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Synthesis, Physical Properties, and Structural Characterization of (μ-Carbonato)-dicopper(II) Complexes. 3.[1,2] Isolation of a Racemic Crystal Form of (μ-Carbonato)-dichlorobis(*N*,*N*,*N'*,*N'*-tetramethyl-1,3-propanediamine)dicopper(II) from a Substitution Reaction of Bis(carbonato)tetrakis[chloro(*N*,*N*-diethylnicotinamide)copper(II)]

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The synthesis of the complex $[(DENC)CuCl]_4(CO_3)_2$ (DENC = *N*,*N*-diethylnicotinamide) from the aprotic oxidation of $[(DENC)CuCl]_4$ by dioxygen in the presence of carbon dioxide is reported. Its cryoscopic, magnetic, and spectral properties are consistent with a tetranuclear structure containing 5-coordinate copper(II) centers. Although $[(DENC)CuCl]_4(CO_3)_2$ is inactive as an initiator for the oxidative coupling of phenols by dioxygen, it can be used as a precursor for active initiators through ligand substitution. The result of one such substitution reaction, that with *N*,*N*,*N'*,*N'*-tetramethyl-1,3-propanediamine (tmpd) in 25% v/v methylene chloride/benzene, results in the formation of crystalline samples of dark green, racemic and light green, enantiomeric forms of the complex (*sym*-μ-carbonato)-*trans*-dichlorobis(tmpd)dicopper(II), (tmpd)CuCl(CO_3)ClCu(tmpd), which have similar spectral and magnetic properties. The racemic form crystallizes in the monoclinic space group $P2_1/n$, with $a = 16.9224$ (38) Å, $b = 7.9417$ (15) Å, $c = 17.3433$ (37) Å, $\beta = 99.73$ (2)°, and $Z = 4$. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer, and the structure was solved via Patterson, Fourier, and least-squares refinement techniques. The discrepancy indices are $R_F = 4.49\%$ and $R_{wF} = 4.03\%$ on the basis of reflection data for which $|F_o| > 3.0\sigma(|F_o|)$ (Mo Kα radiation). The slight differences in geometry between molecules in the monoclinic, racemic form reported here and the orthorhombic, enantiomeric form reported previously[1] are ascribed to differences in packing forces.

Introduction

We have previously reported the results of crystallographic studies on $(tmpd)_2Cu_2Cl_2(\mu\text{-}CO_3)$[1] and $(teed)_2Cu_2Cl_2(\mu\text{-}CO_3)$[2] (tmpd = *N*,*N*,*N'*,*N'*-tetramethyl-1,3-propanediamine, teed = *N*,*N*,*N'*,*N'*-tetraethylethylenediamine) from the reaction of CuCl, the diamine ligand, CO_2, and O_2.

We are currently investigating the chemistry of $[(DENC)CuX]_4O_2$ and $[(DENC)CuX]_4(CO_3)_2$ (DENC = *N*,*N*-diethylnicotinamide, X = Cl, Br).[4] The synthesis and properties of the chloride are reported here. The reaction of $[(DENC)CuCl]_4(CO_3)_2$ with tmpd has now provided a different crystalline form of $(tmpd)_2Cu_2Cl_2(\mu\text{-}CO_3)$, which is shown to be composed of an ordered racemic mixture of the two enantiomers (each of C_2 symmetry) of this complex. (The previously reported structural study[1] was on a crystal composed solely of one of the enantiomers.)

Experimental Section

Synthesis and Physical Measurements. Materials. DENC, tmpd, and 2,4,6-trichlorophenol (TCPH) (Aldrich) were distilled under reduced pressure before use. Methylene chloride and benzene were purified as previously described.[4] Copper(I) chloride was prepared by a literature method.[1]

Synthesis of the Tetranuclear (Carbonato)copper(II) Complex $[(DENC)CuCl]_4(CO_3)_2$. A solution of DENC (0.84 mL, 5 mmol) in 30 mL of anhydrous methylene chloride was flushed with dry CO_2 for 15 min. Copper(I) chloride (0.5 g, 5 mmol) was then added under CO_2. The mixture was stirred with a stream of CO_2 until all the solid had dissolved to give a yellow solution. At this point, both CO_2 and dry O_2 were passed through the solution, rapidly producing a greenish brown solution. After 5 min the gas streams were stopped and the methylene chloride was removed in a rotary evaporator, leaving a greenish brown solid. Anal.[5] Calcd for $C_{42}H_{56}N_8O_{10}Cl_4Cu_4$: C, 41.04; H, 4.56; N, 9.12; Cu, 20.68. Found: 39.43; H, 4.48; N, 8.93; Cu, 20.24. The product yield was quantitative. Cryoscopic measurements on the product were made in nitrobenzene, as described previously.[4] Molecular weight for $[(DENC)CuCl]_4(CO_3)_2$: calcd, 1228; found, 1128 ± 20.

Synthesis of Racemic Crystals of (μ-Carbonato)-dichlorobis(*N*,*N*,*N'*,*N'*-tetramethyl-1,3-propanediamine)dicopper(II), $(tmpd)_2Cu_2Cl_2CO_3$. A solution of $[(DENC)CuCl]_4(CO_3)_2$ was made by dissolving the solid (1.535 g, 1.25 mmol) in 10 mL of methylene chloride. A solution of tmpd (0.84 mL, 5 mmol) in 30 mL of dry benzene was then added. After 10 min the solution turned from greenish brown to apple green. Overnight two different types of crystals were formed: a dark green racemic major product and a light green enantiomeric minor product. The two types of crystals were separated by decantation and washed with anhydrous diethyl ether. Anal.[5] Calcd for light and dark green crystals of $C_{15}H_{36}N4O_3Cl_2Cu_2$: C, 34.7; H, 7.0; N, 10.8; Cu, 24.5. Found for light green crystals: C, 33.34; H, 7.47; N, 10.37; Cu, 24.87. Found for dark green crystals: C, 33.38; H, 7.57; N, 10.34; Cu, 24.67.

Stoichiometry of Reaction with TCPH. Separate solutions of racemic and enantiomeric crystals were titrated with TCPH in anhydrous methylene chloride as solvent and the product was identified by gel permeation chromatography and by spectrophotometry.[6]

Tests of Catalytic Activity. The catalytic activity of a racemic crystalline sample was tested in methylene chloride as previously described.[2]

Spectral Measurements. Electronic spectra were obtained with a Cary Model 14 recording spectrophotometer at 25 °C. Infrared spectra of the product were obtained with a Perkin-Elmer Model 567 spectrometer calibrated with polystyrene at 908 cm^{-1}.

Magnetic Measurements. The magnetic susceptibility of the powdered samples were measured at 25 °C with a Princeton Applied Research Model FM-1 vibrating-sample magnetometer calibrated with $HgCo(SCN)_4$.

Crystal Structure Determination. The crystal of racemic (μ-carbonato)-dichlorobis(*N*,*N*,*N'*,*N'*-tetramethyl-1,3-propanedi-

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(1) Part 1: Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W.; Watkins, K. O. *Inorg. Chem.* **1979**, *18*, 2296-2300.

(2) Part 2: Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W. *Inorg. Chem.* **1980**, *19*, 201-208.

(3) (a) SUNY at Buffalo. (b) Northeastern University.

(4) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; Hutchinson, J. P.; Rupich, M. W. *Inorg. Chem.*, preceding paper in this issue.

(5) Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

(6) Davies, G.; El-Shazly, M. F.; Rupich, M. W. *Inorg. Chem.* **1981**, *20*, 3757.

Table I. Crystal Parameters for the Two Forms of $(tmpd)_2Cu_2Cl_2(\mu\text{-}CO_3)$

	racemic form[a]	chiral form[b]
crystal system	monoclinic	orthorhombic
space group	$P2_1/n$	$P22_12_1$
a, Å	16.9224 (38)	8.0832 (15)
b, Å	7.9417 (15)	11.6855 (14)
c, Å	17.3433 (37)	11.9301 (17)
β, deg	99.73 (2)	[90.00, exactly]
V, Å^3	2297.3 (8)	1126.9 (3)
T, °C	22.4	24
Z (dinuclear molecules)	4	2
ρ(calcd), g/cm^3	1.500	1.528
mol wt	518.47	518.47

[a] This study. [b] See ref 1.

Table II. Details of Data Collection for Racemic $(tmpd)_2Cu_2Cl_2(\mu\text{-}CO_3)$

(A) Measurement of Intensity Data

diffractometer	Syntex $P2_1$
radiation	Mo $K\bar{\alpha}$ ($\bar{\lambda}$ = 0.710 730 Å)
monochromator	highly oriented (pyrolitic) graphite
scan type	coupled θ(crystal)-2θ(counter)
reflctns measd[a]	$h,k,\pm l$ for 2θ = 3.5-45.0°
scan rate	2.0°/min in 2θ
scan width	$[2\theta(K\alpha_1) - 1.0] \to [2\theta(K\alpha_2) + 1.0]°$
bkgd est	stationary crystal, stationary counter at the extremities of each 2θ scan; each for one-quarter the time taken for the 2θ scan
std reflctns	3 every 97 reflections; decay amounting to 17% (average) was observed over the course of data collection and was corrected for
reflctns collected	3272 total yielding 3028 independent upon averaging; $R(I)$ = 2.68% for 147 averaged pairs of reflctns
abs coeff	μ = 21.7 cm^{-1}

(B) Data for Empirical Absorption Correction (Full χ Scans)

hkl	2θ	I_{max}/I_{min}
$21\bar{3}$	9.45	1.47:1
$32\bar{5}$	16.49	1.47:1
$62\bar{5}$	20.13	1.42:1
$53\bar{7}$	24.53	1.43:1
$83\bar{8}$	29.52	1.41:1

[a] Data with 2θ = 35-45° were later discarded (see text).

amine)dicopper(II) selected approximated to a parallelepiped of dimensions 0.20 mm × 0.27 mm × 0.47 mm. It was mounted in a capillary along its extended direction and was set (with beeswax) into an aluminum pin on a eucentric goniometer. The crystal was accurately centered on a Syntex $P2_1$ automated four-circle diffractometer. Determination of approximate unit cell parameters, the orientation matrix, and crystal quality (the last via axial photographs and both θ-2θ and ω scans of reflections along the principal reciprocal cell axes) were carried out as described previously.[7] A unique data set for 2θ = 20-30° was collected at the maximum rate (29.3°/min in 2θ). Careful inspection of these data led to the identification of the space group and to the selection of four strong reflections, well separated in reciprocal space, which were used (along with their symmetry-related forms) to determine accurate cell parameters via a least-squares procedure. Details appear in Tables I and II.

Computations were initially performed in-house by using the Syntex XTL system[8] (NOVA 1200 computer with 24K, 16-bit work memory, disk unit of 1.2 million words; XTL conversational program package, as modified at SUNYAB). The computations were completed on the CDC 6600-Cyber 173 computer at the computer center of the State University of New York at Buffalo using programs described previously.[9] The analytical scattering factors for neutral atoms[10a] were corrected for both the real and imaginary components of anomalous dispersion.[10b] The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}$ and σ is the stochastic esd modified by an "ignorance" factor of p = 0.03.

Table III. Positional Parameters, with Esd's, for Racemic $(tmpd)_2Cu_2Cl_2(\mu\text{-}CO_3)$

atom	x	y	z
Cu(1)	−0.19463 (8)	0.09575 (16)	0.00862 (7)
Cu(2)	−0.06605 (8)	0.20710 (15)	0.22772 (7)
Cl(1)	−0.3014 (2)	0.2801 (4)	0.0201 (2)
Cl(2)	0.0562 (2)	0.3097 (4)	0.1981 (2)
C(1)	−0.1311 (7)	0.0072 (13)	0.1358 (6)
O(1)	−0.1249 (4)	0.1585 (8)	0.1145 (3)
O(2)	−0.1712 (6)	−0.0881 (9)	0.0861 (4)
O(3)	−0.0986 (5)	−0.0283 (8)	0.2042 (4)
N(1)	−0.2531 (5)	−0.0638 (9)	−0.0733 (4)
N(2)	−0.1304 (5)	0.2282 (10)	−0.0640 (4)
C(11)	−0.2792 (6)	0.0220 (13)	−0.1488 (5)
C(12)	−0.2152 (7)	0.1100 (14)	−0.1854 (5)
C(13)	−0.1814 (7)	0.2634 (14)	−0.1415 (5)
Me(11)	−0.3223 (6)	−0.1255 (13)	−0.0436 (6)
Me(12)	−0.2007 (6)	−0.2083 (12)	−0.0828 (6)
Me(21)	−0.1093 (7)	0.3949 (13)	−0.0273 (6)
Me(22)	−0.0552 (6)	0.1501 (13)	−0.0754 (6)
N(3)	−0.0311 (5)	0.1554 (10)	0.3429 (4)
N(4)	−0.1239 (5)	0.4334 (9)	0.2404 (4)
C(21)	−0.0017 (6)	0.3077 (13)	0.3879 (6)
C(22)	−0.0615 (6)	0.4501 (13)	0.3824 (6)
C(23)	−0.0805 (6)	0.5352 (12)	0.3035 (6)
Me(31)	−0.0942 (6)	0.0683 (14)	0.3770 (5)
Me(32)	0.0369 (7)	0.0393 (13)	0.3488 (5)
Me(41)	−0.2094 (5)	0.4029 (13)	0.2527 (6)
Me(42)	−0.1297 (7)	0.5328 (12)	0.1677 (6)
H(11A)[a]	−0.3159	0.1080	−0.1407
H(11B)	−0.3056	−0.0586	−0.1847
H(12A)	−0.2338	0.1345	−0.2390
H(12B)	−0.1720	0.0321	−0.1811
H(13A)	−0.2264	0.3275	−0.1326
H(13B)	−0.1518	0.3256	−0.1737
HMe(11A)	−0.3513	−0.2012	−0.0802
HMe(11B)	−0.3065	−0.1815	−0.0050
HMe(11C)	−0.3553	−0.0319	−0.0364
HMe(12A)	−0.2276	0.2842	−0.1207
HMe(12B)	−0.1541	0.1663	−0.0999
HMe(12C)	−0.1859	0.2653	−0.0344
HMe(21A)	−0.0796	0.4592	−0.0588
HMe(21B)	−0.1577	0.4520	−0.0232
HMe(21C)	−0.0784	0.3806	−0.0233
HMe(22A)	−0.0280	0.2163	−0.1083
HMe(22B)	−0.0218	0.1360	−0.0260
HMe(22C)	−0.0674	0.0429	−0.0988
H(21A)	0.0425	0.3494	0.3665
H(21B)	0.0154	0.2792	0.4413
H(22A)	−0.0427	0.5326	0.4208
H(22B)	−0.1100	0.4025	0.3932
H(23A)	−0.0307	0.5645	0.2889
H(23B)	−0.1105	0.6344	0.3086
HMe(31A)	−0.0761	0.0429	0.4306
HMe(31B)	−0.1394	0.1408	0.3724
HMe(31C)	−0.1089	−0.0330	0.3490
HMe(32A)	0.0561	0.0102	0.4018
HMe(32B)	0.0210	−0.0598	0.3196
HMe(32C)	0.0783	0.0940	0.3275
HMe(41A)	−0.2351	0.5076	0.2579
HMe(41B)	−0.2385	0.3423	0.2098
HMe(41C)	−0.2077	0.3392	0.2993
HMe(42A)	−0.1564	0.6367	0.1723
HMe(42B)	−0.0771	0.5543	0.1577
HMe(42C)	−0.1587	0.4694	0.1258

[a] Each hydrogen atom was assigned an isotropic thermal parameter of B = 6.0 Å^2.

The structure was solved via a three-dimensional Patterson synthesis which readily yielded the positions of the copper atoms. Two difference-Fourier syntheses revealed unambiguously the positions of

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(7) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265-271.

(8) "Syntex XTL Operations Manual", 2nd ed.; Syntex Analytical Instruments (now Nicolet XRD): Cupertino, CA, 1976.

(9) Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1978**, *17*, 3528-3535.

(10) "International Tables for X-Ray Crystallography", Kynoch Press: Birmingham, England, 1974; Vol. 4: (a) pp 99-101; (b) pp 149-150.

Table IV. Anisotropic Thermal Parameters[a] for Racemic $(\mathrm{tmpd})_2\mathrm{Cu}_2\mathrm{Cl}_2(\mu\text{-}\mathrm{CO}_3)$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	5.55 (8)	3.00 (7)	2.29 (7)	0.31 (7)	0.31 (5)	0.21 (6)
Cu(2)	5.18 (8)	3.03 (7)	2.52 (7)	−0.13 (7)	0.41 (5)	0.01 (6)
Cl(1)	6.4 (2)	6.3 (2)	5.4 (2)	2.0 (2)	0.1 (1)	−1.9 (2)
Cl(2)	6.2 (2)	7.7 (2)	5.3 (2)	−1.1 (2)	2.4 (1)	−1.2 (2)
C(1)	9.9 (10)	2.4 (6)	2.7 (6)	0.1 (7)	0.1 (6)	1.1 (6)
O(1)	6.7 (4)	2.2 (4)	2.2 (3)	0.1 (3)	−0.3 (3)	0.4 (3)
O(2)	18.8 (8)	3.6 (4)	3.0 (4)	−2.9 (5)	−3.3 (5)	1.1 (4)
O(3)	16.0 (7)	2.6 (4)	2.1 (4)	−1.4 (4)	−2.1 (4)	0.6 (3)
N(1)	5.2 (5)	3.8 (5)	1.4 (4)	1.2 (4)	−0.5 (4)	−0.2 (4)
N(2)	5.7 (6)	4.3 (5)	3.2 (5)	0.0 (5)	1.1 (4)	0.9 (4)
C(11)	6.7 (8)	6.5 (8)	3.1 (6)	0.2 (6)	−0.5 (5)	−0.9 (6)
C(12)	9.1 (9)	8.3 (9)	1.8 (6)	−0.6 (8)	0.1 (6)	1.2 (6)
C(13)	9.2 (9)	6.8 (9)	3.5 (7)	0.5 (7)	1.5 (6)	2.3 (6)
Me(11)	5.5 (7)	6.1 (8)	5.2 (7)	−1.4 (6)	1.8 (5)	−0.4 (6)
Me(12)	9.2 (9)	4.2 (7)	4.8 (7)	1.5 (7)	0.6 (6)	−1.6 (6)
Me(21)	9.6 (9)	6.0 (7)	6.0 (8)	−1.1 (8)	0.6 (6)	3.3 (7)
Me(22)	5.2 (7)	8.1 (9)	7.1 (8)	−0.2 (7)	1.8 (6)	2.0 (7)
N(3)	5.7 (6)	3.9 (6)	3.5 (5)	0.6 (4)	0.0 (4)	−0.6 (4)
N(4)	6.7 (6)	2.0 (5)	3.4 (5)	0.2 (4)	−0.4 (4)	−0.7 (4)
C(21)	6.5 (8)	5.8 (7)	3.7 (6)	−1.3 (7)	−0.2 (7)	−0.6 (6)
C(22)	7.1 (8)	5.9 (8)	4.3 (6)	−1.4 (6)	1.1 (6)	−2.2 (6)
C(23)	7.7 (8)	3.3 (7)	6.0 (8)	−1.6 (6)	1.5 (6)	−1.3 (6)
Me(31)	10.2 (9)	7.8 (8)	2.1 (6)	−4.2 (8)	1.0 (6)	0.5 (6)
Me(32)	11.0 (10)	6.0 (8)	3.9 (7)	−0.6 (7)	−2.1 (7)	0.1 (6)
Me(41)	3.9 (7)	5.7 (7)	9.3 (8)	0.5 (6)	1.2 (6)	−0.2 (7)
Me(42)	11.3 (10)	2.6 (7)	6.3 (8)	0.2 (7)	−0.4 (7)	0.3 (6)

[a] These anisotropic thermal parameters are analogous to the usual form of the isotropic parameter and have the units of Å^2. They enter the expression for the structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table V. Characteristic IR bands for DENC, $[(\mathrm{DENC})\mathrm{CuCl}]_4(\mathrm{CO}_3)_2$, and $(\mathrm{tmpd})_2\mathrm{Cu}_2\mathrm{Cl}_2\mathrm{CO}_3$[a]

	$\nu_{\mathrm{C=O}}$	ν_{py}					ν_3[b]	ν_2[b]	ν_4[b]	$\nu_{\mathrm{Cu-O}}$
DENC	1640	1595	1470, 1423	1040	955	623				
$[(\mathrm{DENC})\mathrm{CuCl}]_4(\mathrm{CO}_3)_2$	1640	1595	1450	1070	955	650				580
$(\mathrm{tmpd})_2\mathrm{Cu}_2\mathrm{Cl}_2\mathrm{CO}_3$							1560, 1380	895	730	510

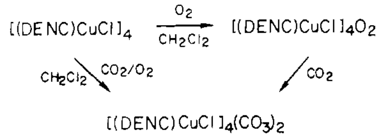
[a] IR spectra for dark green racemic and light green enantiomeric crystals are the same. [b] For carbonate assignments see ref 2.

all remaining nonhydrogen atoms. Full-matrix least-squares refinement led to convergence with $R_F = 11.4\%$ for all data.[11] The magnitude of this value led to our investigating the data for systematic errors. As expected from preliminary work, we found large percentage errors between $|F_o|$ and $|F_c|$ values for the high-angle data, all of which were very weak with few observations above background level. We, therefore, deleted all data with $2\theta > 35°$. Refinement to convergence led to $R_F = 5.91\%$, $R_{wF} = 4.11\%$, and GOF = 2.32 for all data and $R_F = 4.49\%$ and $R_{wF} = 4.03\%$ for those data with $|F_o| > 3.0\sigma(|F_o|)$; the ratio NO:NV was 6.2:1.

Final positional and thermal parameters are collected in Tables III and IV.

Results and Discussion

Copper(I) chloride reacts with DENC in dioxygen-free methylene chloride to give a yellow complex, $[(\mathrm{DENC})\mathrm{CuCl}]_4$.[4] The reaction of such solutions with dioxygen has the stoichiometry, determined by oxygen uptake experiments, $\Delta[\mathrm{Cu(I)}]/\Delta[\mathrm{O}_2] = 4.0$.[4] The oxocopper(II) product $[(\mathrm{DENC})\mathrm{CuCl}]_4\mathrm{O}_2$ reacts with CO_2 to give green-brown $[(\mathrm{DENC})\mathrm{CuCl}]_4(\mathrm{CO}_3)_2$. The same product also results from the reaction of $[(\mathrm{DENC})\mathrm{CuCl}]_4$ with $\mathrm{CO}_2/\mathrm{O}_2$ (eq 1).



(1)

Spectral and Magnetic Properties of $[(\mathrm{DENC})\mathrm{CuCl}]_4(\mathrm{CO}_3)_2$.

The infrared spectra of DENC and $[(\mathrm{DENC})\mathrm{CuCl}]_4(\mathrm{CO}_3)_2$ (Table V) in KBr disks indicate that the $\nu_{\mathrm{C=O}} = 1640\ \mathrm{cm}^{-1}$ absorption of DENC is not affected by coordination. However, the bands assignable to the pyridine ring of DENC[4] are shifted to higher wave number in $[(\mathrm{DENC})\mathrm{CuCl}]_4(\mathrm{CO}_3)_2$, indicating that pyridine nitrogen is the atom coordinated to the copper

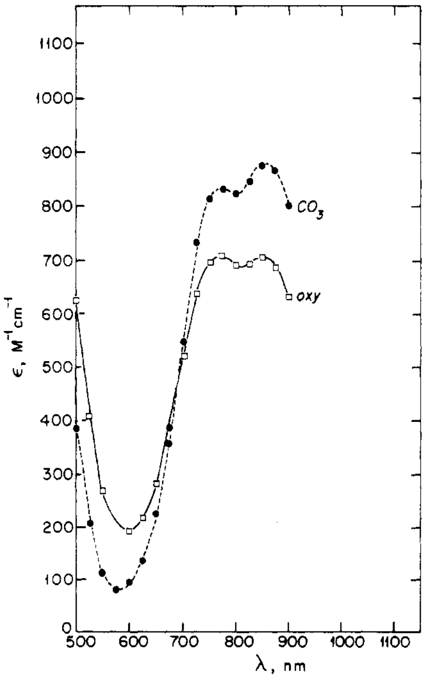


Figure 1. Electronic spectra of $[(\mathrm{DENC})\mathrm{CuCl}]_4\mathrm{O}_2$ (□) and $[(\mathrm{DENC})\mathrm{CuCl}]_4(\mathrm{CO}_3)_2$ (●) in methylene chloride at 25 °C.

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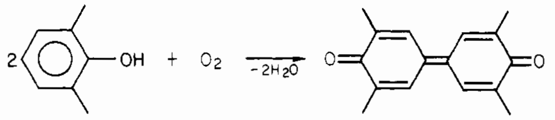
[11] $R_F = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100$ (%). $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} \times 100$ (%). GOF $= [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO = number of observations and NV = number of variables.

Table VI. Interatomic Distances (Å), with Esd's, for Racemic $(tmpd)_2Cu_2Cl_2(\mu\text{-}CO_3)$

A. Copper· · ·Copper Distance			
Cu(1)· · ·Cu(2)	4.1427 (19)		
B. Copper–Ligand Distances			
Cu(1)–O(1)	2.069 (6)	Cu(2)–O(1)	2.083 (6)
Cu(1)–O(2)	1.978 (7)	Cu(2)–O(3)	1.972 (6)
Cu(1)–N(1)	2.032 (7)	Cu(2)–N(3)	2.027 (8)
Cu(1)–N(2)	2.082 (7)	Cu(2)–N(4)	2.076 (7)
Cu(1)–Cl(1)	2.360 (3)	Cu(2)–Cl(2)	2.359 (3)
C. Distances within the Carbonate Ion			
C(1)–O(1)	1.267 (10)	C(1)–O(3)	1.252 (10)
C(1)–O(2)	1.257 (11)		
D. Distances within TMPD Ligands			
N(1)–Me(11)	1.443 (9)	N(3)–Me(31)	1.478 (10)
N(1)–Me(12)	1.476 (10)	N(3)–Me(32)	1.464 (11)
N(1)–C(11)	1.475 (10)	N(3)–C(21)	1.480 (11)
C(11)–C(12)	1.515 (12)	C(21)–C(22)	1.510 (12)
C(12)–C(13)	1.498 (13)	C(22)–C(23)	1.510 (12)
C(13)–N(2)	1.496 (11)	C(23)–N(4)	1.456 (10)
N(2)–Me(21)	1.486 (11)	N(4)–Me(41)	1.517 (10)
N(2)–Me(22)	1.460 (11)	N(4)–Me(42)	1.477 (10)

centers.[4] There is a medium-intensity band at 580 cm^{-1}, attributable to ν_{Cu-O}.[4] Unfortunately, the bands assignable to carbonate[2] are screened by ligand absorption. The room-temperature electronic spectrum of $[(DENC)CuCl]_4(CO_3)_2$ in methylene chloride (Figure 1) exhibits a split band in the near-infrared region (maximal $\epsilon_{850} = 880$ and $\epsilon_{775} = 830$ M^{-1} cm^{-1}) that is slightly solvent dependent and characteristic of both the nicotinamide ligand field and a 5-coordinate Cu^{II}_4 molecular aggregate.[4] The magnetic moment is 1.75 μ_B/Cu atom at 25 °C.[12]

$[(DENC)CuCl]_4(CO_3)_2$ is not an initiator for phenolic oxidative coupling by dioxygen (eq 2).



(2)

Substitution Chemistry of $[(DENC)CuX]_4O_2$ and $[(DENC)CuX]_4(CO_3)_2$. Although $[(DENC)CuX]_4O_2$ and $[(DENC)CuX]_4(CO_3)_2$ are inactive as initiators, they can be used to generate powerful initiator species through dissolution in aprotic solvents containing oxidative coupling promoters such as alkylpolyamines.[2] Spectral changes observed in the presence of such ligands are consistent with at least partial substitution of DENC. We are continuing to study the stoichiometry and products of these substitution reactions since they have the potential of generating species which are not obtainable by oxidation of some copper(I) complexes with dioxygen.[2] Primary attention has been focused on the reaction of $[(DENC)CuCl]_4(CO_3)_2$ with tmpd because the structure of the (μ-carbonato)-dicopper(II) product from the direct oxidation of the corresponding copper(I) complexes is known.[1]

Reaction of $[(DENC)CuCl]_4(CO_3)_2$ with tmpd in 25% v/v Methylene Chloride/Benzene. $[(DENC)CuCl]_4(CO_3)_2$ reacts with 4 equiv of tmpd in dry benzene containing 25% v/v anhydrous methylene chloride to form dark green racemic crystals (the major product) and light green crystals (minor product), both of which analyze as $(tmpd)_2Cu_2Cl_2CO_3$. Both dark and light green crystals are very effective initiators for phenolic oxidative coupling by dioxygen, as found for samples prepared from the corresponding copper(I) complex.[1]

Table VII. Interatomic Angles (Deg), with Esd's, for Racemic $(tmpd)_2Cu_2Cl_2(\mu\text{-}CO_3)$

A. Angles about the Copper Ion			
Cl(1)–Cu(1)–O(1)	96.1 (2)	Cl(2)–Cu(2)–O(1)	99.0 (2)
Cl(1)–Cu(1)–O(2)	118.0 (3)	Cl(2)–Cu(2)–O(3)	120.4 (3)
Cl(1)–Cu(1)–N(1)	99.0 (2)	Cl(2)–Cu(2)–N(3)	99.4 (3)
Cl(1)–Cu(1)–N(2)	102.9 (2)	Cl(2)–Cu(2)–N(4)	99.8 (2)
O(1)–Cu(1)–N(1)	155.3 (3)	O(1)–Cu(2)–N(3)	154.9 (3)
O(1)–Cu(1)–N(2)	97.9 (3)	O(1)–Cu(2)–N(4)	95.8 (3)
O(1)–Cu(1)–O(2)	63.7 (3)	O(1)–Cu(2)–O(3)	63.7 (2)
O(2)–Cu(1)–N(1)	91.9 (3)	O(3)–Cu(2)–N(3)	92.1 (3)
O(2)–Cu(1)–N(2)	135.9 (4)	O(3)–Cu(2)–N(4)	136.3 (3)
N(1)–Cu(1)–N(2)	97.7 (3)	N(3)–Cu(2)–N(4)	97.8 (3)
B. Angles about the Bridging Oxygen Atom			
Cu(1)–O(1)–Cu(2)	172.7 (4)	Cu(1)–O(1)–C(1)	88.2 (6)
Cu(2)–O(1)–C(1)	87.2 (6)		
C. Angles within the Carbonate Ion			
O(1)–C(1)–O(2)	115.6 (9)	O(1)–C(1)–O(3)	116.5 (10)
O(2)–C(1)–O(3)	127.9 (10)		
D. Angles within TMPD Ligands			
Cu(1)–N(1)–C(11)	111.7 (6)	Cu(2)–N(3)–C(21)	111.8 (6)
Cu(1)–N(1)–Me(11)	106.9 (5)	Cu(2)–N(3)–Me(31)	112.2 (6)
Cu(1)–N(1)–Me(12)	109.4 (6)	Cu(2)–N(3)–Me(32)	107.0 (6)
C(11)–N(1)–Me(11)	109.6 (8)	C(21)–N(3)–Me(31)	111.8 (8)
C(11)–N(1)–Me(12)	110.8 (7)	C(21)–N(3)–Me(32)	106.8 (8)
Me(11)–N(1)–Me(12)	108.3 (8)	Me(31)–N(3)–Me(32)	106.9 (8)
N(1)–C(11)–C(12)	117.2 (8)	N(3)–C(21)–C(22)	114.7 (8)
C(11)–C(12)–C(13)	113.6 (9)	C(21)–C(22)–C(23)	115.5 (8)
C(12)–C(13)–N(2)	114.7 (9)	C(22)–C(23)–N(4)	115.8 (8)
C(13)–N(2)–Me(21)	106.2 (8)	C(23)–N(4)–Me(41)	110.8 (8)
C(13)–N(2)–Me(22)	110.0 (8)	C(23)–N(4)–Me(42)	107.3 (7)
C(13)–N(2)–Cu(1)	110.9 (7)	C(23)–N(4)–Cu(2)	111.9 (6)
Me(21)–N(2)–Cu(1)	107.7 (6)	Me(41)–N(4)–Cu(2)	110.8 (6)
Me(22)–N(2)–Cu(1)	115.1 (6)	Me(42)–N(4)–Cu(2)	109.7 (6)
Me(21)–N(2)–Me(22)	106.6 (8)	Me(41)–N(4)–Me(42)	106.1 (8)

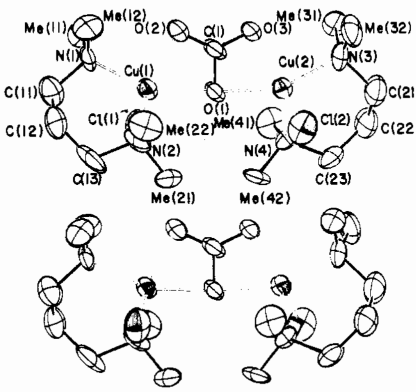


Figure 2. Labeling of atoms in the $(tmpd)_2Cu_2Cl_2(\mu\text{-}CO_3)$ molecule. The lower half of the figure shows the "other hand" of the molecule.

Description of the Molecular Structure of the Racemic Product. Interatomic distances and angles are compiled in Tables VI and VII. Least-square planes appear as Table VIII (supplementary material). Figure 2 shows the scheme used for labeling nonhydrogen atoms and also shows the relative geometry of the two chiral (C_2) forms which make up the racemic crystal.

Our previous study of chiral $(tmpd)_2Cu_2Cl_2(\mu\text{-}CO_3)$ revealed a molecule lying in a special position of crystallographically imposed C_2 symmetry in the orthorhombic space group $P22_12_1$. In the present study, the molecules lie in general positions in the monoclinic space group $P2_1/n$ and no crystallographic symmetry is imposed upon the molecules although they approximate closely to C_2 symmetry (vide infra). The previous study revealed a crystal (space group $P22_12_1$) containing only one enantiomer; the present structural study reveals a centrosymmetric space group ($P2_1/n$) with an ordered racemic

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[12] We have speculated about the structure of $[(DENC)CuCl]_4O_2$ in ref 4: since the copper centers in $[(DENC)CuCl]_4(CO_3)_2$ are evidently also 5-coordinate, the core structure of the latter, tetranuclear complex depends on whether the carbonate groups are bridging bidentate or trientate ligands. In the latter case, four copper–halogen bonds would have to be broken of formation of the carbonato complex in order to maintain 5-coordinate copper(II). Tridentate, bridging carbonate in $[(DENC)CuCl]_4(CO_3)_2$ is indicated by the structure of the substitution product $(tmpd)CuClCO_3Cl(tmpd)$ (see text).

array of the two enantiomeric forms which are interrelated by symmetry elements of the second kind ($\bar{1}$, *n*). The present monoclinic cell indicates a volume of 574.3 Å^3/molecule, as compared to 563.5 Å^3/molecule in the chiral orthorhombic cell. Thus, the molecular packing is "looser" in the present racemic monoclinic crystal. This manifests itself, inter alia, through higher thermal parameters for all atoms in the structure (as compared to the chiral orthorhombic crystal). It is this, presumably, that causes a paucity of meaningful diffraction data above $2\theta = 35°$. (Similar problems are found in certain $L_4Cu_4X_4$ structures—see ref 13–16.)

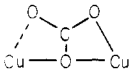
The slight differences in geometry between molecules in the present monoclinic racemic crystal and the previously reported orthorhombic chiral crystal[1] must be ascribed primarily to packing forces.

In the present monoclinic racemate each molecule lies in a general position. Each copper(II) ion maintains a distorted square-pyramidal coordination geometry, in which two oxygen atoms of the carbonate group and two nitrogen atoms of the diamine ligand define the basal plane; atoms Cu(1), Cu(2), Cl(1), and Cl(2) are, respectively, −0.473 (1), 0.488 (1), −2.823 (3), and 2.822 (3) Å out of their basal plane (see Table VIII, planes B and C). These deviations compare favorably with those found in our previous study (i.e., −0.4225 (3) and −2.8140 (9) Å for copper and chlorine atoms, respectively). Angles (degrees) from the apical chlorine atoms are Cl(1)–Cu(1)–O(1) = 96.1 (2), Cl(1)–Cu(1)–O(2) = 118.0 (3), Cl(1)–Cu(1)–N(1) = 99.0 (2), Cl(1)–Cu(1)–N(2) = 102.9 (2), Cl(2)–Cu(2)–O(1) = 99.0 (2), Cl(2)–Cu(2)–O(3) = 120.4 (3), Cl(2)–Cu(2)–N(3) = 99.4 (3), and Cl(2)–Cu(2)–N(4) = 99.8 (2) (cf. 99.49 (3), 109.63 (7), 99.75 (7), and 100.27 (7)° for the corresponding angles in the prior orthorhombic case). The small bite of the carbonate leads to small dibasal angles: O(1)–Cu(1)–O(2) = 63.7 (3) and O(1)–Cu(2)–O(3) = 63.7 (3)°, as compared to the remaining such angles O(1)–Cu(1)–N(2) = 97.9 (3), O(2)–Cu(1)–N(1) = 91.9 (3), N(1)–Cu(1)–N(2) = 97.7 (3), O(1)–Cu(2)–N(4) = 95.8 (3), O(3)–Cu(2)–N(3) = 92.1 (3), and N(3)–Cu(2)–N(4) = 97.8 (3)°. All are consistent with our prior determination in which there was a dibasal angle of 63.96 (9)° for the carbonate ligand and values ranging from 91.32 (9) to 97.92 (9)° for the remaining dibasal angles. The copper(II)–nitrogen linkages are Cu(1)–N(1) = 2.032 (7), Cu(1)–N(2) = 2.082 (7), Cu(2)–N(3) = 2.027 (8), and Cu(2)–N(4) = 2.076 (7) Å; these values show a slight inequivalence relative to those previously determined[1] (2.0470 (23) and 2.0426 (23) Å for Cu–N(1) and Cu–N(2), respectively).

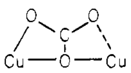
Turning our attention to the carbonate ligand, we see that its overall geometry of chelation is maintained. The copper atoms are bonded to the bridging oxygen atom in a close-to-symmetrical manner (Cu(1)–O(1) = 2.069 (6) Å and Cu(2)–O(1) = 2.083 (6) Å). The linkages to the nonbridging oxygen atoms are slightly shorter, being 1.978 (7) and 1.972 (6) Å for O(2) and O(3), respectively. The angle at the bridging oxygen , O(1), is Cu(1)–O(1)–Cu(2) = 172.7 (4)°. The carbonate moiety itself is distorted from perfect D_{3h} symmetry, having an angle O(2)–C(1)–O(3) = 127.9 (10)° as compared to 125.59 (36)° in the orthorhombic form. The remaining O–C–O (carbonate) angles are reduced to 115.6 (9) and 116.5 (10)° for O(1)–C(1)–O(2) and O(1)–C(1)–O(3) (see Table VII). The bridging role of O(1) leads to a slight increase in the C(1)–O(1) distance as compared to the C(1)–O(2) and C(1)–O(3) distances (1.267 (10) Å as compared to 1.257 (11) and 1.252 (10) Å). The copper(II) ions lie 0.057 (1) and 0.152 (1) Å from the carbonate plane (see Table VIII, plane A).

The propylenediamine framework of the ligand takes up a chair conformation, as evidenced by the displacements of atoms N(2) and C(11), in plane D of Table VIII, which lie 0.665 (8) and −0.0619 (10) Å from the plane defined by Cu(1)–N(1)–C(12)–C(13). The displacements of atoms N(4) and C(21) are −0.627 (8) and 0.648 (10) Å, respectively, from the plane defined by Cu(2)–N(3)–C(22)–C(23), as shown by plane E in Table VIII.

There are two principal differences in molecular parameters between the present racemic structure and the previous[1] chiral structure. (1) The Cl(1)–Cu(1)–O(2) and Cl(2)–Cu(2)–O(3) angles in the present structure (118.0 (3) and 120.4 (3)°) are some 10° more obtuse than in the previous chiral structure (109.63 (7)°). (2) The thermal parameters for atoms O(2), O(3), and C(1) are unexpectedly large (especially when compared to those of O(1)). It is possible that there might be some slight disorder in the Cu(μ-CO$_3$)Cu bridge—i.e., that we have a disordered array of forms perhaps like Ia and Ib rather than just II.

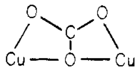


Ia

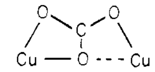


Ib

Note that forms Ia and Ib are *not* equivalent to the asymmetric bridging carbonate group found in (teed)$_2$Cu$_2$Cl$_2$(*asym*-μ-CO$_3$): that form is represented by III and would require the bridging atom O(1) to have the largest displacement.



II



III

Infrared and Electronic Spectra of Racemic (tmpd)$_2$Cu$_2$Cl$_2$CO$_3$. The infrared spectra of the racemic and enantiomeric crystals in KBr disks (Table V) contain bands characteristic of bridging, tridentate carbonate.[2] Both crystals exhibit a medium-intensity band at ~510 cm^{-1}, which is assigned to ν_{Cu-O}.[2] The room-temperature electronic spectra of solutions of racemic and enantiomeric crystals in methylene chloride exhibit similar near-infrared bands at 775 mm (ϵ 450 M^{-1} cm^{-1}) with a shoulder at about 960 nm (ϵ 240 M^{-1} cm^{-1}). The charge-transfer spectrum of the racemic crystal has slightly different molar absorptivities but almost the same wavelengths of maximum absorption as the enantiomeric sample, which is identical with that of the previously reported[1] enantiomer prepared through the Cu(I) complex: 375 nm (ϵ 7200 M^{-1} cm^{-1}), 315 (4500), and 265 (4700) and 375 nm (ϵ 4500), 300 (5000), and 255 (5100) for racemic and enantiomeric crystals, respectively. Both crystal forms are diamagnetic at room temperature.

Stoichiometry of the Reactions of Racemic and Enantiomeric Crystals with TCPH in Methylene Chloride. We have previously used the stoichiometries of reactions of (tmpd)CuClCO$_3$ClCu(tmpd) and (teed)CuClCO$_3$ClCu(teed) with TCPH to distinguish between the respective *trans*- and *cis*-dichloro geometries found in these two complexes.[1,2,6] As expected,[6] the racemic sample whose structure is reported herein reacts with TCPH according to eq 3.

$$\text{(tmpd)CuClCO}_3\text{ClCu(tmpd)} + 2\text{TCPH} \rightarrow 2\text{(tmpd)CuCl(TCP)} + \text{H}_2\text{CO}_3 \quad (3)$$

Acknowledgment. This work was supported by National Science Foundation Grant CHE77-04981 (to M.R.C.) and by Biomedical Research Support Grant RR07143 from the

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Department of Health, Education and Welfare and Faculty Development Grant 7590 from Northeastern University (to G.D.), which are gratefully acknowledged.

Registry No. $(tmpd)_2Cu_2Cl_2CO_3$, racemic form, 80225-06-5; $[(DENC)CuCl]_4(CO_3)_2$, 80105-81-3; $[(DENC)CuCl]_4O_2$, 80105-85-7; DENC, 59-26-7; CO_2, 124-38-9; O_2, 7782-44-7.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes and of least-squares planes (Table VIII) (14 pages). Ordering information is given on any current masthead page.

Contribution from the Research School of Chemistry,
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Resolutions Involving Metal Complexation. Preparation and Resolution of (*R*,*S*)-Methylphenyl(8-quinolyl)phosphine and Its Arsenic Analogue. Crystal and Molecular Structure of $(+)_{589}$-[(*R*)-Dimethyl(1-ethyl-α-naphthyl)aminato-C^2,*N*]-[(*S*)-methylphenyl(8-quinolyl)phosphine]palladium(II) Hexafluorophosphate

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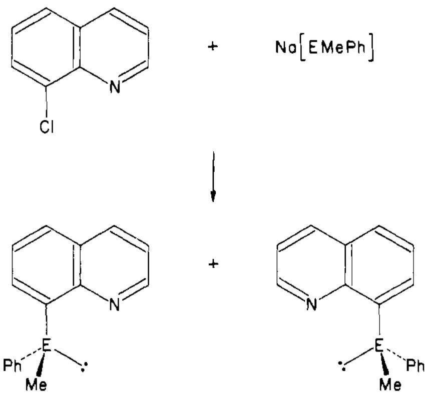
Received August 6, 1981

The asymmetric bidentates (*R*,*S*)-methylphenyl(8-quinolyl)phosphine and (*R*,*S*)-methylphenyl(8-quinolyl)arsine have been prepared in high yield from 8-chloroquinoline and the respective substituted phosphide or arsenide anion in tetrahydrofuran at −78 °C. Both compounds are air-stable crystalline solids. An efficient and large-scale resolution of both substances is described, which is based upon the fractional crystallization of a pair of internally diastereoisomeric palladium(II) complexes containing the chiral chelating ligand and an optically active ortho-metalated dimethyl(1-ethyl-α-naphthyl)amine. The optically pure enantiomers of the tertiary phosphine have $[\alpha]_D$ ±107° (mp 98 °C) and the corresponding arsine $[\alpha]_D$ ±115° (mp 75–76 °C) in diethyl ether solution. The molecular structure and absolute configuration of $(+)_{589}$-[(*R*)-dimethyl(1-ethyl-α-naphthyl)aminato-C^2,*N*][(*S*)-methylphenyl(8-quinolyl)phosphine]palladium(II) hexafluorophosphate has been determined by a single-crystal X-ray analysis. The complex crystallizes in space group $P2_12_12_1$ with a = 25.784 (5) Å, b = 19.159 (3) Å, c = 12.277 (2) Å, and Z = 8. The structure was solved by heavy-atom methods and refined by least-squares methods to an R of 0.079 and R_w of 0.047 for 2955 reflections. The tertiary phosphine liberated from this complex, $[\alpha]_D$ −107° (diethyl ether), accordingly has the *R* absolute configuration.

Introduction

Recent work in our laboratory has shown that palladium(II) complexes containing optically active ortho-metalated dimethyl(α-methylbenzyl)amines are exceedingly effective resolving agents for dissymmetric di(tertiary phosphines[1] and arsines[2]). For bidentates of lower symmetry, however, the existence of cis–trans isomerism within the internally diastereoisomeric complexes is a potential drawback to the generality of the method. In this article we describe the synthesis and resolution of the asymmetric bidentate (*R*,*S*)-methylphenyl-(8-quinolyl)phosphine and its arsenic analogue, symmetrical counterparts of which have been known for some time.[3] Chiral bidentates of this type, which are unsymmetrical with respect to the arrangement of donor atoms, are of considerable synthetic interest because of the potential of their metal chelates to exercise an electronic, as well as steric, control over the asymmetric synthesis of a chiral molecule from an appropriate coordinated substrate. Moreover, in view of our earlier results concerning the dynamic properties of certain square-planar and square-pyramidal complexes of bivalent nickel,[4] palladium, and platinum containing[5] dissymmetric di(tertiary phosphines and arsines), it was appropriate to investigate the behavior of related compounds containing asymmetric bidentates.

Scheme I



(*S*)-1 (E = P) (*R*)-1
(*S*)-2 (E = As) (*R*)-2

The present article describes a direct and efficient synthesis of (*R*,*S*)-methylphenyl(8-quinolyl)phosphine, and its arsenic analogue, as well as the resolution of both compounds, which in each case was based upon the fractional crystallization of a pair of internally diastereoisomeric palladium(II) complexes containing the appropriate bidentate and an optically active ortho-metalated dimethyl(1-ethyl-α-naphthyl)amine.

Results and Discussion

Methylphenyl(8-quinolyl)phosphine, (*R*,*S*)-**1**, and its arsenic analogue, (*R*,*S*)-**2**, were prepared from 8-chloroquinoline and the respective anion in tetrahydrofuran at −78 °C (Scheme I). They distilled as high-boiling viscous oils and were sub-

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