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Coordination Chemistry of Tripyridinedimethane

Andrei N. Vedernikov,* John C. Huffman, and Kenneth G. Caulton*

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405-7102

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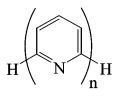
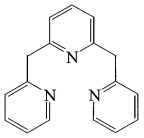
The ligand tripyridinedimethane (tpdm), consisting of three pyridine residues linked at their ortho carbons by two CH_2 groups, is shown to be a sterically flexible ligand capable of binding in a meridional arrangement in trigonal bipyramidal (tpdm) $Cu^{II}Cl_2$ but binding in a facial arrangement in tetrahedral (tpdm) $Cu^{I}Cl$. Nucleophilic substitution of chloride by $^tBuO^-$ and $PhC{\equiv}C^-$ is possible, and deprotonation of the acidic benzylic protons does not take place because the resulting carbanion cannot achieve coplanarity with the aryl rings. $RhCl_3$ forms, with tpdm in boiling methanol, a 1:1 kinetic mixture of *fac*- and *mer*-isomers $RhCl_3$(tpdm). The former isomerizes slowly at RT (room temperature) in DMSO solution into the latter with Rh–N bond dissociation as the rate-determining step.

Introduction

One important recent trend in the field of organo-transition-metal chemistry is the application of chelating N-donor ligands and their comparison to analogous polyphosphines. For example, the use of polydentate N-donor ligands is extremely fruitful in the chemistry of hydridoalkyl complexes of d^6 platinum metals. Azaheterocycles were especially useful in this respect, in particular, owing to their resistance to oxidation, low basicity, and higher ligand field. Progress in coordination chemistry of polyazaheterocyclic compounds is limited by the availability of these ligands. The well-studied polypyridines, **A**, have a very rigid structure, limiting their coordination geometry on a metal. In contrast, the rarely studied polypyridinepolyalkanes[1,2] contain alkanediyl bridges between pyridine rings and therefore combine features of polyazaheterocycles with enhanced molecular flexibility. For example, they have the flexibility to adopt either meridional chelation (which is exclusive for polypyridines) or facial chelation, which is characteristic for trihetaryl-substituted methane or boronate.



A



Recently, we have developed a one-step method for the synthesis of substituted tripyridinedimethanes, involving condensation of lithiated monopyridine derivatives.[3] Here, we report the coordination chemistry of one of these new ligands, which is a parent for the family of tripyridinedialkanes, tripyridinedimethane (tpdm). By studying two oxidation states of copper and isomeric octahedral Rh(III) complexes, we can test the flexibility of this ligand.

Experimental Section

General. All manipulations were carried out under purified argon using standard Schlenk and glovebox techniques. Solvents were dried and distilled following standard protocols and stored in gastight bulbs under argon. All reagents for which a synthesis is not given are commercially available from Aldrich or Pressure Chemicals and were used as received without further purification. All NMR solvents were dried, vacuum-transferred, and stored in an argon-filled glovebox.

^1H and ^{13}C NMR spectra were recorded on an Inova 700 spectrometer (^1H 400 MHz; ^{13}C 100.62 MHz). ^1H and ^{13}C NMR chemical shifts are reported in ppm and referenced to residual solvent resonance peaks. High-resolution mass spectra were obtained on a Kratos MS80 RFAQQ instrument.

Computational Details. Theoretical calculations in this work have been performed using a density functional theory (DFT) method,[4] specifically functional PBE,[5] implemented in an original

* To whom correspondence should be addressed. E-mail: caulton@indiana.edu (K.G.C.).

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program package "Priroda".[6] In PBE calculations, relativistic Stevens−Basch−Krauss (SBK) effective core potentials (ECP)[7] optimized for DFT calculations have been used. The basis set was 311-split for main group elements with one additional polarization p-function for hydrogen and two additional polarization d-functions for elements of higher periods. Full geometry optimization has been performed without constraints on symmetry. For all species under investigation, frequency analysis has been carried out. All minima have been checked for the absence of imaginary frequencies.

Tripyridinedimethane, $C_{17}H_{15}N_3$. A flame-dried 300-mL Schlenk flask connected to a vacuum−argon line was charged with 50 mL of diethyl ether and 2,6-lutidine (23.3 mL, 0.20 mol; distilled from calcium hydride). The flask was cooled to 0 °C, and butyllithium solution in hexane (20.0 mL of 10 M, 0.2 mol) was added dropwise with stirring. After the addition of butyllithium was complete, the dark red solution was permitted to warm to ambient temperature for 1 h. Diethyl ether was removed in a vacuum, and the yellow crystalline residue was dried at 0.1 Torr for 1 h. Toluene (50 mL) was added via cannula, and pyridine distilled over calcium hydride under argon atmosphere (8.1 mL, 0.1 mmol) was added with a syringe. The flask was then immersed for 40 min into a silicone oil bath heated to 120 °C. Dihydrogen evolution and residual ether distillation was observed; the mixture became purple-red. The reaction mixture was then cooled, and methanol (8 mL) was added with syringe to decompose precipitated lithium hydride. After addition of water (18 mL), a yellow liquid could be easily separated by filtration from the white precipitate of lithium hydroxide. The liquid was dried over solid potassium hydroxide and fractionally distilled, first at ambient pressure and then under vacuum. Yield of tripyridinedimethane: 6.8 mL (6.4 g, 50%). Bp: 165−168 °C at 0.1 Torr. ^{1}H NMR (25 °C, $CDCl_3$): 4.31 (br, 4H, CH_2), 7.03 (d, 7.7 Hz, 2H, C(3,5)-central-H), 7.10 (dd, 7.6 Hz, 4.9 Hz, 2H, C5-terminal-H), 7.21 (d, 7.7 Hz, 2H, C3-terminal-H), 7.48 (t, 7.7 Hz, 1H, C4-central-H), 7.55 (dt, 7.7 Hz, 1.8 Hz, 2H, C4-terminal-H), 8.49−8.54 (m, 2H, C6−H). High-resolution mass spectrum, *m*/*z*: found 261.12730, calcd 261.12660, $C_{17}H_{15}N_3$.

Cu(tripyridinedimethane)Cl·CH_2Cl_2, $C_{18}H_{17}Cl_3N_3Cu$. To a dry flask containing a magnetic stirring bar was added, in a glovebox, CuCl (396 mg, 4.0 mmol) and 20.0 mL of dry dichloromethane. To the stirred mixture, tripyridinedimethane (1.10 g, 4.2 mmol) dissolved in 5.0 mL of dichloromethane was then added. Stirring was continued at room temperature for 5 h. The orange precipitate formed was filtered off, washed twice with 1.0 mL portions of dichloromethane, and dried. Yield: 1.25 g (70%). Large orange crystals suitable for X-ray structural determination have been obtained by slow cooling of a saturated solution of CuCl(tpdm) in dichloromethane. ^{1}H NMR (25 °C, $CDCl_3$): 4.38 (br s, 4H, CH_2), 7.18−7.36 (m, 6H), 7.59 (t, 1H, 7.7 Hz, C4-central-H), 7.63 (dt, 2H, 7.5, 1.0 Hz, C4−H-terminal), 8.72−8.74 (m, 2H, C6−H).

Cu(tripyridinedimethane)Cl_2·CH_2Cl_2, $C_{18}H_{17}Cl_4N_3Cu$. To a dry flask containing a magnetic stirring bar was added, under argon atmosphere, $CuCl_2$ (536 mg, 4.0 mmol) and 20.0 mL of dry dichloromethane. To the stirred mixture was then added tripyridinedimethane (1.10 g, 4.2 mmol) dissolved in 5.0 mL of dichloromethane. Stirring was continued at room temperature for 24 h. The resulting greenish-blue precipitate was filtered off, washed twice with 1.0 mL portions of dichloromethane, and dried. Yield: 1.5 g (80%). Large crystals suitable for X-ray structural determination have been obtained by slow cooling of a saturated solution of $CuCl_2$(tpdm) in dichloromethane.

A ^{1}H NMR spectrum could not be obtained because of the low solubility of Cu(tpdm)Cl_2.

When stored in an open flask, the compound loses one molecule of dichloromethane to give Cu(tpdm)Cl_2. Anal. Calcd for $C_{17}H_{15}Cl_2N_3Cu$: C, 51.6; H, 3.82; N, 10.6. Found: C, 51.4; H, 3.48; N, 10.6.

Rh(tripyridinedimethane)Cl_3, $C_{17}H_{15}Cl_3N_3Rh$. To a flask containing a magnetic stirring bar was added $RhCl_3$·$3H_2O$ (129 mg, 0.490 mmol) and 5 mL of methanol. After dissolution of the rhodium salt was complete, a solution of tripyridinedimethane (139 mg, 0.533 mmol) in 2 mL of methanol was added with stirring. Light reddish-brown precipitate formed and was then refluxed for 2 h with rapid stirring. After the reaction mixture cooled, the precipitate was filtered off and washed with methanol. Yield of 1:1 mixture of *fac*- and *mer*-isomers: 200 mg (87%). ^{1}H NMR (25 °C, DMSO-d_6) are presented in the following paragraphs. Anal. Calcd for $C_{17}H_{15}Cl_3N_3Rh$: C, 43.4; H, 3.21; N, 8.93. Found: C, 43.8; H, 3.45; N, 8.84.

fac-Rh(tpdm)Cl_3: 4.66 (d, $^2J_{H-H}$ = 16.7 Hz, CH_2), 6.77 (d, $^2J_{H-H}$ = 16.7 Hz, CH_2), 7.52 (app t, $^3J_{H-H}$ = 7.1 Hz; 2H, C5−H, terminal py); 7.75 (br d, $^3J_{H-H}$ = 7.7 Hz; 2H, C3−H, terminal py); 7.79 (d, $^3J_{H-H}$ = 7.7 Hz; 2H, *meta*-CH, central py); 8.05 (dt, $^3J_{H-H}$ = 7.6 Hz; $^4J_{H-H}$ = 1.4 Hz; 2H, *para*-CH, terminal py); 8.08 (t, $^3J_{H-H}$ = 7.6 Hz; 1H, *para*-CH, central py); 9.44 (m, 2H, *ortho*-CH, py).

mer-Rh(tpdm)Cl_3: 4.79 (d, $^2J_{H-H}$ = 16.2 Hz, CH_2), 6.03 (d, $^2J_{H-H}$ = 16.2 Hz, CH_2), 7.58 (app t, $^3J_{H-H}$ = 7.0 Hz; 2H, C5−H, terminal py); 7.63 (br d, $^3J_{H-H}$ = 7.7 Hz; 2H, C3−H, terminal py); 7.68 (d, $^3J_{H-H}$ = 7.7 Hz; 2H, *meta*-CH, central py); 7.97 (dt, $^3J_{H-H}$ = 7.6 Hz; $^4J_{H-H}$ = 1.3 Hz; 2H, *para*-CH, terminal py); 8.05 (t, $^3J_{H-H}$ = 7.6 Hz; 1H, *para*-CH, central py); 9.61 (m, 2H, *ortho*-CH, py).

X-ray Diffraction Structure Determination. (a) General. The crystal was affixed to the end of a glass fiber using silicone grease and cooled for data collection on a Bruker SMART 6000 diffractometer. The data were collected with an ω scan of 0.30°. Data were corrected for Lorentz and polarization effects and equivalent reflections averaged using the Bruker SAINT software as well as utility programs from the XTEL library. The structures were solved using SHELXTL and Fourier techniques. Crystallographic data and bond lengths and angles are presented in Tables 1 and 2.

(b) Cu(tpdm)Cl·CH_2Cl_2. All hydrogen atoms were located and refined. A final difference Fourier was essentially featureless with maximum peak height of 0.44/Å^3.

(c) Cu(tpdm)Cl_2·CH_2Cl_2. Systematic absences and statistical tests indicated the centrosymmetric space group $P\bar{1}$. The solution and refinement confirmed this assignment. The structure consists of the molecule of interest and one dichloromethane solvent molecule. All of the hydrogen atoms were clearly visible in a difference Fourier and were refined isotropically in the final cycles of refinement. A final difference Fourier was essentially featureless, with all peaks being less than 0.54 e/Å^3.

Reactions of Cu(tpdm)Cl with Nucleophiles. In an argon-filled glovebox, a Teflon-capped NMR Young tube was charged with 9.0 mg (20 μmol) of Cu(tpdm)Cl·CH_2Cl_2, 4.5 mg (40 μmol) of KOBu^t or 4.3 mg of LiCCPh (40 μmol), and 1.0 mL of benzene-d_6 (KOBu^t) or 1.0 mL of CD_2Cl_2 (LiCCPh). The tube was closed, removed from the glovebox, and put into a rotating clamp to allow constant mixing of the reaction mixture. Each hour, the ^{1}H NMR

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Table 1. Crystallographic Data for Cu(tpdm)Cl·CH_2Cl_2 and Cu(tpdm)Cl_2·CH_2Cl_2

	$C_{18}H_{17}Cl_3CuN_3$		$C_{18}H_{17}Cl_4CuN_3$
a, Å	15.7949(4)	*a*, Å	8.4172(5)
b, Å	14.4722(4)	*b*, Å	10.8024(6)
c, Å	15.9546(5)	*c*, Å	12.0266(7)
		α, deg	67.237(1)
		β, deg	78.420(1)
		γ, deg	75.625(1)
V, Å^3	3647.01	*V*, Å^3	970.06
Z	8	*Z*	2
fw	445.26	fw	480.71
space group	*Pbca*	space group	$P\bar{1}$
T, °C	−162	*T*, °C	−160
λ, Å	0.71073	*λ*, Å	0.71073
ρ_{calc}, g/cm^{-3}	1.622	ρ_{calc}, g/cm^{-3}	1.646
μ(Mo Kα), cm^{-1}	16.4	*μ*(Mo Kα), cm^{-1}	16.8
R^a	.0254	R^a	0.0285
$R_w{}^b$	.0245	$R_w{}^b$	0.0281

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ where $w = 1/\sigma^2(|F_o|)$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Cu(tpdm)Cl·CH_2Cl_2

Cu(1)	Cl	2.2609(8)
Cu(1)	N(3)	2.0907(26)
Cu(1)	N(15)	2.0971(26)
Cu(1)	N(22)	2.0735(26)

Cl	Cu(1)	N(3)	113.68(8)
Cl	Cu(1)	N(15)	124.17(8)
Cl	Cu(1)	N(22)	118.75(7)
N(3)	Cu(1)	N(15)	91.15(10)
N(3)	Cu(1)	N(22)	111.52(10)
N(15)	Cu(1)	N(22)	93.30(10)

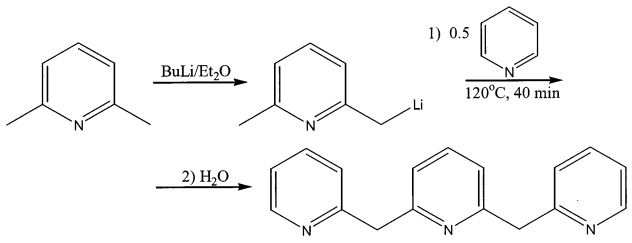
spectrum of the reaction mixture was taken. The transformations were complete in 2 h in the case of KOBu^t and in 8 h in the case of LiCCPh.

NMR yield of light-yellow Cu(tpdm)(OBu^t) was 90%. The compound decomposes slowly (24 h) in benzene solution liberating dark brown precipitate. ^{1}H NMR (25° C, C_6D_6) *δ*, ppm: 1.13 (s, 9H, Bu^t); 4.32 (br s, 4H, CH_2); 6.49 (dd, $^3J_{H-H}$ = 7.5 Hz; $^3J_{H-H}$ = 5.1 Hz; 2H, *meta*-CH, terminal py); 6.85 (d, $^3J_{H-H}$ = 7.5 Hz; 2H, *meta*-CH, terminal py); 6.90 (t, $^3J_{H-H}$ = 7.4 Hz; 1H, para-CH, central py); 6.91 (dt, $^3J_{H-H}$ = 7.4 Hz; $^4J_{H-H}$ = 1.9 Hz; 2H, *para*-CH, terminal py); 6.95 (d, $^3J_{H-H}$ = 7.4 Hz; 2H, *meta*-CH, central py); 8.39 (m, 2H, *ortho*-CH, py).

NMR yield of light-yellow Cu(tpdm)CCPh was 70%. The compound is stable for at least 2 days in dichloromethane solution. ^{1}H NMR (25 °C, CD_2Cl_2) *δ*, ppm: 4.35 (br s, 4H, CH_2); 7.06−7.15 (m, 3H, Ph); 7.21 (d, $^3J_{H-H}$ = 7.8 Hz; 2H, *meta*-CH, central py); 7.23 (ddd, $^3J_{H-H}$ = 7.8 Hz; $^3J_{H-H}$ = 5.0 Hz; $^4J_{H-H}$ = 1.1 Hz; 2H, *meta*-CH, terminal py); 7.25−7.29 (m, 2H, Ph); 7.33 (br d, $^3J_{H-H}$ = 7.8 Hz; 2H, *meta*-CH, terminal py); 7.63 (t, $^3J_{H-H}$ = 7.8 Hz; 1H, *para*-CH, central py); 7.68 (dt, $^3J_{H-H}$ = 7.8 Hz; $^4J_{H-H}$ = 1.9 Hz; 2H, *para*-CH, terminal py); 8.67 (m, 2H, *ortho*-CH, py).

Reaction of Cu(tpdm)Cl_2 with MeLi. In an argon-filled glovebox, a 5 mL Schlenk flask was charged with a magnetic stirring bar, 45.0 mg (100 *μ*mol) of Cu(tpdm)Cl_2·CH_2Cl_2, and 5.0 mL of THF. The flask was fitted with a serum cap, removed from the glovebox, attached to a vacuum−argon line, and put into an acetone bath cooled to −60 °C. Then, 0.2 mL of 1 M MeLi solution in ether (200 *μ*mol) has been added dropwise to a stirred greenish-blue suspension in the course of 5 min. After addition was complete, the color changed to pale red, and all the precipitate dissolved. The mixture was allowed to warm to room temperature, the solvent was removed under vacuum, and the pink residue dissolved in C_6D_6 and was filtered. Selected ^{1}H NMR data (21° C) *δ*, ppm: 0.07 (br s, 3H, CH_3); 4.23 (br s, 4H, CH_2).

Scheme 1



Isomerization of *fac*-Rh(tpdm)Cl_3 into *mer*-Rh(tpdm)Cl_3. An NMR tube was charged with 2.0 mg of an isomeric mixture of Rh(tpdm)Cl_3 (plus 16.0 mg of LiCl in the case of mechanistic experiments) dissolved in 1.0 mL of warm DMSO-d_6. Every 12 h, the ^{1}H NMR spectrum was taken to monitor the isomerization. In 100 h at 21 °C, the reaction was complete.

Results

Ligand Synthesis. The tpdm ligand for this work has been synthesized in a one-step reaction from inexpensive 2,6-lutidine and pyridine (see Scheme 1). 2,6-Lutidine was deprotonated in ether solution with 10 M *n*-butyllithium in hexane to give 6-methyl-2-pyridylmethyllithium. The ether was removed and replaced with toluene mixed with a stoichiometric amount of pyridine. Heating the mixture at 120 °C for 40 min caused an exothermic condensation reaction, which is in fact aromatic nucleophilic hydride substitution with a carbanionic nucleophile,[8] accompanied by dihydrogen evolution and lithium hydride precipitation to give the dilithium salt of tpdm. After water work up and distillation under vacuum, the target compound has been obtained in pure form in 50% yield.

Cu(tpdm)Cl. (a) Synthesis and Characterization. CuCl dissolves in CH_2Cl_2 in the presence of the tripyridine, and an orange precipitate then forms. The product is sufficiently soluble in $CDCl_3$ to record a ^{1}H NMR spectrum, which shows mirror symmetry making the two terminal pyridyl ligands equivalent. The two protons on a given CH_2 group are *not* equivalent, although a well-resolved AB pattern is not seen; a broad peak is observed. This inequivalence is consistent with a pseudotetrahedral structure for CuCl(tpdm), with a tridentate ligand.

(b) Structure. The structure was shown by X-ray diffraction to involve tridentate binding of the ligand to Cu(I) to give a molecular species. As shown in Figure 1, the molecule has an idealized mirror plane of symmetry containing Cl, Cu, and N15. It is noteworthy that all three Cu−N distances are very similar (within 0.02 Å), thus showing no great strain on any pyridine ring. The N−Cu−N angle within a six-membered CuN_2C_3 ring, at 92°, is much smaller than that between the two chelate ends (111.5°). The Cl−Cu−N angles, 4−14° larger than 109°, reflect the compact facial "bite" of the tpdm ligand.

Cu(tpdm)Cl_2. (a) Synthesis and Characterization. In contrast to the copper(I) analogue, this compound is of

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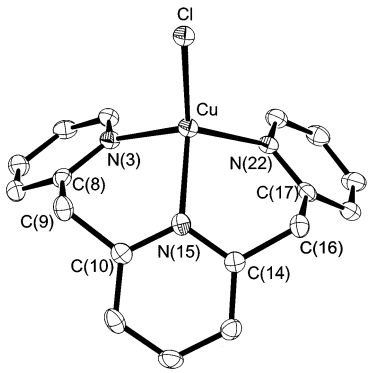

Figure 1. ORTEP drawing (50% probability criterion) of the non-hydrogen atoms of (tpdm)CuCl, showing selected atom labeling.

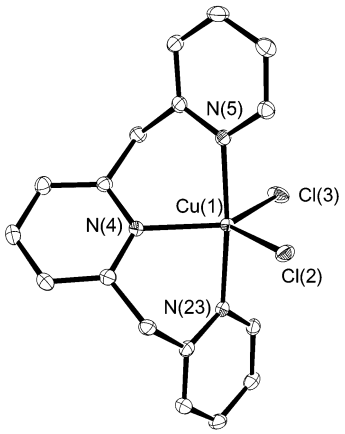

Figure 2. ORTEP drawing (50% probability criterion) of the non-hydrogen atoms of (tpdm)$CuCl_2$, showing selected atom labeling.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Cu(tdpm)Cl_2

Cu(1)	Cl(2)		2.4021(6)
Cu(1)	Cl(3)		2.3339(6)
Cu(1)	N(4)		2.0730(17)
Cu(1)	N(5)		2.0368(18)
Cu(1)	N(23)		2.0338(18)
Cl(2)	Cu(1)	Cl(3)	117.070(23)
Cl(2)	Cu(1)	N(4)	115.44(5)
Cl(2)	Cu(1)	N(5)	93.05(5)
Cl(2)	Cu(1)	N(23)	90.38(5)
Cl(3)	Cu(1)	N(4)	127.44(5)
Cl(3)	Cu(1)	N(5)	87.08(5)
Cl(3)	Cu(1)	N(23)	95.42(5)
N(4)	Cu(1)	N(5)	88.02(7)
N(4)	Cu(1)	N(23)	86.39(7)
N(5)	Cu(1)	N(23)	174.29(7)

significantly lower solubility in CH_2Cl_2. The reaction of copper(II) chloride with tpdm is therefore heterogeneous and proceeds more slowly though completely at room temperature.

(b) Structure. The molecule has no crystallographic symmetry (Figure 2, Table 3), but the two fused chelate rings cause a strong nonplanarity of each six-membered CuN_2C_3 ring, in opposite directions, so that there is approximate C_2 symmetry. The idealized C_2 axis lies on the Cu−N4 vector. The Cu, N4, and the two Cl atoms are rigorously planar, as are the equatorial sites of a trigonal bipyramid, but the two Cu−Cl distances differ by 0.07 Å (75 esd's), and the N4−Cu−Cl angles differ by 12°. The Cu−N4 distance is slightly *longer* than the other two Cu−N distances, which is the reverse of what is true in the terpyridyl analogue.[9,10]

It is natural to compare the coordinating ability of tpdm to those of terpy, **A** with $n = 3$, where there are direct bonds between pyridine rings. The rigidity of terpy is evident by comparison of the structures of Cu(tpdm)Cl_2 here with that of Cu(terpy)Cl_2.[9,10] The cisoid N−Cu−N angles in Cu(terpy)-Cl_2 are 79°, which is 7° smaller, a difference which results in Cu(terpy)Cl_2 being unable to adopt trigonal bipyramidal geometry, but instead having a planar 4 + 1 coordination geometry with one Cl 0.34 Å farther from copper. This change leads to the Cu−N distance to the central pyridine being short (1.95 vs 2.05 Å to the other two N), and trans N−Cu−N angles of only 157.3° (compare 174.3° in Cu-(tpdm)Cl_2). In sum, the flexibility of tpdm permits approximate trigonal bipyramidal geometry, while terpy prohibits it.

Structural Comparison: Cu^I Versus Cu^{II}. The Cu/N distances are only slightly (∼0.06 Å) longer to Cu^I, but the Cu/Cl distances are 0.06 and 0.14 Å longer to Cu^{II}, which may be partly a reflection of Jahn−Teller elongation mainly in the Cu^{II}/Cl orbitals. The N−Cu−N angles between adjacent pyridines are 86.4° and 88.0° for Cu^{II}, but a severely compressed (from 109°) 91.15° and 93.30° for Cu^I. It thus seems that this ligand is better suited to square than to tetrahedral coordination geometries, although a tetrahedron on Cu^I is proven here to tolerate considerable distortion.

The six-membered C_3N_2Cu rings formed in the complex all have boat conformations. In the $CuCl_2$ complex, the two boats have the opposite sense, consistent with the C_2 symmetry axis. This boat conformation contradicts the possibility of conjugation of the two aryl substituents with a *deprotonated* benzylic carbon.

***fac*- and *mer*-Rh(tpdm)Cl_3. Synthesis and Characterization.** To explore and analyze more information about possible coordination modes of tpdm, we have synthesized a tpdm complex with a d^6 metal species, rhodium(III) chloride. For 18-electron octahedral $RhCl_3$(tpdm) product, we could expect *fac*-/*mer*-isomerism.

A 1:1 mixture of *fac*- and *mer*-$RhCl_3$(tpdm) was in fact obtained from a reaction between rhodium(III) chloride trihydrate and a stoichiometric amount of tpdm in refluxing methanol in the course of 2 h. The product is insoluble in methanol, water, chloroform, or dichloromethane. Its solubility is low in nitromethane and slightly higher in DMSO, and in the latter case, it is soluble enough to characterize the product with ^{1}H NMR spectroscopy.

The product obtained was a 1:1 mixture of *fac*- and *mer*-isomers, one of which completely converted into the other over 120 h at RT (room temperature) ($\tau_{1/2} \approx 25$ h). These two modes of tpdm coordination have been deduced from analysis of ^{1}H NMR spectroscopic data. According to these, each of the isomers is characterized with either mirror or C_2 symmetry and shows only one AX set of resonances of

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protons of methylene bridges and one set of resonances of terminal pyridine rings of the ligand. The AX pattern for the *mer*-isomers shows that it has either a C_2 symmetry axis or a mirror plane including a $RhCl_3$ fragment, but no mirror plane relating the two hydrogens in a given CH_2. This is best explained by the "twist" structure found for the coordinated ligand in (tpdm)$CuCl_2$ together with the conclusion that inversion of the MC_3N_2 boat is slow on the ^{1}H NMR time scale. Low solubility of the product in methanol may be the reason for obtaining a kinetic mixture of stable *mer*- and unstable *fac*-isomers under described conditions. The assignment of configuration of the isomers observed as either *fac* or *mer* was based on the pattern of ^{1}H NMR spectra indicating the presence of a mirror plane (*fac*) or C_2 elements of symmetry (*mer*), and on the direction of the isomerization, and DFT calculated 13.1 kcal/mol greater stability (ΔG^o_{298}) of the latter.

Thus, we can conclude that under conditions used in this work we obtain *kinetic* distribution of two possible isomers of $RhCl_3$(tpdm).

Reactivity. (a) Copper. The reactivity of CuCl(tpdm) was investigated. Replacement of a chloride ligand by a nucleophilic reagent *may* be complicated or even suppressed by competitive deprotonation of the acidic CH_2 fragments linking neighboring pyridine rings. Such a deprotonation can be readily achieved when tpdm is treated with KOBu^t in THF or benzene solution.

In fact, reaction of CuCl(tpdm) with excess KOBu^t (1:2) in C_6D_6 (1 h, RT) gives rise to the substitution product only, Cu(OBu^t)(tpdm), which has been characterized by ^{1}H NMR spectroscopy, showing a mirror symmetric tpdm ligand and O^{t}Bu in the correct intensity ratio.

Reaction of CuCl(tpdm) with an even stronger base, LiCCPh, taken in excess (1:2) in CD_2Cl_2 for 8 h at RT gives the corresponding substitution product in 70% yield.

When the divalent copper complex, $CuCl_2$(tpdm), reacted with methyllithium (1:2 ratio) in THF at −60 °C, no deprotonation was observed, but chloride substitution and reduction of Cu(II) were observed. After slow warming up and removal of the solvent, the resulting pink powder was dissolved in C_6D_6 and characterized by ^{1}H NMR as the *monovalent* Cu(CH_3)(tpdm).

We therefore conclude that coordination to a copper atom prevents planarization of py−CH_2−py fragments of the tpdm ligand and therefore significantly suppresses the otherwise high acidity of the methylene bridges observed for the free ligand.

(b) Rh(III). To find out whether the *fac* → *mer* isomerization in DMSO occurs via the rate-determining dissociation of a chloride ligand from the rhodium(III) center, then the rapid switch of tpdm from *fac*- to *mer*-geometry, and finally chloride association, we studied the influence of the addition of 90 equiv of lithium chloride on the isomerization rate in DMSO. The rate of isomerization under these conditions is even 60% higher ($\tau_{1/2} \approx 15$ h) than in a salt-free solution. Thus, no rate-determining chloride ligand dissociation takes place in DMSO solution at RT, and the effect of lithium chloride may be purely due to a change of the solution ionic strength. We therefore suggest a mechanism beginning with Rh−N bond cleavage as the rate-determining step, with subsequent rearrangement of three chlorides from *facial* to *meridional* position, change of tpdm conformation, and recoordination of the third nitrogen atom.

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Supporting Information Available: Full crystallographic details (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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