and $[Ni^{I}(DAPA)(SPh)_2(CN)]^{2-}$ (**5**) (g = 2.235, 2.164, 2.013), respectively (Figure 2). The reduced species **3** also reacts with CO to produce the CO adduct $[Ni^{I}(DAPA)(SPh)_2(CO)]^-$ (**6**) (g = 2.198, 2.145, 2.023). Stepwise oxidation of **6** with $[Fe(CN)_6]^{3-}$ first generates an EPR-silent species and then the oxidized complex **2** (Figure S2, supplementary material). The coordinated CO in **6** therefore dissociates from the nickel center upon oxidation. This is also supported by the fact that no change in the EPR spectrum of **2** is observed under very high partial pressure of CO. It is interesting to note that CO replaces CN^- upon reduction of **4** in the presence of CO (the product being **6**), while CN^- recaptures the sixth coordination site upon oxidation (the product is **4**, Figure 2). Also, reaction of **5** with CO affords **6** as the sole product. It is thus clear that (a) CN^- binds to both the oxidized and the reduced species (**2** and **3**), (b) CO binds only to the reduced species, and (c) CO binds to the reduced species more strongly than CN^-.

In conclusion, complex **1** is the first example of a model system for the nickel site of the [FeNi] H_2ases that could be readily oxidized and reduced to the corresponding Ni(III) and Ni(I) species. Binding studies with these species reveal that the EPR spectra of the pentacoordinated complexes (be it oxidized or reduced) are mostly axial while the hexacoordinated species exhibit more rhombic EPR signals. The same trend has been observed with the terpy system. It is therefore not unreasonable to assume the presence of hexacoordinated nickel centers in both the oxidized (Ni-A/Ni-B) and reduced (Ni-C) forms of the enzyme. Since the combined presence of aromatic heterocyclic nitrogens and thiolato sulfurs in the first coordination sphere of nickel in **1** provides stabilization to three oxidation states (+3, +2, and +1), it is quite likely that ligation of imidazole nitrogens and cysteinyl sulfurs creates a similar electronic environment around the biological nickel site, which in turn allows it to assume the same three oxidation states during turnover.

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supplementary Material Available: EPR spectrum of $[Ni^{III}(terpy)(2,6\text{-}(Me)_2C_6H_3S)_2]^+$ (Figure S1), EPR titration (stepwise oxidation) of **6** with $[Fe(CN)_6]^{3-}$ (Figure S2), crystal structure data for **1** including tables of atomic coordinates (Table S1), complete bond distances (Table S2) and angles (Table S3), anisotropic thermal parameters (Table S4), and H-atom coordinates (Table S5) (14 pages); table of observed and calculated structure factors (Table S6) (39 pages). Ordering information is given on any current masthead page.

---

(8) Cammack, R.; Fernandez, V. M.; Schneider, K. *Biochimie* **1986**, *68*, 85. (b) Fernandez, V. M.; Hatchikian, E. C.; Patil, D. S.; Cammack, R. *Biochim. Biophys. Acta* **1986**, *883*, 145.

(9) Baidya, N.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **1991**, *30*, 929.

(10) (a) Baidya, N.; Olmstead, M. M.; Whitehead, J. P.; Bagyinka, C.; Maroney, M. J.; Mascharak, P. K. *Inorg. Chem.* **1992**, *31*, 3612. (b) Maroney, M. J.; Colpas, G. J.; Bagyinka, C.; Baidya, N.; Mascharak, P. K. *J. Am. Chem. Soc.* **1991**, *113*, 3962. (c) Colpas, G. J.; Maroney, M. J.; Bagyinka, C.; Kumar, M.; Willis, W. S.; Suib, S. L.; Baidya, N.; Mascharak, P. K. *Inorg. Chem.* **1991**, *30*, 920.

(11) Alyea, E. C.; Ferguson, G.; Restivo, R. J. *Inorg. Chem.* **1975**, *14*, 2491.

(12) X-ray analysis: red-brown plates from acetonitrile, $NiC_{35}H_{32}N_4S_2$ (**1**), monoclinic space group $P2_1/c$, a = 23.012 (7) Å, b = 17.814 (5) Å, c = 15.698 (4) Å, β = 108.52 (2)°, V = 6099 (5) Å^3, Z = 8, d_{calcd} = 1.375 g/cm^3, R = 6.46%, R_w = 5.40%. The structure was solved by direct methods (SHELXTL PLUS, version 4.2).

(13) Mascharak, P. K. *Inorg. Chem.* **1986**, *25*, 245.

(14) Salerno, J. In *The Bioinorganic Chemistry of Nickel*; Lancaster, J. R., Jr., Ed.; VCH Publishers: Deerfield Beach, FL, 1988; Chapter 3, p 53.

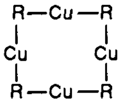
Synthesis of $[Me_2SCu(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)]$ and $[(Me_2S)_2Cu(\mu\text{-}C_6H_2\text{-}2,4,6\text{-}Ph_3)Cu(C_6H_2\text{-}2,4,6\text{-}Ph_3)]$: Mononuclear and Dinuclear Organocopper(I) Species of Formula $[CuR{\cdot}Solvate]_{1\text{ or }2}$

Xiaoming He, Marilyn M. Olmstead, and Philip P. Power*

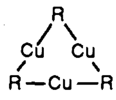
Department of Chemistry
University of California
Davis, California 95616

Received July 24, 1992

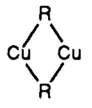
The solid- and solution-phase structures of organocopper compounds are a topic of considerable current interest.[1,2] Part of the reason for this is the extreme importance of these compounds, in particular their ionic derivatives (organocuprates), for organic synthesis.[3] In addition, their structures are inherently interesting not least because of their isovalent relationship to organolithium compounds.[4] Owing to their similar sizes, it is often possible to interchange Li for Cu in related aggregates while preserving the overall integrity of the molecules themselves. An illustration of this phenomenon is provided by the series of compounds $Cu_4Ph_4(SMe_2)_2$, $Li_2Cu_2Ph_4(SMe_2)_3$, and $Li_4Ph_4(SMe_2)_4$, which contain different Li:Cu ratios but remain tetrametallic species.[5] These complexes are not isostructural, however, owing to the preference of a σ-bonded, two-coordinate Cu^+ ion for linear or near linear coordination. This restriction, in contrast to the coordinative flexibility of Li^+, exerts a profound influence on the structure of organocopper compounds.[4] One consequence is that organocopper structures having simple monodentate groups and lower aggregation numbers than four are practically unknown, whereas they are quite common in the case of lithium compounds. This may be understood in part by assuming that the preference for linear coordination at Cu imposes increasingly acute angles at the organo group as illustrated schematically by



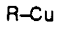
I



II



III



IV

Structures related to type II, in which the angle at R is ideally 60°, have not been reported for a purely organometallic species,[6] and only one representative of the species IV featuring a one-coordinate unsolvated copper has been published.[7] No compounds corresponding to the formula $(CuR)_2$, where R is a monodentate ligand, have yet appeared.[8] In this paper, the first examples of

---

(1) van Koten, G. *J. Organomet. Chem.* **1990**, *400*, 283.

(2) Power, P. P. *Prog. Inorg. Chem.* **1991**, *39*, 75.

(3) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley: New York, 1980. van Koten, G.; Noltes, J. G. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. Pergamon: Oxford, 1984.

(4) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

(5) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1990**, *112*, 8008. A further example of this type of relationship is seen with use of the chelating ligand $C_6H_4\text{-}2\text{-}CH_2NMe_2$.[1]

(6) Some related species that have been reported are the thiolate $[Cu\{SC_6H_4\text{-}2\text{-}CHMeNMe_2\}]_3$ (Knotter, D. M.; van Koten, G.; van Maanen, H. L.; Grove, D. M.; Spek, A. L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 341), the species $[Cu_3(\mu\text{-}C_6H_2Me_3)(\mu\text{-}O_2CPh)_2]$ (Aalten, H. L.; van Koten, G.; Goubitz, K.; Stam, C. H. *Organometallics* **1989**, *8*, 2293), and the amide $[Cu\{N(SiMePh_2)_2\}]_3$ (Chen, H.; Olmstead, M. M.; Shoner, S. C.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1992**, 451). For further examples, see ref 1.

(7) Lingnau, R.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 436.

(8) Dimeric organocopper species are known in the case of chelating ligands such as $CH(SiMe_3)(2\text{-pyridine})$. These compounds, however, contain no multicenter bonding. The dimeric formula is a consequence of the chelating effect of the ligand, which allows an almost linear geometry at the coppers and imposes a short Cu⋯Cu interaction, 2.412 (1) Å: Papasergio, R. I.; Raston, C. L.; White, A. L. *J. Chem. Soc., Chem. Commun.* **1983**, 1419.

0002-7863/92/1514-9668$03.00/0

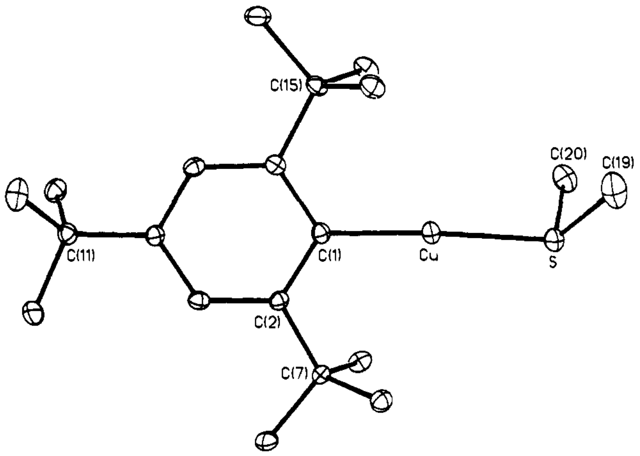


Figure 1. Computer-generated plot of **1**. Selected bond distances (Å) and angles (deg) are Cu–S = 2.185 (1), Cu–C(1) = 1.916 (3), S–C(19) = 1.805 (4), S–C(20) = 1.804 (3), S–Cu–C(1) = 175.7 (1), Cu–S–C(19) = 108.6 (1), Cu–S–C(20) = 105.5 (1), C(19)–S–C(20) = 100.5 (2).

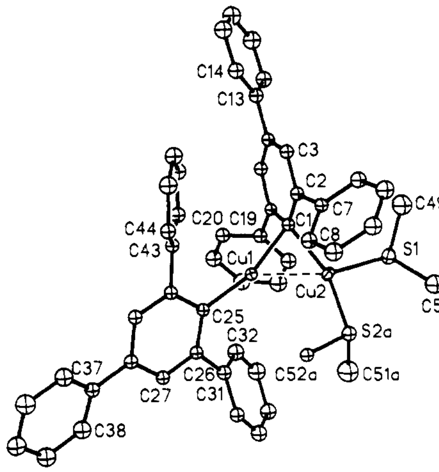


Figure 2. Computer-generated drawing of **2**. Selected bond distances (Å) and angles (deg) are Cu(1)···Cu(2) = 2.443 (1), Cu(1)–C(1) = 2.017 (5), Cu(2)–C(1) = 2.027 (6), Cu(1)–C(25) = 1.935 (5), Cu(2)–S(1) = 2.340 (2), Cu(2)–S(2) = 2.273 (2), 2.329 (8), C(1)–Cu(1)–C(25) = 163.0 (2), Cu(2)–Cu(1)–C(25) = 142.7 (2), Cu(1)–C(1)–Cu(2) = 74.3 (2), C(1)–Cu(1)–Cu(2) = 53.0 (2), C(1)–Cu(2)–Cu(1) = 52.6 (2). For clarity, the site of major occupancy (80%) of the disordered SMe_2 ligand is shown.

organocopper(I) solvates corresponding to the formulas III and IV are now reported.

The title compounds $[Me_2SCu(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)]$, **1**, and $[(Me_2S)_2Cu(\mu\text{-}C_6H_2\text{-}2,4,6\text{-}Ph_3)Cu(C_6H_2\text{-}2,4,6\text{-}Ph_3)]$, **2**, were synthesized by treatment of CuBr with the appropriate lithium aryl.[9] The structures of **1** and **2**[10] were obtained by X-ray crystallography and are illustrated in Figures 1 and 2. The structure of **1** consists of well-separated monomers of formula $[Me_2SCuS(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)]$, and thus it represents the simplest possible structure for a solvated organocopper species. The coordination at Cu is almost linear (S–Cu–C(1) = 175.7 (1)°) with Cu–S and Cu–C(1) distances of 2.185 (1) and 1.916 (1) Å. The Cu–C distance is comparable to those observed in other organocopper species although the Cu–S distance is substantially shorter (by ca. 0.2 Å) than those observed in other Cu–SMe_2 complexes.[5] The lowest degree of aggregation in **1** is presumably due to the large size of its organic substituent. If the size of this group is reduced slightly, the dimeric structure in **2** is obtained. The structure of the dimer **2** involves two copper atoms symmetrically bridged in an η^1-fashion by a Triph(2,4,6-$Ph_3C_6H_2$) group and with a short copper–copper contact of 2.443 (1) Å.[11] One of the coppers is also bound to a terminal Triph group and has a C–Cu–C angle of 163.0 (2)°. The other is solvated by two SMe_2 molecules. This type of structure has not been previously described[12] for organocopper compounds and may be viewed in several ways. Its formula corresponds to half of the commonly found tetrameric structures of Cu_4R_4. It bears a strong resemblance to half of $Cu_4Ph_4(SMe_2)_2$,[5] which has Cu···Cu distances of 2.445 (2) and 2.475 (1) Å and an extra SMe_2 molecule coordinated in the site made vacant by the cleavage of the tetramer. Another view of the molecule is that it may be regarded as a contact ion pair between the cuprate anion $[Cu(Triph)_2]^-$ and the cation $[Cu(SMe_2)_2]^+$. This view is not strongly supported by the structural parameters, however. This is because the bridging (C(1)) Triph ligand is symmetrically bound to the two coppers and the C(1)–Cu(1)–C(25) and Cu(2)–Cu(1)–C(25) angles are both quite wide. Interestingly, the Cu(1)–C(25) bond is tipped only 7° out of the C(25)–C(30) plane, whereas Cu(1)–C(1) and Cu(2)–C(1) are tipped 47.5° and 24.3° out of the C(1)–C(6) ring plane, respectively. An obvious explanation for the overall structure is that, if it is assumed that the minimum $Cu^+\cdots Cu^+$ distance is ~2.4 Å, then the angles at the bridging carbon in a species such as III must be about the same as in **2**. It follows that a symmetric structure of type III would impose a CCuC angle at copper of about 106°. Apparently, this angle is incompatible with the σ-bonding requirements of the coppers, which prefer a linear coordination.

The asymmetric structure of **2** is dissociated[12] in solution (presumably to Me_2S-solvated CuTriph monomers similar to **1**) as ^{13}C and ^{13}C–^1H heteronuclear correlated 2D NMR spectra of the crystalline species in $CDCl_3/Me_2S$ solution indicate one set of peaks for the Triph groups in the aromatic region. The central ring is distinguished by peaks at 154.9 (ipso), 148.3 (ortho), and 139.7 (para). A further peak at 141.35 is probably due to the ipso carbons of the *o*-phenyl rings. The TriphH present in the

---

(9) Under anerobic and anhydrous conditions, *n*-BuLi (3.8 mL of a 1.6 M hexane solution) was added to 2,4,6-*t*-$Bu_3C_6H_2Br$[9a] (Mes*Br 1.95 g, 60 mmol) in Et_2O (30 mL) with cooling in an ice bath. After stirring for 3 h, the solvents were removed under reduced pressure. The residue was dissolved in Et_2O (30 mL) and added dropwise to a suspension of CuBr (0.43 g, 3 mmol) in Et_2O (20 mL) with cooling in a dry ice–acetone bath. After 30 min of stirring, Me_2S (15 mL) was added. The mixture was then allowed to come to room temperature and stirred for 2 h. Filtration and volume reduction to ca. 10 mL followed by storage in a −20 °C freezer for 2 days afforded the product **1** as colorless blocks: yield 0.71 g (32%); mp 124–125 °C dec; ^1H NMR ($CDCl_3$) δ = 7.4 (s, 2 H, m-H), 2.03 (s, 6 H, Me_2S), 1.71 (s, 18 H, *o*-*t*-Bu), 1.28 (s, 9 H, *p*-*t*-Bu); ^{13}C and ^1H NMR (C_4D_6O) δ = 168.5 (s, ipso C), 151.0 (s, *m*-C), 121.3 (s, *o*-C), 120.4 (s, *p*-C), 39.1 (s, *o*-*C*$(CH_3)_3$), 34.0 (s, *C*-$(CH_3)_3$), 36.1 (s, *o*-C$(\mathit{CH}_3)_3$), 32.1 (s, *p*-C$(\mathit{CH}_3)_3$), 19.0 (s, Me_2S). $(Et_2O)_2LiC_6H_2$-2,4,6-Ph_3,[9b] ($(Et_2O)_2$LiTriph), 2.3 g, 5 mmol in 10 mL of SMe_2, was added dropwise to rapidly stirred CuBr (0.72 g, 5 mmol) in DMS (10 mL) with cooling in a dry ice acetone bath. After 0.5 h the solution was allosed to warm to ca. −10 °C and stirred for 1 h. Hexane (17 mL) was added, and the resultant mixture was filtered rapidly to afford a yellow solution. This was concentrated to ca. 15 mL under reduced pressure. Storage in a −20 °C freezer for 2 days afforded the product as colorless crystals. The compound, **2**, cocrystallizes with one molecule of C_6H_3-2,4,6-Ph_3 and Me_2S:[9c] yield 1.5 g (24%); mp = 95–96 °C. (a) Pearson, D. E.; Frazer, M. G.; Frazer, V. S.; Washburn, L. C. *Synthesis* **1976**, 621. (b) Olmstead, M. M.; Power, P. P. *J. Organomet. Chem.* **1991**, *408*, 1. (c) Repeated preparations of the compound have always shown that some free 2,4,6-$Ph_3C_6H_2$ is present in the reaction mixture in spite of stringent precautions to exclude moisture and air. It may be that the TriphH may be generated by an unknown mechanism during the reaction process.

(10) Crystal data for **1** and **2** at 130 K with Mo Kα (λ = 0.710 69 Å) radiation: **1**, $C_{20}H_{35}CuS$, a = 12.359 (3) Å, b = 12.887 (5) Å, c = 25.535 (9) Å, orthorhombic, space group *Pbca*, Z = 8, R = 0.039 for 3481 ($I > 2\sigma(I)$) reflections; **2**·2,4,6-$Ph_3C_6H_2$·SMe_2, $C_{78}H_{70}Cu_2S_3$, a = 9.944 (3) Å, b = 14.604 (5) Å, c = 22.936 (7) Å, α = 97.02 (2)°, β = 90.88 (2)°, γ = 109.50 (2)°, triclinic, space group $P\bar{1}$, Z = 2, R = 0.068 for 8170 ($I > 3\sigma(I)$) reflections. In **2** the SMe_2 of solvation was disordered between two sites, but it was refined satisfactorily with occupancies of 80% at site a and 20% at site b.

(11) Very short organocopper Cu···Cu interactions (2.418 and 2.38 Å) have been recorded in copper alkyl and aryl tetramers: Jarvis, J. A.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1977**, 999. Guss, J. M.; Mason, R.; Sotofte, I.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1972**, 446. See also refs 8, 11, and 14 for further discussions of short Cu···Cu interactions.

(12) Both **1** and **2** are monomeric in Me_2S solution (ca. 0.2 M by the Signer method).

crystals displays peaks at 142.2 and 140.9 ppm, which are close to those of an authentic sample. The remaining carbons of the Triph groups display a complex pattern of peaks between 128.7 and 124.0 ppm. There is no overall change in the ^{13}C NMR resonance pattern at temperatures as low as −80 °C that might indicate association in solution.

In conclusion, it is notable that the Cu⋯Cu contact in **2** lends support to the idea that interactions between d^{10} centers in organocopper structures may be of considerable significance in determining their structures. Such interactions have already been implicated in the structures of various Cu(I) compounds[13] and the Cu_4R_4 tetramers.[11] The presence of these interactions has been supported by calculations.[14] Finally, it is notable that the isolation of **1** and **2** underline the usefulness of SMe_2 in stabilizing organocopper species.[15]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Supplementary Material Available: Tables of data collection parameters, atomic coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters for **1** and **2** (17 pages); listing of observed and calculated structure factors for **1** and **2** (69 pages). Ordering information is given on any current masthead page.

---

(13) Harding, C. H.; McKee, V.; Nelson, J. *J. Am. Chem. Soc.* **1991**, *113*, 9684.

(14) Mehrotra, P. K.; Hoffman, R. *Inorg. Chem.* **1978**, *17*, 2187. Dedieu, A.; Hoffman, R. *J. Am. Chem. Soc.* **1978**, *100*, 2074. Merz, K. M.; Hoffman, R. *Inorg. Chem.* **1988**, *27*, 2120.

(15) Bertz, S. H.; Dabbagh, G. *Tetrahedron* **1989**, *45*, 425.

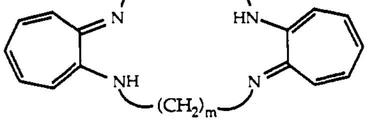
Tuning the Stereochemistry of Pentacoordinate Co(III) Halide Complexes: A Rare Case of Trigonal Bipyramidal Stereochemistry for Cobalt(III)

B. Scott Jaynes, Tong Ren, Shuncheng Liu, and
Stephen J. Lippard*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received July 13, 1992

Previously we employed the macrocyclic tropocoronand ligand, $H_2(TC\text{-}n,m)$, to prepare $[M(TC\text{-}n,m)]$ complexes of Cu(II) and Ni(II) with controlled geometries ranging from square planar to tetrahedral.[1] We now report a series of unusual pentacoordinate



Tropocoronand, $H_2(TC\text{-}n,m)$

Co(III) tropocoronand chloride complexes which vary in geometry from square pyramidal to trigonal bipyramidal, depending on the size of the macrocycle. The [CoCl(TC-4,4)] complex, **3**, is a rare example of a structurally characterized trigonal bipyramidal Co(III) complex, and solid-state magnetics measurements indicate that it is paramagnetic at room temperature. In contrast to the variable geometry of the Co(III) chloride complexes, the analogous Co(III) alkyls are diamagnetic and have geometries that are relatively uninfluenced by the ligand constraints.

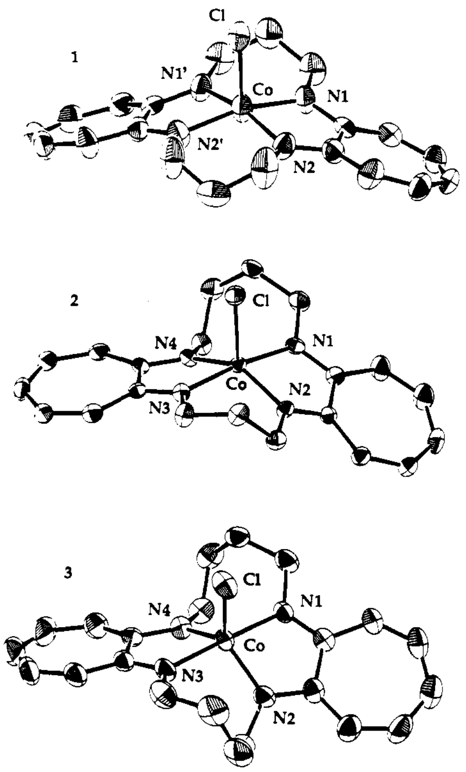


Figure 1. ORTEP drawings of [CoCl(TC-3,3)] (**1**), [CoCl(TC-3,4)] (**2**), and [CoCl(TC-4,4)] (**3**) showing the 50% probability thermal ellipsoids for all non-hydrogen atoms. Selected interatomic distances (Å) and angles (deg) are as follows. **1**: Co–Cl, 2.384 (5); Co–N1, 1.892 (8); Co–N2, 1.889 (8); N1–Co–Cl, 101.9 (3); N2–Co–Cl, 94.8 (3); N1–Co–N1′, 94.6 (5); N1–Co–N2, 82.1 (3); N1–Co–N2′, 163.3 (4); N2–Co–N2′, 96.2 (5). **2**: Co–Cl, 2.343 (1); Co–N1, 1.921 (4); Co–N2, 1.862 (3); Co–N3, 1.919 (4); Co–N4, 1.881 (4); N1–Co–Cl, 98.5 (1); N2–Co–Cl, 108.3 (1); N3–Co–Cl, 90.0 (1); N4–Co–Cl, 109.3 (1); N1–Co–N2, 81.9 (2); N1–Co–N3, 171.5 (2); N1–Co–N4, 96.7 (2); N2–Co–N4, 142.1 (2). **3**: Co–Cl, 2.288 (1); Co–N1, 1.906 (4); Co–N2, 1.870 (4); Co–N3, 1.914 (4); Co–N4, 1.894 (4); N1–Co–Cl, 91.7 (1); N2–Co–Cl, 121.7 (1); N3–Co–Cl, 90.2 (1); N4–Co–Cl, 117.9 (1); N1–Co–N2, 82.0 (2); N1–Co–N3, 178.0 (2); N1–Co–N4, 97.9 (2); N2–Co–N4, 120.4 (2).

When O_2 was introduced to a stirred mixture of $Li_2(TC\text{-}3,4)$ or $Li_2(TC\text{-}4,4)$ and $CoCl_2$ in THF, the resulting dark green solution[2] turned red-brown. Removal of solvent and extraction into CH_2Cl_2, followed by slow addition of diethyl ether, gave brown crystalline [CoCl(TC-3,4)] or [CoCl(TC-4,4)] in approximately 50% yield. [CoCl(TC-3,3)] could not be prepared by using this procedure, but instead was isolated in low yield by slow diffusion of $CHCl_3$ into a CH_2Cl_2/Et_2O solution of [Co(TC-3,3)].[3]

Single-crystal X-ray structural analysis[4] of the three products revealed substantially different geometries, as summarized in Figure 1. The structure of [CoCl(TC-3,3)] (**1**) is square py-

---

(1) Villacorta, G. M.; Lippard, S. J. *Pure Appl. Chem.* **1986**, *58*, 1477.

(2) The Co(II) compounds will be reported elsewhere.

(3) Analytical and spectroscopic data for compounds **1–3** and the Co(III) alkyl complexes are reported as supplementary material.

(4) Crystal data for **1** at 200 K: size ca. 0.08 × 0.15 × 0.30 mm, orthorhombic $Cmc2_1$, $a = 16.275$ (6) Å, $b = 11.874$ (2) Å, $c = 9.069$ (4) Å, $V = 1752$ (1) Å^3, $Z = 4$, $\rho_{calcd} = 1.56$ g cm^{-3}. For 838 unique, observed reflections with $F^2 > 1\sigma(F^2)$ and 130 variable parameters, the final discrepancy indices were $R = 0.057$ and $R_w = 0.058$. Crystal data for **2** at 200 K: size ca. 0.13 × 0.20 × 0.25 mm, monoclinic, space group $P2_1$, $a = 10.742$ (2) Å, $b = 8.270$ (1) Å, $c = 11.106$ (2) Å, $\beta = 104.30$ (1), $V = 956.0$ (3) Å^3, $Z = 2$, $\rho_{calcd} = 1.48$ g cm^{-3}. For 2233 unique, observed reflections with $F^2 > 3\sigma(F^2)$ and 243 variable parameters, the final discrepancy indices were $R = 0.035$ and $R_w = 0.038$. Crystal data for **3** at 296 K: size ca. 0.20 × 0.40 × 0.40 mm, orthorhombic, space group $Pbca$, $a = 9.6713$ (8) Å, $b = 25.948$ (3) Å, $c = 15.901$ (1) Å, $V = 3990$ (1) Å^3, $Z = 8$, $\rho_{calcd} = 1.47$ g cm^{-3}. For 2087 unique, observed reflections with $F^2 > 3\sigma(F^2)$ and 253 variable parameters, the final discrepancy indices were $R = 0.044$ and $R_w = 0.054$.

0002-7863/92/1514-9670$03.00/0