}$_4$] (**6d**), and (^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Ni(η^2-c,c,c-cdt) (**7b**) complexes, the molecular structures have been determined. The c,c,c-cdt ligand in **5** and **7b** retains the C_2 symmetrical helical conformation of the free c,c,c-cdt, whereas in **1b** and **6b**,**d**, it assumes a C_3 symmetrical ratchet conformation. The coordination geometry of the metal in **6b** is tetrahedral, and it is trigonal pyramidal in **1b** and **6d**. Details of the synthesis and chemical and spectroscopic properties of the complexes are reported.

Introduction

Wilke's discovery of trigonal planar Ni(t,t,t-cdt) (**1a**; t,t,t-cdt = *trans*,*trans*,*trans*-1,5,9-cyclododecatriene) and tetrahedral Ni(cod)$_2$ (**2**; cod = *cis*,*cis*-1,5-cyclooctadiene) in 1960 laid the foundation for the then quite spectacular and even today still fascinating class of homoleptic transition metal(0)−alkene complexes.[1] These complexes have to be seen in a historic context with other milestones of organometallic chemistry, such as ferrocene,[2] the Ziegler catalysts,[3] bis(benzene)chromium,[4] and bis(π-allyl)nickel,[5] all of which were discovered within a single decade. A series of derivatives of **1a** such as the isomeric Ni(c,c,c-cdt) (**1b**; c,c,c-cdt = *cis*,*cis*,*cis*-1,5,9-cyclododecatriene),[6] tris(*trans*-cyclooctene)nickel(0) (**3a**),[6a] tris(norbornene)nickel(0) (**3b**),[7a] and, above all, the parent tris(ethene)nickel(0) (**3c**)[7d] soon also became available, mainly by displacement of the t,t,t-cdt ligand in **1a** with the respective alkene. Notwithstanding intrinsic properties of the alkenes, such as the cyclotrienes bearing 2-fold substituted C=C bonds in contrast to the parent ethene, and that *trans*-cyclooctene and norbornene are strained alkenes, the driving force for the t,t,t-cdt−alkene displacement reactions of **1a** appears to result from the out-of-plane twist of the C=C bonds in **1a** and the associated poor backbonding from Ni(0), making **1a** less stable than the other trigonal planar complexes **1b** and **3a**−**c**, which, due to an in-plane arrangement of the C=C bonds, have enhanced backbonding, as anticipated both on the basis of experimental evidence[7] and on the basis of MO calculations.[8]

Complexes **1a**, **2**, and **3c** are frequently used as a source of "naked nickel",[1b] but little is known about the properties of **1b**. Whereas **1a** forms a series of tetrahedral adducts (t,t,t-cdt)NiL with a broad range of ligands such as L = PR$_3$, P(OR)$_3$, CO, HAlR$_3^-$, and Me$^-$,[1c,9] for the isomeric **1b**, only a single adduct (c,c,c-cdt)Ni{P(OC$_6$H$_4$-2-C$_6$H$_5$)$_3$} (**4**)[6] with a sterically much encumbered phosphite has been briefly mentioned. Beyond it, the only other metal complexes of c,c,c-cdt that are known so far are (c,c,c-cdt)(AgNO$_3$)$_3$ (**5**)[10a] and (c,c,c-cdt)CuOTf (**6a**).[10b] The reason for the scarcity of the c,c,c-cdt complexes may lie in the laborious synthesis[6a,10] of the ligand. We were intrigued to learn more about the structure of **1b** and the ligand properties of c,c,c-cdt[11] and have therefore studied some c,c,c-cdt−metal complexes in detail.

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(1) (a) Wilke, G. *Angew. Chem.* **1960**, *72*, 581. (b) Wilke, G. *Angew. Chem.* **1963**, *75*, 10. (c) Bogdanović, B.; Kröner, M.; Wilke, G. *Liebigs Ann. Chem.* **1966**, *699*, 1.

(2) (a) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039. (b) Miller, S. A.; Tebboth, J. A.; Tremaine, J. F. *J. Chem. Soc.* **1952**, 632. (c) Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2125. (d) Fischer, E. O.; Pfab, W. *Z. Naturforsch., B: Chem. Sci.* **1952**, *7*, 377.

(3) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. *Angew. Chem.* **1955**, *67*, 426.

(4) (a) Fischer, E. O.; Hafner, W. *Z. Naturforsch., B: Chem. Sci.* **1955**, *10*, 665. (b) Fischer, E. O.; Hafner, W. *Z. Anorg. Allg. Chem.* **1956**, *286*, 146. (c) Fischer, E. O.; Fritz, H.-P. *Angew. Chem.* **1961**, *73*, 353.

(5) (a) Wilke, G.; Bogdanović, B. *Angew. Chem.* **1961**, *73*, 756. (b) Wilke, G. *Angew. Chem.* **1966**, *78*, 157; *Angew. Chem., Int. Ed.* **1966**, *5*, 151.

(6) (a) Jonas, K. Ph.D. Thesis, Universität Bochum, 1968. (b) Jonas, K.; Heimbach, P.; Wilke, G. *Angew. Chem.* **1968**, *80*, 1033; *Angew. Chem., Int. Ed.* **1968**, *7*, 949. (c) Hoffmann, E. G.; Jolly, P. W.; Küsters, A.; Mynott, R.; Wilke, G. *Z. Naturforsch., B: Chem. Sci.* **1976**, *31*, 1712. (d) Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, *19*, 257.

(7) (a) Wilke, G.; Yamamoto, A.; Krüger, K.; Tsay, Y.-H. Unpublished results; cited in ref 7b,c. (b) Fischer, K.; Jonas, K.; Misbach, P.; Stabba, R.; Wilke, G. *Angew. Chem.* **1973**, *85*, 1002; *Angew. Chem., Int. Ed.* **1973**, *12*, 943. (c) Fischer, K.; Jonas, K.; Mollbach, A.; Wilke, G. *Z. Naturforsch., B: Chem. Sci.* **1984**, *39*, 1011. (d) Fischer, K.; Jonas, K.; Wilke, G. *Angew. Chem.* **1973**, *85*, 620; *Angew. Chem., Int. Ed.* **1973**, *12*, 565.

(8) (a) Rösch, N.; Hoffmann, R. *Inorg. Chem.* **1974**, *13*, 2656. (b) Pitzer, R. M.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1979**, *101*, 7176. (c) Schaefer, H. F., III. *J. Mol. Struct.* **1981**, *76*, 117.

(9) Wilke, G. *Angew. Chem.* **1988**, *100*, 189; *Angew. Chem., Int. Ed.* **1988**, *27*, 185 and references therein.

(10) (a) Untch, K. G.; Martin, D. J. *J. Am. Chem. Soc.* **1965**, *87*, 3518. (b) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889. (c) Trauer, H.; Haufe, G. *Z. Chem.* **1988**, *28*, 290.

(11) For reports on physical properties of c,c,c-cdt (registry no. 4736-48-5), see: (a) (conformational analysis) Anet, F. A. L.; Rawdah, T. N. *J. Org. Chem.* **1980**, *45*, 5243. (b) (exclusion of tris-homoconjugation) McEwen, A. B.; Schleyer, P. v. R. *J. Org. Chem.* **1986**, *51*, 4357. (c) (vicinal olefinic ^{1}H−^{1}H coupling constant) Radeglia, R.; Poleschner, H.; Haufe, G. *Magn. Res. Chem.* **1993**, *31*, 1054.

10.1021/om7004172 CCC: $37.00

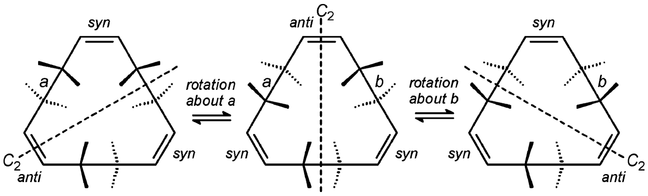

Figure 1. Schematic representation of the helical conformation of c,c,c-cdt and its enantiomerization.

Results and Discussion

(c,c,c-cdt)(AgNO$_3$)$_3$ (5). We begin with a discussion of the structure of free c,c,c-cdt and its AgNO$_3$ complex, **5**. For uncoordinated c,c,c-cdt, the most prominent supposable conformations are associated with C_2 (denoted helix), C_s (saddle), C_3 (ratchet),[12] D_3 (propeller), C_{3v} (crown),[13] and C_{3h} (plate) symmetry with increasing energy along this series. Untch and Martin[10a] first suggested the helix conformation as the ground state conformation of the free c,c,c-cdt, and this has since been confirmed by Anet and Rawdah by a combination of low-temperature NMR and empirical force field calculations.[11a] In the helix conformation, all three C_2H_4 units of c,c,c-cdt adopt a single-trans conformation, with two *cis*-$C{=}C$ bonds having the C_2H_4 substituents in a syn alignment and the third in an anti alignment (Figure 1). Enantiomerization[14] of this chiral conformation occurs by a 180° $CH_2{-}CH_2$ bond rotation of one of the two C_2H_4 substituents (*a* or *b*) at the anti aligned *cis*-$C{=}C$ bond, through which the original C_2 axis passes. Thereby, the former anti and syn alignments of the C_2H_4 substituents at the corresponding *cis*-$C{=}C$ bonds interchange, causing a migration of the C_2 axis of symmetry. By repetition, all three $CH_2{-}CH_2$ bonds equally participate in the process.[11a] Because of dynamic D_{3h} symmetry, in the ambient temperature solution NMR spectra, only one signal each is observed for the $-CH{=}$ and $-CH_2-$ groups, including equivalence of the geminal allyl protons (Table 1).

Complex **5**, which was originally obtained during the synthesis process of c,c,c-cdt, [10a] contains strictly three entities of AgNO$_3$; this is also the case in the presence of an excess of c,c,c-cdt, where only **5** is isolated. It is closely related to the by Untch and Martin also prepared (c,c,c-1,4,7-cyclononatriene)(AgNO$_3$)$_3$ (**A**; mp 248 °C dec),[15] which was structurally characterized by others.[16c] We obtained large colorless cubes of **5** by cooling a water−THF solution of AgNO$_3$ and c,c,c-cdt to 5 °C. After isolation, the complex was almost insoluble in most solvents, including MeOH, H$_2$O, THF, and MeCN, consistent with a durable catenate structure, although it modestly dissolves in CH$_2$Cl$_2$. Compound **5** is thermally stable to about 160 °C (DSC) and thus less stable than either **A** or AgNO$_3$ itself (mp 212 °C).[15] In the ESI mass spectrum (CH$_2$Cl$_2$), a series of intense ions is observed of which only $[(C_{12}H_{18})Ag]^+$ (*m*/*e* 269) and $[(C_{12}H_{18})_2Ag_2(NO_3)]^+$ (*m*/*e* 600) allowed ready assignment. Among the numerous structurally known AgNO$_3$−alkene complexes,[17] there are examples in which one or several AgNO$_3$ entities are bound to a single cyclopolyene ligand,[16] one AgNO$_3$ is coordinated by two cyclopolyene ligands,[18] AgNO$_3$ and the cyclopolyene are both in bridging modes,[19] and one central Ag$^+$ is coordinated to all $C{=}C$ bonds of the cyclopolyene ligand.[20]

The molecular structure of **5** is shown in Figure 2a, and details of the crystal structure analysis are given in Table 2. Bearing in mind the conclusion from previous structural investigations that ring conformations of cyclopolyenes are generally not significantly altered by AgNO$_3$ coordination,[21] it is not unexpected that the conformation of the c,c,c-cdt ligand in **5** corresponds to the helical conformation of the free c,c,c-cdt, with the obvious distinction that all three $C{=}C$ bonds of the c,c,c-cdt ligand are coordinated by individual Ag$^+$ centers. Apart from the Ag coordination, the c,c,c-cdt ligand has a conformational C_2 symmetry with the 2-fold axis running through the midpoints of the double bond C1−C2 and the single bond C7−C8. The $C{=}C$ bonds C5−C6 and C9−C10 each have the cis-bonded C_2H_4 substituents in syn alignment, and Ag2 and Ag3 coordinate at the opposite face of the respective $C{=}C$ bond with retention of the conformational C_2 symmetry. The C_2H_4 substituents at C1−C2 have anti orientation, and the inherent C_2 symmetry is broken by the coordination of Ag1. Consequently, the full (c,c,c-cdt)Ag$_3$ core has only C_1 symmetry.

The mean Ag−C coordination bond length in **5** is 2.39(6) Å (**A**: 2.379 and 2.411 Å), and the mean distances for the $C{=}C$, $=CH{-}CH_2$, and $CH_2{-}CH_2$ bonds are 1.364(5), 1.508(3), and 1.549(7) Å, respectively. The torsional angles of the $CH_2{-}CH_2$ bonds are almost identical (170(2)°) and correspond to a near single-trans conformation.

The crystal structure of **5** including the AgNO$_3$ framework is shown in Figure 2b. Whereas in the crystals of $(C_9H_{12})(AgNO_3)_3$ (**A**) [16c] and $C_{60}(AgNO_3)_5$[22] silver nitrate forms a 3-D network with the cyclononatriene and buckminsterfullerene molecules occupying channels, in the crystal of **5**, the silver nitrate network is only 2-D with sheets of AgNO$_3$ separated by c,c,c-cdt ligands. Clearly, the AgNO$_3$ framework is important for the formation of the solid. So far, we have not been able to isolate Ag−η^2-c,c,c-cdt complexes with only one or two circumferentially coordinated AgNO$_3$ entities or $[(\eta^2,\eta^2,\eta^2$-c,c,c-cdt)Ag]NO$_3$ (**5a**) with a central Ag$^+$ cation.

If the conformation of the c,c,c-cdt ligand of **5** in solution were the same as that in the solid, rather complicated ^{1}H and ^{13}C NMR spectra would be expected due to the inequivalent $C{=}C$ bonds, even if the complex underwent a dynamic process similar to that depicted in Figure 1. This is not the case, and the ^{1}H NMR spectrum of a solution of **5** in CD$_2$Cl$_2$ shows one

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[12] The ratchet conformation has been denoted by Untch and Martin as "symmetrical *s-trans*" (see their **IId**)[10a] and by Anet and Rawdah as "crown-I".[11a] According to the latter authors, the "crown-I" conformation undergoes enantiomerization via interconversion with a C_1 symmetrical "crown-II" conformation (likewise having an energy minimun and thus invoking a further transition state), and they discount the C_{3v} symmetrical conformation, which Untch and Martin originally termed crown, due to its high energy. To avoid confusion, we refer to the C_3 symmetrical "crown-I" conformation with the term "ratchet" since the conformation has a sense of rotation and to the C_{3v} symmetrical as "crown".

[13] According to DFT calculations, the C_{3v} symmetrical crown conformation represents neither a minimum nor a regular transition state on the potential surface since it comprises three imaginary frequencies. At the B3LYP/6-31G* level, the C_{3v} symmetrical crown lies about 6 kcal mol^{-1} above the C_3 symmetrical ratchet minimum (4 kcal mol^{-1} including zero-point and enthalpic corrections); Bühl, M., personal communication.

[14] Enantiomerization is defined as the reversible interconversion of one enantiomer into the other.

[15] Untch, K. G.; Martin, D. J. *J. Org. Chem.* **1964**, *29*, 1903.

[16] (a) Mathews, F. S.; Lipscomb, W. N. *J. Phys. Chem.* **1959**, *63*, 845. (b) Hartsuck, J. A.; Paul, I. C. *Chem. Ind. (London)* **1964**, 977. (c) McPhail, A. T.; Sim, G. A. *J. Chem. Soc. B* **1966**, 112. (d) Jackson, R. B.; Streib, W. E. *J. Am. Chem. Soc.* **1967**, *89*, 2539.

[17] Currently, there are 32 examples in the Cambridge Structural Database (CSD), version 5.28, updated November 2006.

[18] Kuribayashi, S.; Yasuoka, N.; Mitsui, T.; Takahashi, H.; Yamaguchi, M. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1242.

[19] (a) Coggon, P.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. B* **1970**, 1024. (b) Mak, T. C. W. *J. Organomet. Chem.* **1983**, *246*, 331.

[20] Faure, R.; Loiseleur, H.; Haufe, G.; Trauer, H. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *41*, 1593.

[21] Ganis, P.; Dunitz, J. D. *Helv. Chim. Acta* **1967**, *50*, 2379.

[22] Olmstead, M. M.; Maitra, K.; Balch, A. L. *Angew. Chem.* **1999**, *111*, 243; *Angew. Chem., Int. Ed.* **1999**, *38*, 231.

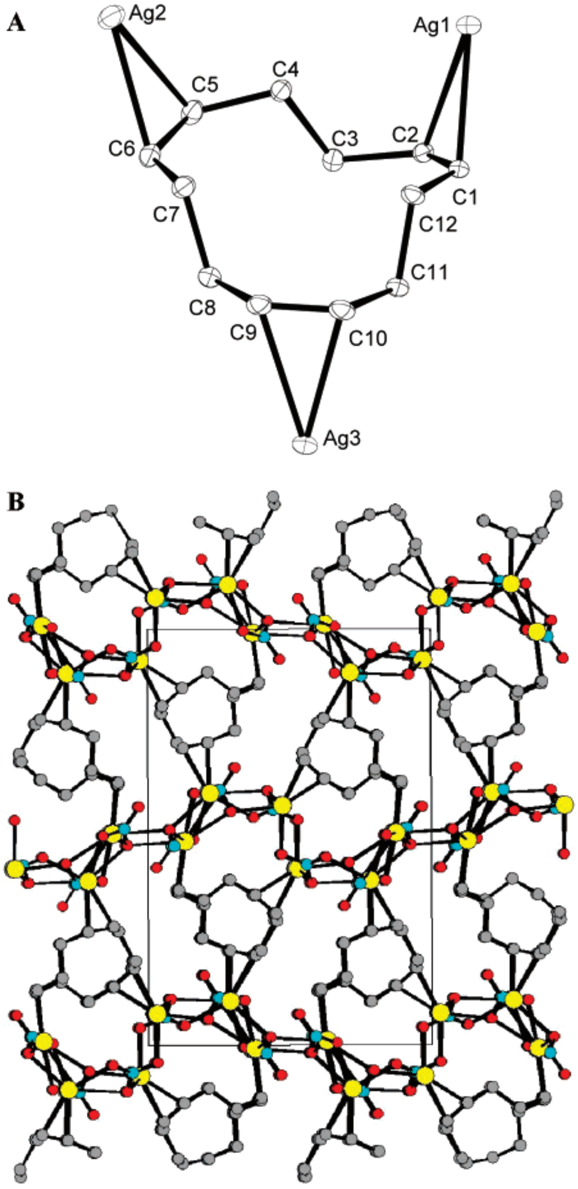
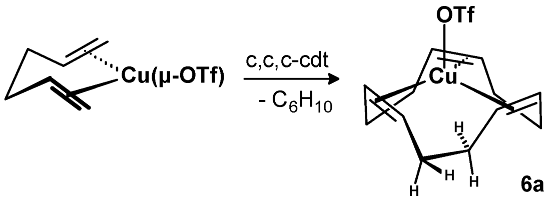


Figure 2. (a) Molecular structure of (c,c,c-cdt)$(AgNO_3)_3$ (**5**) (nitrate ions are omitted for clarity, atomic displacement ellipsoids are shown at the 50% probability level). Selected bond lengths (Å) and torsional angles (deg): C1−C2 = 1.360(2), C2−C3 = 1.512(2), C3−C4 = 1.545(2), C4−C5 = 1.509(2), C5−C6 = 1.369(2), C6−C7 = 1.508(2), C7−C8 = 1.557(2), C8−C9 = 1.506(3), C9−C10 = 1.364(2), C10−C11 = 1.511(2), C11−C12 = 1.544(2), C12−C1 = 1.504(2), Ag1−C1 = 2.379(2), Ag1−C2 = 2.479(2), Ag2−C5 = 2.339(2), Ag2−C6 = 2.377(2), Ag3−C9 = 2.442(2), Ag3−C10 = 2.327(2); C2−C3−C4−C5 = 169(1), C6−C7−C8−C9 = 167(1), C10−C11−C12−C1 = 7(1). (b) Crystal structure of (c,c,c-cdt)$(AgNO_3)_3$ (**5**), including nitrate ions, showing the layered structure. Ag, yellow; O, red; N, blue; and C, gray.

signal for the olefinic protons (δ(H) 6.07) and two resonances for the geminal allylic protons (δ(H) 2.70 and 2.39), while in the ^{13}C NMR spectrum, just two single resonances are found (Table 1). Clearly, the structure of **5** in solution is highly symmetric, with all six −CH= and six CH_aH_b groups each equivalent, but with inequivalent geminal allylic protons. We denote the structure in solution as **5a**. From a comparison of the NMR data of **5a** with those of the (c,c,c-cdt)Cu complexes **6a**−**d**, we conclude that **5** upon dissolution eliminates two $AgNO_3$ molecules to form mononuclear **5a** comprising a central Ag(I). While we would expect a C_3 symmetrical ground state structure for **5a**, it undergoes enantiomerization to result in a dynamic C_{3v} symmetrical structure in solution. This process is described next for complexes **6a**−**d** in more detail.

(c,c,c-cdt)CuOTf (6a), [(c,c,c-cdt)Cu(MeOH)]BF_4 (6b), (c,c,c-cdt)CuBF_4 (6c), and [(c,c,c-cdt)Cu][Al{OC(CF_3)$_3$}$_4$] (6d). In connection with this work, we became interested in Kochi and Salomon's Cu(I) complex **6a**, which in its ionic form is isoelectronic with the Ni(0) complex **1b**. While the original synthesis was hampered by the fact that the complex tends to oil out of a benzene−pentane mixture, requiring repeated recrystallizations,[10b] we found that the 1,5-hexadiene ligand in (C_6H_{10})CuOTf[23] is readily displaced by 1 equiv of c,c,c-cdt. Colorless cubes of pure **6a** crystallize at ambient temperature from a concentrated CH_2Cl_2−diethyl ether solution (eq 1).



(1)

Kochi and Salomon have already noted the extraordinary thermal stability of solid **6a**.[10b] As determined by DSC, the melting point of **6a** is 170 °C (lit. mp 160 °C),[10b] and decomposition occurs only at 240 °C. DSC revealed also the occurrence of four reversible endothermic events at −56, −24, 0, and 8 °C, indicative of increasing disorder. In the EI mass spectrum (170 °C), the molecular ion (m/e = 374, 5%) is observed, which fragments by elimination of the OTf ligand to give $[(c,c,c\text{-cdt})Cu]^+$ (m/e = 225, 42%) as a further prominent ion. The latter is also the base ion in the ESIpos spectrum. According to NMR, a possible exchange of the c,c,c-cdt ligand in **6a** with free c,c,c-cdt or ethene is slow in solution (CD_2Cl_2) at ambient temperature. The high stability of **6a** can be attributed to the macrocyclic effect;[24] that is, c,c,c-cdt is ideally suited for coordination to a central Cu^+. On the basis of the single C=C stretching band in the IR spectrum (ν(C=C) = 1585 cm^{-1}), Kochi and Salomon have already concluded that all three C=C bonds in **6a** are symmetrically coordinated at the Cu(I) center. This leaves open the question as to whether **6a** has an essentially ionic structure with a possibly trigonal planar coordinated Cu center[10b] or whether the complex has a tetrahedral Cu center with tight binding of the OTf ligand, as is suggested by the EI mass spectrum. Also, the exact conformation of the c,c,c-cdt ligand is unknown. Unfortunately, a single crystal grown at ambient temperature and investigated by X-ray analysis revealed a disordered molecule. At a lower temperatures, the crystals become opaque.

We therefore synthesized the BF_4 derivative by reacting CuI with $AgBF_4$ and c,c,c-cdt. At the first attempt, the complex crystallized as the MeOH solvate **6b** due to the presence of adventitious MeOH in the CH_2Cl_2−diethyl ether solvent mixture. Compound **6b** is conveniently prepared by the deliberate addition of 1 equiv of MeOH (eq 2a). It is worth noting

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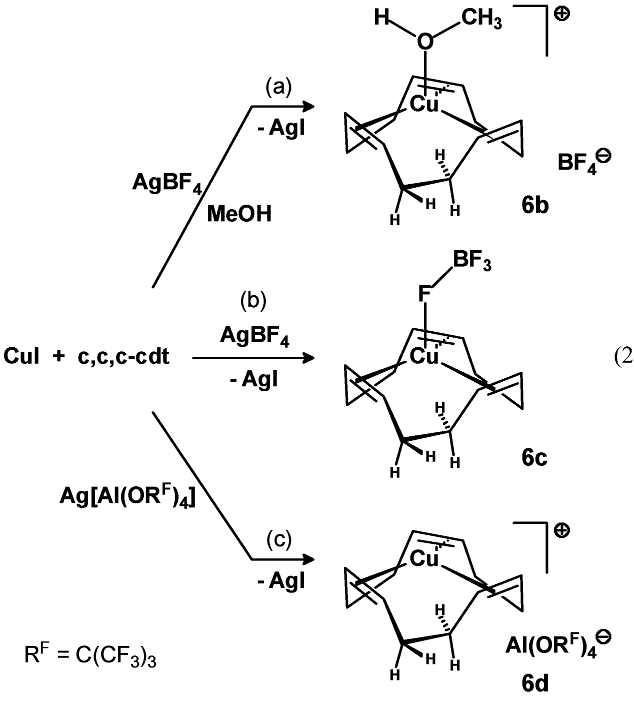
(23) Nickel, T.; Pörschke, K.-R.; Goddard, R.; Krüger, C. *Inorg. Chem.* **1992**, *31*, 4428.

(24) (a) Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 6540. (b) Hinz, F. P.; Margerum, D. W. *J. Am. Chem. Soc.* **1974**, *96*, 4993. (c) Hinz, F. P.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2941. (d) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85*, 271. (e) Hancock, R. D.; Martell, A. E. *Comments Inorg. Chem.* **1988**, *6*, 237. (f) Haack, K.-J.; Goddard, R.; Pörschke, K.-R. *J. Am. Chem. Soc.* **1997**, *119*, 7992.



(2)

that the positive Cu^+ center prefers to coordinate the neutral methanol rather than the negatively charged BF_4 anion, so MeOH appears to be the stronger donor ligand. The MeOH ligand is nonvolatile when drying the compound under vacuum at ambient temperature for 1 h.

Repeating the reaction in the absence of MeOH afforded the actual BF_4 adduct **6c** as a colorless solid, but its structure has not been determined (eq 2b). Similarly, CuI was reacted with c,c,c-cdt and $[Ag(CH_2Cl_2)][Al\{OC(CF_3)_3\}_4]$[25a] to afford equally well-formed colorless crystals of the ionic **6d** (eq 2c). $Al\{OC(CF_3)_3\}_4^-$ has a reputation as ranking among the "least coordinating anions".[25] While **6b** appears to be stable to 230 °C, **6d** shows no tendency to melt or decompose up to 320 °C.

We have successfully performed X-ray single crystal structure determinations of **6b**,**d**, details of which are given in Table 2. Structural data are shown in Table 3. Crystals of **6b** (Figure 3) are made up of discrete Cu(I) complex cations and BF_4 anions. The Cu(I) center is coordinated in a tetrahedral fashion to the three C═C bonds of the c,c,c-cdt ligand and the oxygen atom of the methanol ligand, and the Cu atom lies 0.656(1) Å out of the olefinic plane defined by the midpoints of the three C═C bonds. The c,c,c-cdt ligand adopts an almost exact C_3 symmetrical (ratchet) conformation (root-mean-square deviation of 0.037 Å), with three short Cu1−C distances to C1, C5, and C9 (2.194(4) Å, mean) and three longer distances to C2, C6, and C10 (2.25(1) Å, mean). The olefinic bonds are twisted by 6(1)° out of the mean plane through the midpoints of the bonds so the C═C carbon atoms are approximately coplanar (root-mean-square deviation of 0.078 Å). Within the C_{12} ring, the olefinic C═C bonds are shortest (1.359 Å, mean) as expected and only slightly lengthened as compared to an uncoordinated C═C bond (1.32 Å), and the CH_2−CH_2 bonds are longest (1.538 Å, mean). Interestingly, the ═CH−CH_2 bonds are shorter to the tighter coordinated C1, C5, and C9 (1.506 Å, mean) than those to the more loosely coordinated C2, C6, and C10 (1.529 Å, mean). The difference is also reflected in the torsion angles, which all mirror the C_3 symmetry of the ligand. Thus, whereas two protons at ═CH−CH_2 of the more tightly bound C1, C5, and C9 are anti to one another (C═C−C−C torsion angle −136(1)°, mean), those at ═CH−CH_2 of the more loosely bound C2, C6, and C10 are eclipsed (C═C−C−C torsion angle 79(2)°, mean). The CH_2−CH_2 bonds are all gauche with a mean C−C−C−C torsion angle of 38(2)°. The C_3 symmetry of the cation is necessarily broken by the methanol ligand, although O1 only deviates from the 3-fold axis of the c,c,c-cdt ligand by an angle of 12(1)° at the metal. The Cu1−O1 bond at 2.149(1) Å is normal, as is the Cu1−O1−C13 angle at 125.3(1)°. The cations are arranged in the crystal in layers of enantiomers.

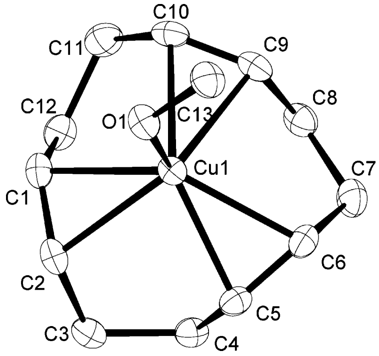


Figure 3. Molecular structure of **6b** in the crystal (BF_4 anion is omitted, atomic displacement ellipsoids are shown at the 50% probability level).

Whereas in **6b** the Cu is tetrahedrally coordinated by the c,c,c-cdt and MeOH ligands, in the $Al\{OC(CF_3)_3\}_4$ salt **6d**, the Cu cation is only bonded to the c,c,c-cdt ligand, and the structure is truly ionic with a large cation−anion separation (Figure 4). The (c,c,c-cdt)Cu cation in **6d** is partially disordered by the inverted molecule in the X-ray analysis. Since the disorder was only light, it was modeled by a second Cu atom (Cu2) 2.103 Å away from Cu1, such that the combined occupancy of Cu1 and Cu2 was 1. The refined occupancy of Cu2 is 0.2058(1). A second crystal showed a similar effect, so some disorder of the (c,c,c-cdt)Cu cation (ca. 20%) appears to take place on crystallization, which is not surprising in view of the symmetrical nature of the cation.

The (c,c,c-cdt)Cu cation in the major component of **6d** is C_3 symmetric within the error margin of the analysis. The conformation of the c,c,c-cdt ligand is very similar to that in **6b** (root-mean-square deviation of 0.053 Å) with each C═C bond asymmetrically coordinated at Cu1 (Table 3). The Cu atom is displaced 0.47(8) Å out of the mean plane of the three olefinic bonds away from the C_2H_4 groups. The ligand does not appear to be flexible enough to accommodate an ideally trigonally planar coordinated metal atom, and the coordination geometry of the Cu atom is therefore perforce distorted toward trigonal pyramidal.

The crystal structures of **6b** and **6d** make a convenient starting point for a discussion of the solution ^1H and ^{13}C NMR spectra of **6a**−**d**. Assuming that the structure of **6a**−**d** in solution is the same as in the solid state, one would expect for the c,c,c-cdt ligand in the rigid ratchet conformation six ^1H and four ^{13}C resonances. However, down to −80 °C, the ^1H NMR spectra of **6a**−**d** in CD_2Cl_2 (Table 1) show only three equally intense and sharply resolved ^1H NMR multiplets for the c,c,c-cdt ligand, namely, one for the olefinic protons (**6a**: δ(H) 6.10) and two for the inequivalent geminal protons at the methylene groups (**6a**: δ(H) 2.74 and 2.46), and in the ^{13}C NMR spectra there

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(25) (a) Krossing, I. *Chem.—Eur. J.* **2001**, *7*, 490. (b) Krossing, I.; Raabe, I. *Angew. Chem.* **2004**, *116*, 2116; *Angew. Chem., Int. Ed.* **2004**, *43*, 2066. (c) Krossing, I.; Reisinger, A. *Coord. Chem. Rev.* **2006**, *250*, 2721.

Table 1. ^{1}H and ^{13}C NMR Data of c,c,c-cdt and c,c,c-cdt Ligands in 1b, 5a, 6a−d, and 7b and the Reference Complex 4[a]

	δ(H)		δ(C)	
	=CH−	−CH$_2$−	=CH−	−CH$_2$−
c,c,c-cdt[b,c]	5.58	2.18	130.8	28.4
[(c,c,c-cdt)Ag]NO$_3$ (**5a**)[b]	6.07	2.70, 2.39	129.4	27.0
(c,c,c-cdt)CuOTf (**6a**)[b]	6.10	2.74, 2.46	125.0	27.4
[(c,c,c-cdt)Cu(MeOH)]BF$_4$ (**6b**)[b]	6.12	2.75, 2.52	124.7	27.7
(c,c,c-cdt)CuBF$_4$ (**6c**)[b]	6.14	2.74, 2.52	124.7	27.7
[(c,c,c-cdt)Cu][Al{OC(CF$_3$)$_3$}$_4$] (**6d**)[b]	6.16	2.83, 2.65	126.5	27.8
(c,c,c-cdt)Ni (**1b**)[c]	4.80	2.40deg	89.3	29.2
(c,c,c-cdt)NiL (**4**)[6d]			99.5	29.9
(d^{t}bpe)Ni(η^2-c,c,c-cdt) (**7b**)[c,e]	5.60, 5.56 (uncoord.) 2.73 (coord.)	2.40, 1.79 (α) 2.74, 2.09 (β) 2.17, 2.08 (γ)	132.5, 129.8 (uncoord.) 55.2 (“t”, coord.)	33.8 (“t”), 33.5, 29.6

[a] Temperature: 25 °C. deg = degenerate. [b] Solvent: CD$_2$Cl$_2$. [c] Solvent: THF-d_8. [d] L = P(OC$_6$H$_4$-2-C$_6$H$_5$)$_3$. Solvent: toluene-d_8. Temperature: −20 °C. [e] d^{t}bpe: δ(H) 1.67deg (PCH$_a$H$_b$), 1.21deg (P^{t}Bu$_a$^{t}Bu$_b$). δ(C) 35.2, 35.1 (each “t”, P*C*Me$_3$), 31.4, 30.5 (each “t”, PC*Me$_3$*), 24.1 (“t”, PC$_2$H$_4$P). δ(P) 83.9.

are only two equally intense signals for the olefinic and allylic C atoms, so all olefinic protons and carbon atoms and all methylene groups are equivalent on the time average. The solution NMR spectra of **6a−d** reveal the dynamic nature of the c,c,c-cdt ligand in the chiral ratchet conformation, which results in rapid enantiomerization. While the coordination chemical shifts are small, in agreement with the expected weak backbonding from Cu(I), there are distinct chemical shift differences in the c,c,c-cdt signals of **6a−d**, suggesting that **6a−c** remain undissociated in CD$_2$Cl$_2$ solution with respect to the OTf, MeOH, and BF$_4$ coordination. Consistent with a stable MeOH coordination in **6b** and consequently slow proton exchange, the MeOH ^{13}C signal (δ(C) 51.5) differs from that of free MeOH (δ(C) 50.7), and the MeOH ligand gives rise to a ^{1}H doublet (δ(H) 3.44, ^3J(HH) = 5.3 Hz) and a quartet (δ(H) 2.10), unlike free MeOH (δ(H) 3.41, 1.50) for which the couplings are unresolved. The addition of some free MeOH causes the MeOH ligand multiplets to collapse.

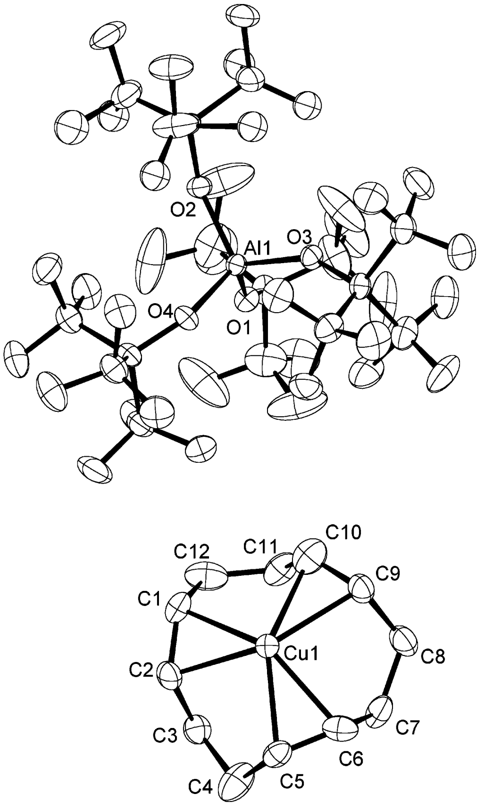
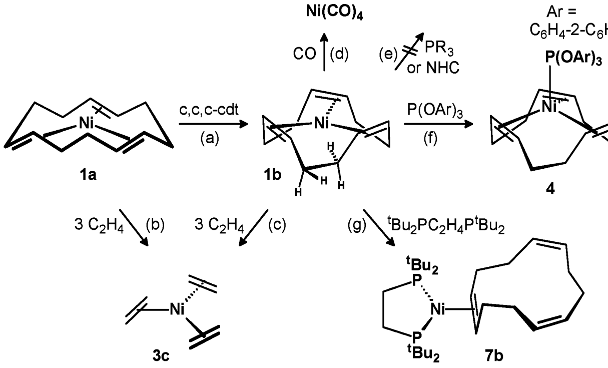


Figure 4. Molecular structure of **6d** in the crystal (atomic displacement ellipsoids shown at the 50% probability level).



(3)

Thus, our studies on the Ag(I) and Cu(I) complexes are in agreement with the results from Anet’s conformational analysis of the free c,c,c-cdt, which concluded that not only the helical but also the ratchet conformation (crown-I)[12] is relatively low in energy, and hence, the c,c,c-cdt can take up one of these conformations in the corresponding Ag(I) and Cu(I) complexes (the likewise low-energy saddle conformation has so far not been encountered in c,c,c-cdt−metal complexes). While for M−η^2-c,c,c-cdt coordination the helical conformation is preferred as in **5**, the ratchet conformation of the c,c,c-cdt ligand suits both a tetrahedral (**6b**) and a distorted trigonal coordination geometry (**6d**) of the central metal. In the ratchet conformation, all three C=C bonds are almost in-plane, which appears favorable for backbonding in the case of the trigonal planar coordination mode, but each individual C=C bond is unsymmetrically coordinated, thereby counteracting an optimal backbonding. The hypothetical C_{3v} symmetrical crown conformation is not a viable conformation[13] for the free c,c,c-cdt or when it is ligated to a metal due to the considerable Pitzer strain.

(c,c,c-cdt)Ni (1b). The insight gained with the Ag(I) and Cu(I) complexes will help us to discuss the conformational aspects of the Ni(0)−c,c,c-cdt complexes **1b** and **7b**. Complex **1b** is obtained by reaction of a pentane or diethyl ether solution of **1a** (not **2**) with 1 equiv of c,c,c-cdt at 20 °C. The red color of **1a** fades within a few minutes, and a yellow−brown solution is formed from which the pale yellow, similarly trigonal **1b** crystallizes at −40 °C in high yield (eq 3a).[6a,b] Although **1b** is thermodynamically more stable, it is even more sensitive to oxygen than **1a**. Furthermore, complex **1b** is only stable in solution at ambient temperature for a short period, preventing an extensive solution investigation (e.g., by ^{61}Ni NMR).[26] Below

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(26) (a) Benn, R.; Rufinska, A. *Angew. Chem., Int. Ed.* **1986**, *25*, 861. (b) Benn, R.; Rufinska, A. *Magn. Reson. Chem.* **1988**, *26*, 895. (c) Behringer, K. D.; Blümel, J. *Magn. Reson. Chem.* **1995**, *33*, 729.

Table 2. Crystal Data for (c,c,c-cdt)Ni (1b), (c,c,c-cdt)($AgNO_3$)$_3$ (5), [(c,c,c-cdt)Cu(MeOH)]BF_4 (6b), [(c,c,c-cdt)Cu]Al{OC(CF_3)$_3$}$_4$ (6d), and (^{t}Bu$_2$PC_2H_4P^{t}Bu$_2$)Ni(η^2-c,c,c-cdt) (7b)

	1b	**5**	**6b**	**6d**	**7b**
empirical formula	$C_{12}H_{18}Ni$	$C_{12}H_{18}Ag_3N_3O_9$	$C_{13}H_{22}BCuF_4O$	$C_{28}H_{18}AlCuF_{36}O_4$	$C_{30}H_{58}NiP_2$
color	yellow	colorless	colorless	colorless	orange−brown
fw (g mol^{-1})	220.97	671.90	344.66	1192.94	539.41
temp (K)	100	100	100	100	100
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	rhombohedral	monoclinic	monoclinic	monoclinic	triclinic
space group	$R\bar{3}m$ (No. 166)	$P2_1/c$ (No. 14)	Cc (No. 9)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	7.7327(5)	7.1207(1)	9.7840(5)	13.6998(5)	12.8797(2)
b (Å)	7.7327(5)	12.9571(2)	10.9423(6)	14.6452(5)	13.9842(2)
c (Å)	7.7327(5)	19.3026(2)	13.7195(7)	19.7498(7)	18.4902(3)
α (deg)	115.346(1)	90.0	90.0	90.0	72.7950(8)
β (deg)	115.346(1)	100.200(1)	95.568(2)	99.439(2)	75.4380(8)
γ (deg)	115.346(1)	90.0	90.0	90.0	81.7670(8)
V (Å^3)	250.42(3)	1752.78(4)	1461.87(13)	3908.9(2)	3070.55(8)
Z	1	4	4	4	4
V/Z (Å^3)	250.4	438.2	365.5	977.2	767.6
calcd density (Mg m^{-3})	1.465	2.546	1.566	2.027	1.167
abs coeff (mm^{-1})	1.885	3.373	1.529	0.791	0.752
F(000) (e)	118	1296	712	2336	1184
cryst size (mm^3)	0.34 × 0.03 × 0.03	0.20 × 0.17 × 0.05	0.14 × 0.10 × 0.06	0.09 × 0.07 × 0.02	0.18 × 0.16 × 0.16
θ range for data collection (deg)	4.40−31.44	3.14−33.11	2.98−31.55	2.97−27.48	2.96−31.53
index ranges	$-11 \le h \le 11$ $-11 \le k \le 11$ $-11 \le l \le 11$	$-10 \le h \le 10$ $-19 \le k \le 19$ $-29 \le l \le 29$	$-14 \le h \le 14$ $-16 \le k \le 16$ $-20 \le l \le 20$	$-17 \le h \le 17$ $-19 \le k \le 18$ $-25 \le l \le 25$	$-18 \le h \le 18$ $-20 \le k \le 19$ $-27 \le l \le 27$
no. of reflns collected	5594	52502	18575	43009	79638
no. of ind reflns	318 ($R_{int} = 0.0529$)	6641 ($R_{int} = 0.0343$)	4810 ($R_{int} = 0.0376$)	8944 ($R_{int} = 0.0905$)	20428 ($R_{int} = 0.0378$)
no. of reflns with $I > 2\sigma(I)$	300	6380	4248	5720	17696
completeness (%)	99.7 ($\theta = 31.44°$)	99.7 ($\theta = 33.11°$)	99.8 ($\theta = 31.55°$)	99.9 ($\theta = 27.48°$)	99.8 ($\theta = 31.53°$)
abs correction	semiempirical from equivalents	Gaussian	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents
max/min transmission	1.0/0.91	0.85/0.56	0.75/0.43	1.00/0.95	1.00/0.97
full-matrix least-squares	F^2	F^2	F^2	F^2	F^2
no. of data/restraints/params	318/0/22	6641/0/244	4810/2/197	8944/0/659	20428/0/591
GOF on F^2	1.161	1.100	1.059	1.018	1.038
final R indices ($I > 2\sigma(I)$)					
R1	0.0565	0.0233	0.0272	0.0588	0.0358
wR2	0.1419	0.0556	0.0595	0.1229	0.0803
R indices (all data)					
R1	0.0598	0.0244	0.0347	0.1085	0.0448
wR2	0.1436	0.0562	0.0620	0.1453	0.0842
abs structure param			0.017(7)		
largest diff peak/hole (e Å^{-3})	0.315/−0.281	0.972/−1.059	0.247/−0.352	0.927/−0.407	0.931/−0.466

Table 3. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) for [(c,c,c-cdt)Cu(MeOH)]BF_4 (6b) and [(c,c,c-cdt)Cu][Al{OC(CF_3)$_3$}$_4$] (6d)

	6b	**6d**
Cu1−C1	2.197(2)	2.178(4)
Cu1−C2	2.250(2)	2.191(4)
Cu1−C5	2.189(2)	2.174(4)
Cu1−C6	2.237(2)	2.200(4)
Cu1−C9	2.197(2)	2.218(4)
Cu1−C10	2.261(2)	2.194(5)
C1−C2	1.361(2)	1.376(6)
C5−C6	1.359(3)	1.354(6)
C9−C10	1.356(3)	1.352(6)
Cu1−O1	2.149(2)	
Cu1−O1−C13	125.3(1)	
C2−C3−C4−C5	36(1)	37(3)
C6−C7−C8−C9	38(1)	32(3)
C10−C11−C12−C1	40(1)	33(3)
mean twist of the C═C bonds out of the olefinic plane (deg)	6(1)	7(1)
displacement of Cu1 from the olefinic plane (Å)	0.656(1)	0.47(8)

−40 °C, the solubility of **1b** in typical solvents is poor. In the ambient temperature ^{1}H NMR spectrum (THF-d_8), one signal each, with considerable line-broadening, is observed for the olefinic protons (δ(H) 4.80) and the allylic protons (δ(H) 2.40), so that the latter appears degenerate. As for **5a** and **6a−d**, there are just two ^{13}C signals (Table 1). The spectra are unchanged at −30 °C.

The spectra are in accord with rapid enantiomerization of **1b** in solution at the given temperatures assuming the ratchet conformation for the c,c,c-cdt ligand and thus a C_3 symmetrical chiral ground state structure. A previous ^{13}C NMR study[6c,d] has shown that while the coordination chemical shift for the c,c,c-cdt ligand in **1b** of $\Delta\delta(C) = -41.5$ is larger than for the t,t,t-cdt ligand in **1a** ($\Delta\delta(C) = -25.0$), it is substantially smaller than for the ethene ligands in **3c** ($\Delta\delta(C) = -65.5$), suggesting that backbonding from Ni(0) to the c,c,c-cdt ligand in **1b**—although larger than for the t,t,t-cdt ligand in **1a**—is clearly weaker than the optimal backbonding of the ethene ligands in the D_{3h} symmetrical **3c**.[8] This result seems to agree with the anticipated ratchet conformation of the c,c,c-cdt ligand with an asymmetric Ni−η^2-C═C coordination, in which backdonation from the trigonal planar Ni(0) to the in-plane C═C bonds is hampered.

Complex **1b** reacts with ethene at 0 °C to afford **3c** (eq 3c) in accord with restricted backbonding, just as is the case for **1a** (eq 3b). Thus, although **1a**,**b** bear cyclopolyene ligands (t,t,t-cdt and c,c,c-cdt) in which the chelate and macrocyclic effects might be assumed to play a stabilizing role, the stabilization of the Ni(0) complexes by these effects is not sufficient to retard the reactions with ethene to give **3c**. In this respect, there is a sharp contrast between stability and reactivity of the t,t,t-/c,c,c-cdt complexes of Ni(0) (**1a**,**b**) and those of Cu(I) (**6a−d**).

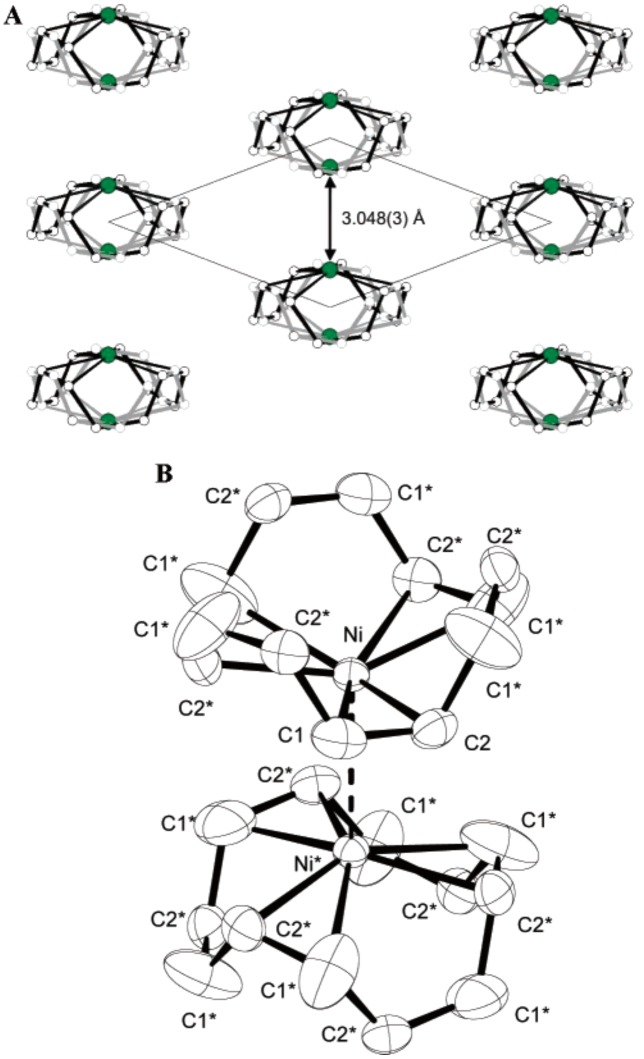

Figure 5. (a) Crystal structure of **1b**, viewed along the crystallographic *a*-axis, showing the arrangement of disordered (c,c,c-cdt)Ni moieties in the unit cell. As a result of the disorder, it is not possible to distinguish between a CH_2-CH_2 and a $CH=CH$ group bound to Ni. (b) View of molecules of **1b**, showing the possible weak interaction between two (c,c,c-cdt)Ni moieties. Selected distances (Å) and angles (deg): Ni−C1 = 2.298(12), Ni−C2 = 2.119(6), C1−C2 = 1.440(12), C1−C2* = 1.484(10), Ni···Ni = 3.048(3), C1−C2−C1* = 115.4(6), C2−C1−C2* = 119.6(6).

Because of the significance of **1b** as a pendant to the isomeric **1a**, we considered it worthwhile to determine its crystal structure by X-ray crystallography (Table 2). The molecules crystallize in the trigonal space group $R\bar{3}m$, with one (c,c,c-cdt)Ni moiety in the unit cell. Figure 5a shows the packing of the molecules in the unit cell. The molecules are close-packed and positionally disordered, as was observed to a smaller extent for the (c,c,c-cdt)Cu cation in the crystal structure of **6d**. Despite the disorder, the structure of **1b** refines to a satisfactory *R*-index of 0.0565 (5594 measured data, 318 independent observations, $R_{av} = 0.0529$, and data/parameter ratio >14). In **1b**, each (c,c,c-cdt)-Ni unit occupies two positions with equal occupancy, and they are stacked vertically above one another, with a Ni···Ni distance of 3.048(3) Å between the closest units. The disorder (see comment in the CIF) precludes a detailed discussion of the structure, apart from confirming the existence of the (c,c,c-cdt)-Ni moiety and revealing its general structure.

Since the (c,c,c-cdt)Ni units can either pack with all the Ni atoms orientated in the same direction or alternating, it is unfortunately not possible to say with certainty whether the molecules crystallize as monomers or weakly bound dimers (Figure 5b). Arguments that support the presence of a dimer in the crystal are that (a) the (c,c,c-cdt)Ni units pack vertically above one another, (b) weak $d^{10}-d^{10}$ transition metal interactions are not unknown,[27] (c) weak Ni···Ni interactions have been discussed in connection with the crystal structures of a series of complexes containing Ni(II) bound to macromolecules,[28] and (d) the Ni atoms lie 0.4(1) Å above the mean plane of the midpoints of the three olefinic bonds, although as we have seen in the case of the (c,c,c-cdt)Cu cation of **6d**, the conformation of the c,c,c-cdt ligand does not allow the metal to lie exactly in the olefinic plane.

The only previously known adduct of **1b** is **4** with the sterically much encumbered $P(OC_6H_4\text{-}2\text{-}C_6H_5)_3$ ligand (eq 3f).[6a,b] Complex **4** separates from solution as a microcrystalline powder, so far unsuitable for a crystallographic structure determination. All attempts to synthesize further adducts of **1b** with monodentate ligands have failed. Thus, whereas (t,t,t-cdt)-Ni(PMe_3) is a stable compound,[29a] **1b** can be recovered unchanged from a pentane solution containing 1 equiv of the sterically small and strongly donating PMe_3 (−20 °C). Similarly, **1b** resists forming adducts with alkyl phosphites or the very strongly electron donating carbenes $C\{N(^tBu)CH\}_2$ and $C\{N(C_6H_3\text{-}2,6\text{-}^iPr_2)CH\}_2$. In contrast, whereas **1a** forms with the strongly accepting CO the isolable (t,t,t-cdt)Ni(CO) below −20 °C,[1c,29b] **1b** reacts with 4 equiv of CO already at −60 °C by displacement of the c,c,c-cdt to yield $Ni(CO)_4$ (eq 3d). This reaction is related to the aforementioned displacement reaction with ethene to give **3c** (eq 3c).

These experimental findings can be rationalized as follows: as is evident from the ^{13}C NMR data, backbonding from Ni(0) to the c,c,c-cdt ligand is already inherently imperfect for **1b** because of the anticipated asymmetric coordination of the conformationally restricted C=C bonds and the out-of-plane position of the Ni atom. An even poorer backbonding is expected for a tetrahedral Ni(0)−alkene complex.[30] In a hypothetical tetrahedral (c,c,c-cdt)NiL species with a strongly electron donating L, the charge imposed by L on the Ni atom could not be properly transferred further onto the accepting orbitals of the structurally constrained c,c,c-cdt ligand, and consequently, the Ni atom simply resists to coordinate L.

Thus, a stable tetrahedral (c,c,c-cdt)NiL complex such as **4** can only be realized for a predominantly electron accepting ligand L, requiring only mediocre backbonding of Ni(0) to the c,c,c-cdt ligand, similar to the electronic situation in the likewise tetrahedral Cu(I) derivatives **6a**−**c**. Such accepting ligands L are furnished by, for example, CO, CNMe, C_2H_4, and aryl phosphites. However, for the smaller L the c,c,c-cdt ligand can be readily displaced by further L to give products NiL_n such as **3c** (eq 3c) and $Ni(CO)_4$ (eq 3d), via a non-isolatable (c,c,c-cdt)NiL intermediate. Only for a bulky acceptor ligand such as $P(OC_6H_4\text{-}2\text{-}Ph)_3$, for which the c,c,c-cdt displacement is hampered, can the reaction halt at the stage of the 1:1 adduct (**4**).

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[27] (a) Dedieu, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2074. (b) Merz, K. M., Jr.; Hoffmann, R. *Inorg. Chem.* **1988**, *27*, 2120.

[28] For Ni···Ni distances around 3 Å, see: (a) 2.788 Å: Peng, S.-M.; Goedken, V. L. *J. Am. Chem. Soc.* **1976**, *98*, 8500. (b) 2.800 Å: Herebian, D.; Bothe, E.; Neese, F.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2003**, *125*, 9116. (c) 3.358 Å: Stephens, F. S.; Vagg, R. S. *Inorg. Chim. Acta* **1980**, *43*, 77.

[29] (a) Pörschke, K.-R.; Wilke, G.; Mynott, R. *Chem. Ber.* **1985**, *118*, 298 and references therein. (b) Pörschke, K.-R.; Wilke, G. *Chem. Ber.* **1984**, *117*, 56.

[30] Pörschke, K.-R.; Mynott, R. *Z. Naturforsch., B: Chem. Sci.* **1984**, *39*, 1565.

(^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Ni(η^2-c,c,c-cdt) (7b). While an adduct of **1b** with a monodentate phosphane appears to be inaccessible, we have reacted **1b** with the sterically encumbered bidentate phosphane ^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$ (d^{t}bpe) to afford yellow−brown cubes of adduct **7b** (eq 3g). In the course of this reaction, the Ni atom in **1b** moves from its central position within the ring to an outside position. It can be shown on a model that in this process the Ni atom can maintain a continued binding to one C═C bond of the c,c,c-cdt ligand while the cycloalkene undergoes eversion. Complex **7b** (mp 185 °C dec) is thermally rather stable. In the EI mass spectrum (140 °C), the molecular ion (m/e = 538, 10%) is observed, which fragments by elimination of the cycloalkene to give [(d^{t}bpe)Ni]$^+$ as the base ion. The η^2-c,c,c-cdt ligand in **7b** is readily displaced by ethene to afford the known (d^{t}bpe)Ni(C$_2$H$_4$).[31]

Complex **7b** is isomeric to the previously studied (d^{t}bpe)Ni(η^2-t,t,t-cdt) (**7a**), which is practically inert and resists a displacement reaction of the η^2-t,t,t-cdt ligand by ethene or even butadiene and cyclooctatetraene at ambient temperature.[31] The low reactivity of **7a** can be rationalized in terms of its C_2 symmetrical structure, which, by virtue of the four ^{t}Bu substituents of the d^{t}bpe ligand assuming a gear-like orientation relative to the trans substituents of the coordinated C═C bond, results in a shielding of the Ni atom by the two ligands.

The ambient temperature NMR spectra of **7b** are in agreement with the presence of a η^2-c,c,c-cdt ligand and effective C_s symmetry of the complex in solution, resulting from the time average of the different conformations of the η^2-c,c,c-cdt ligand. Thus, the latter displays nine ^{1}H and six ^{13}C signals (Table 1): besides two low-field signals for the inequivalent −CH═groups of the uncoordinated C═C bonds (δ(H) 5.60, 5.56; δ(C) 132.5, 129.8), there is an upfield signal for the coordinated C═C bond (δ(H) 2.73; δ(C) 55.2), with the latter ^{13}C signal representing a virtual triplet due to two ^{31}P couplings. The geminal CH$_a$H$_b$ protons, which are inequivalent because of their endo and exo positions in the ring, are quite different for the methylene groups α and β to the coordinated C═C bond (δ(H)$_\alpha$ 2.40, 1.79; δ(H)$_\beta$ 2.74, 2.09) and less so for the distant γ methylene group (δ(H)$_\gamma$ 2.17, 2.08). While the α and γ methylene groups give rise to ^{13}C singlets (δ(C)$_\alpha$ 33.5; δ(C)$_\gamma$ 29.6), the β methylene groups produce a virtual triplet (δ(C)$_\beta$ 33.8, Σ^4J(PP) = 10 Hz). This pattern of signal splittings seems unusual but is characteristic for a series of substituted bis(phosphane)Ni−alkene complexes. The signal assignment has been verified by C,H- and H,H-COSY NMR. The total of five d^{t}bpe ^{13}C signals (the PCH$_a$H$_b$ and P^{t}Bu$_a$^{t}Bu$_b$ protons are degenerate) indicates inequivalent ^{t}Bu substitutents at the phosphorus atoms, thereby ruling out rotation of the coordinated C═C bond about the bond axis to Ni. The ^{31}P resonance is a singlet. The spectra are practically unchanged at −80 °C. It will be shown at the end that the effective C_s symmetry of **7b** in solution is due to enantiomerization of a chiral structure, which is rapid even at −80 °C.

Data on the X-ray structure analysis of **7b** are given in Table 2, and the molecular structure is shown in Figure 6. The complex crystallizes with two independent molecules 1 and 2 in the asymmetric unit, which differ mainly in the orientation of one ^{t}Bu group and the conformation of the η^2-c,c,c-cdt ligand at the distal CH$_2$−CH$_2$ bond, where there is slight (ca. 20%) disorder. The complex is chiral in the solid state.

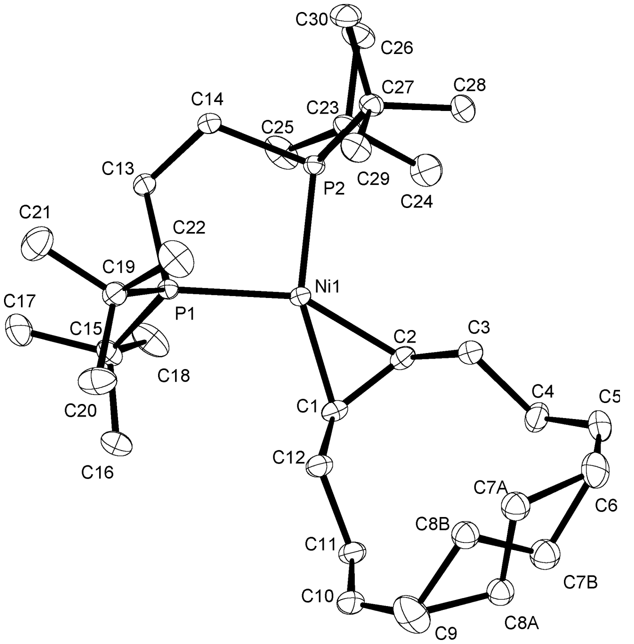

Figure 6. Molecular structure of (^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Ni(η^2-c,c,c-cdt) (**7b**) (molecule 1, atomic displacement ellipsoids are shown at the 50% probability level). Selected bond distances (Å), a bond angle (deg), interplanar angle (deg), and dihedral angles (deg): Ni1−P1 = 2.1855(4), Ni1−P2 = 2.1876(3), Ni1−C1 = 1.977(1), Ni1−C2 = 1.986(1), C1−C2 = 1.429(2), C2−C3 = 1.516(2), C3−C4 = 1.552(2), C4−C5 = 1.507(2), C5−C6 = 1.299(3), C6−C7A = 1.529(3), C7A−C8A = 1.536(3), C8A−C9 = 1.543(3), C9−C10 = 1.316(2), C10−C11 = 1.503(2), C11−C12 = 1.548(2), C12−C1 = 1.519(2); P1−Ni1−P2 = 93.23(1); P1,P2,Ni1/Ni1,C1,C2 = 7(1); C2−C3−C4−C5 = 189(1), C6−C7A−C8A−C9 = 192(1), C10−C11−C12−C1 = 170(1).

In both molecules, the geometry at the Ni atom is approximately trigonal planar with the Ni atom lying 0.1 Å out of the plane defined by the phosphorus atoms and the midpoint D1 of the coordinated C═C bond toward the ring. Whereas the C atoms of the C═C bond lie approximately parallel to the P···P vector (1 and 4°) in **7b**, this is not the case for the isomeric complex **7a** where the comparable angles are 27 and 19°. The puckering in the (PC$_2$H$_4$P)Ni chelate ring is slightly larger for **7b** (P−C−C−P = 42 and 37°) than for **7a** (P−C−C−P = 29 and 30°). While the Ni−P bond distances in **7b** (2.186 Å, mean) are very similar to those in the isomeric **7a**, the Ni−C1/C2 coordination bonds at 1.977(1) and 1.986(1) Å are slightly shorter (**7a**, 2.007 Å, mean), and the coordinated bond C1−C2 at 1.429(2) Å is somewhat longer (**7a**, 1.398(4) Å). Within the η^2-c,c,c-cdt ligand, we see typical bond lengths for ═CH−CH$_2$ (1.52 Å, mean), CH$_2$−CH$_2$ (1.55 Å, mean), and uncoordinated C═C (1.31 Å, mean).

The conformation of the η^2-c,c,c-cdt ligand in **7b** corresponds to the helical conformation of the uncoordinated c,c,c-cdt, which has emerged as the most stable,[10a,11a] and the same conformation is also present in the 3-fold AgNO$_3$ coordinated **5** (Figure 2a). Although in principle the (d^{t}bpe)Ni moiety can coordinate to the c,c,c-cdt ligand in this conformation in three different modes, the only isomer that is observed is the one in which Ni is bound to the opposite face (exo) of one of the two C═C bonds with the two C$_2$H$_4$ substituents in syn alignment, and so minimizing steric effects.

While the free c,c,c-cdt in its helical conformation has C_2 symmetry, with the C_2 axis passing through the midpoint of the *cis*-C═C bond bearing the two anti aligned C$_2$H$_4$ substituents and the midpoint of the opposite CH$_2$−CH$_2$ bond, coordination of the (d^{t}bpe)Ni moiety at one of the *cis*-C═C bonds off the original C_2 axis lowers the symmetry to C_1 in **7b**. Enantiomer-

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[31] Pörschke, K.-R.; Pluta, C.; Proft, B.; Lutz, F.; Krüger, C. *Z. Naturforsch., B: Chem. Sci.* **1993**, *48*, 608.

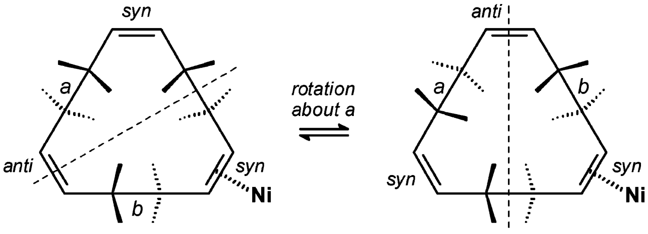

Figure 7. Schematic representation (in the notation of refs 10a and 11a) of the conformation of the η^2-c,c,c-cdt ligand in **7b** and of the complex enantiomerization. Dashed line marks the C_2 symmetry axis in the uncoordinated c,c,c-cdt.

ization of **7b** is formally possible by 180° $CH_2{-}CH_2$ bond rotation of the C_2H_4 entity *a* at the anti aligned *cis*-C═C bond and opposite to the coordinated C═C bond (and not at *b* connecting to this bond), so changing the rotational direction of the helix (Figure 7). Enantiomerization of **7b** therefore proceeds by a similar mechanism as for free c,c,c-cdt (Figure 1), with the restriction that 180° rotation occurs only at one and not at all three $CH_2{-}CH_2$ bonds of the cyclotriene (i.e., the bond opposite to the coordinated *cis*-C═C bond). (If rotation occurs at bond *b*, an isomer of **7b** is formed.)

As the molecular structure of **7b** shows, in the c,c,c-cdt ligand, the atoms C7 and C8 that make up the $CH_2{-}CH_2$ bond *a* opposite to the coordinated *cis*-C═C bond are disordered. The disorder can be attributed to the presence of a diastereomer of **7b** (with a retained puckering of the $(PC_2H_4P)Ni$ chelate ring).

Conclusion

The principal coordination modes and conformations of c,c,c-cdt as a ligand in d^{10} Ag(I), Cu(I), and Ni(0) complexes are described. For η^2-c,c,c-cdt coordination at one (**7b**) or several metal centers (**5**), the cyclopolyene maintains a helical conformation of local C_2 symmetry, which was shown previously to be the most stable for free c,c,c-cdt. For trisdentate coordination at a single d^{10} center, the ligand can accommodate both trigonal (**1b**, **6d**) and tetrahedral (**6a**−**c**) coordination geometries of the metal center, thereby assuming a ratchet conformation with C_3 symmetry. In solution, the chiral complexes undergo enantiomerization.

There are striking differences in the stability and reactivity of the d^{10} complexes. The Cu(I) complexes **6a**−**d** are of exceptionally high thermal stability. They show no exchange with ethene, and together with donors, the c,c,c-cdt ligand imposes a tetrahedral structure on the Cu(I) center. In contrast, the Ni(0) complex **1b** is thermally much less stable; it does not form adducts with most donors, and the c,c,c-cdt ligand is displaced by ethene. As a trisdentate ligand at a single d^{10} center, c,c,c-cdt prefers the ratchet conformation with an out-of-plane coordination of the metal center and as such is a poor acceptor.

Experimental Procedures

All manipulations were carried out under argon with Schlenk-type glassware. Solvents were dried prior to use by distillation from $NaAlEt_4$. c,c,c-cdt[10a] (d = 0.89 g mL^{-1}), (t,t,t-cdt)Ni,[1c] (C_6H_{10})-CuOTf,[23] and $^tBu_2PC_2H_4P^tBu_2$[31] were prepared as published. (t,t,t-cdt)Ni (**1a**) contained 5% cocrystallized t,t,t-cdt, so the calculated molecular weight of 233 g mol^{-1} was used. Microanalyses were performed by the local Mikroanalytisches Labor Kolbe. EI mass spectra were recorded at 70 eV and refer to ^{58}Ni, ^{63}Cu, and ^{107}Ag. ^{1}H NMR spectra were measured at 300 MHz and ^{13}C NMR spectra at 75.5 MHz (both relative to TMS) on Bruker AMX-300 and DPX-300 instruments. NMR data of the products are listed in Table 1.

Ni(c,c,c-cdt) (1b).[6a,b] To a red solution of **1a** (932 mg, 4.00 mmol) in 20 mL of diethyl ether was added c,c,c-cdt (0.73 mL, 4.0 mmol) at −40 °C. On keeping the solution at room temperature for 30 min, the solution turned yellow. Slow cooling of the solution to −25 °C afforded colorless needles, which were separated from the mother liquor, washed twice with cold ether, and dried under vacuum (20 °C): yield 780 mg (88%); dec 65 °C. EI-MS (65 °C): *m/e* (%) 220 ([M]$^+$, 28). $C_{12}H_{18}Ni$ (221.0).

(c,c,c-cdt)(AgNO$_3$)$_3$ (5).[10a] c,c,c-cdt (0.30 mL, 1.67 mmol) was added to a solution of $AgNO_3$ (849 mg, 5.00 mmol) in 2 mL of H_2O and 4 mL of THF. Cooling the mixture to 5 °C for 2 days afforded large colorless cubes: yield 704 mg (63%); mp 150 °C, dec >160 °C. Anal. Calcd for $C_{12}H_{18}Ag_3N_3O_9$ (671.9): C, 21.45; H, 2.70; Ag, 48.16; N, 6.25; O, 21.43. Found: C, 21.85; H, 2.56; Ag, 48.12; N, 6.25.

(c,c,c-cdt)CuOTf (6a). To a solution of (C_6H_{10})CuOTf (295 mg, 1.00 mmol) in 5 mL of CH_2Cl_2 was added c,c,c-cdt (0.2 mL, 1.06 mmol). About 1−2 mL of diethyl ether was added dropwise until a white precipitate formed. The latter was redissolved by gentle warming. Letting the solution stand at ambient temperature and further slow cooling to −20 °C afforded colorless cubes: yield 300 mg (80%). EI-MS (170 °C): *m/e* (%) 374 ([M]$^+$, 5), 225 ([$C_{12}H_{18}Cu$]$^+$, 42). ESIpos-MS (CH_2Cl_2): *m/e* (%) 225 ([$(C_{12}H_{18})$-Cu]$^+$, 100). ESIneg-MS (CH_2Cl_2): *m/e* (%) 149 ([OTf]$^-$, 100). $C_{13}H_{18}CuF_3O_3S$ (374.9).

[(c,c,c-cdt)Cu(MeOH)]BF$_4$ (6b). A suspension of CuI (286 mg, 1.50 mmol) in 4 mL of CH_2Cl_2 and 0.1 mL of MeOH was stirred with c,c,c-cdt (0.27 mL, 1.50 mmol) and solid $AgBF_4$ (292 mg, 1.50 mmol) for 30 min. The precipitated AgI was removed by filtration, and 2 mL of diethyl ether was added. Cooling the solution to 0 °C afforded well-formed colorless rods, which were isolated and dried under vacuum: yield 450 mg (87%); dec 230 °C. ESIpos-MS (CH_2Cl_2): *m/e* (%) 225 ([$(C_{12}H_{18})$Cu]$^+$, 100). ESIneg-MS (CH_2Cl_2): *m/e* (%) 87 ([BF_4]$^-$, 100). Anal. Calcd for $C_{13}H_{22}BCuF_4O$ (344.7): C, 45.30; H, 6.43; B, 3.14; Cu, 18.44; F, 22.05; O, 4.64. Found: C, 45.10; H, 5.82; Cu, 18.68; F, 22.30.

(c,c,c-cdt)CuBF$_4$ (6c). Synthesis was as for **6b**, but without the addition of MeOH; colorless crystals: yield 330 mg (70%). ESIpos-MS (CH_2Cl_2): *m/e* (%) 225 ([$(C_{12}H_{18})$Cu]$^+$, 100). ESIneg-MS (CH_2Cl_2): *m/e* (%) 87 ([BF_4]$^-$, 100). $C_{12}H_{18}BCuF_4$ (312.6).

[(c,c,c-cdt)Cu][Al{OC(CF$_3$)$_3$}$_4$] (6d). A suspension of CuI (190 mg, 1.00 mmol) in 15 mL of CH_2Cl_2 was stirred with c,c,c-cdt (0.18 mL, 1.00 mmol) and solid [$Ag(CH_2Cl_2)$][$Al\{OC(CF_3)_3\}_4$] (1160 mg, 1.00 mmol) for 30 min. The precipitated AgI was removed by filtration. Cooling the solution to 0 °C afforded colorless rods: yield 895 mg (75%); dec 320 °C. ESIpos-MS (CH_2Cl_2): *m/e* (%) 225 ([$(C_{12}H_{18})$Cu]$^+$, 100). ESIneg-MS (CH_2Cl_2): *m/e* (%) 967 ([$AlC_{16}F_{36}O_4$]$^-$, 100). $C_{12}H_{18}Cu{\cdot}AlC_{16}F_{36}O_4$ (1192.9).

($^tBu_2PC_2H_4P^tBu_2$)Ni(η^2-$C_{12}H_{18}$) (7b). To a solution of **1b**, prepared in situ from **1a** (700 mg, 3.00 mmol) and c,c,c-cdt (0.55 mL, 3.00 mmol) in 15 mL of diethyl ether, was added at −40 °C a solution of $^tBu_2PC_2H_4P^tBu_2$ (955 mg, 3.00 mmol), also in 15 mL of diethyl ether. After warming the mixture to ambient temperature, the solution was cooled to −60 °C to afford yellow−brown cubes: yield 1.165 g (72%); mp 185 °C dec. EI-MS (140 °C): *m/e* (%) 538 ([M]$^+$, 10), 376 ([$(d^tbpe)Ni$]$^+$, 100). Anal. Calcd for $C_{30}H_{58}$-NiP_2 (539.4): C, 66.80; H, 10.84; Ni, 10.88; P, 11.48. Found: C, 66.62; H, 10.86; Ni, 10.87; P, 11.47.

Supporting Information Available: CIF data for **1b**, **5**, **6b**, **6d**, and **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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