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Dipyrimidylamine and tripyrimidylamine as chelating N-donor ligands

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Abstract

Dipyrimidylamine (dipm) and tripyrimidylamine (tripm) are reported. A bidentate tripm ruthenium complex, [RuCl(η^6-*p*-cymene)(κ^2-tripm)]SbF_6, is synthesized and structurally characterized. The presence of an intramolecular C–H···N hydrogen bond is proposed between the cymene C–H and a ring nitrogen in an uncoordinated pyrimidine ring. IR data on [$Mo(CO)_4$(dipm)] suggest that the Tolman electronic parameter of the dipm ligand is similar to that of $2 \times PPh_3$. M–L bonding may be weaker for pyrimidine versus pyridine because κ^2-tripm complexation is apparently more favorable relative to the κ^3-form than is the case for tripyridylamine.

Keywords: Dipyrimidylamine ligands; Tripyrimidylamine ligands; Ruthenium complexes; X-ray crystal structures

1. Introduction

The design and synthesis of ligands effective in promoting homogeneous catalysis but resistant to thermal degradation at high temperature is one of the challenging emerging areas in catalysis. Phosphines are excellent for promoting catalysis but decompose readily at elevated temperature by P–C bond cleavage [1]. Ligand robustness is particularly desirable in the area of C–H functionalization catalysis [2a], where high temperatures are useful both for improving rates and for increasing the thermodynamic driving force. Jensen and coworkers [3a] have shown how pincer phosphines can improve thermal stability for phosphines in alkane dehydrogenation and Heck chemistry, which also requires high temperatures. Mosny and Crabtree [2b] in our group extensively studied the chemistry of tri-2-pyridylamine (tripyam), and showed how its complexes were generally thermally stable as hoped, but the complexes studied were too stable and lacked catalytic activity. Catalytic activity for alkane conversion has been found by Periana et al. [3b] for a 2,2′-dipyrimidine platinum complex. This soft chelating ligand, proposed to have greater π acceptor character than 2,2′-dipyridine, was successful in catalysis at elevated temperature. This prompted us to examine the possibility of incorporating additional nitrogen atoms into the pyridine rings of tripyridylamine. We therefore decided to look at tri-2-pyrimidylamine (tripm), which we hoped would give complexes with better catalytic activity than tripyridylamine complexes. Most tripyridylamine complexes also show low solubility in common solvents, but we expected tripm complexes would be more soluble because of the extra nitrogen atoms on the rings allowing stronger interactions with the solvent.

2. Synthesis of dipyrimidylamine (dipm) and tripm

Our first goal was to synthesize the potentially chelating organic ligand, tripm. We have therefore developed a synthetic pathway to tripm (**2**) via dipm (**1**) as intermediate, in 15% overall yield (Eqs. (1) and (2)).

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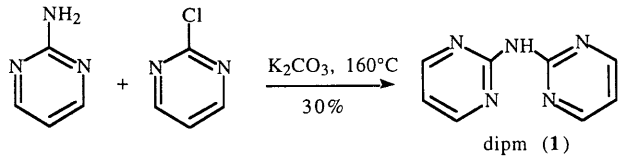
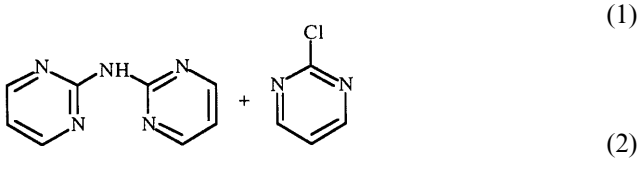


(1)



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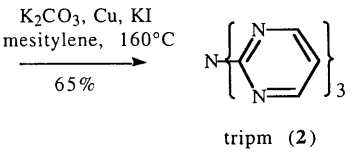

In the first step, 2-aminopyrimidine is condensed with 2-chloropyrimidine using K_2CO_3 at 160°C without a solvent (Eq. (1)) in a modification of a standard [4] type of procedure to give dipm (**1**) in 30% yield. The resulting dipm is then arylated with 2-bromopyrimidine and K_2CO_3 at 160°C (Eq. (2)), also a modification of a known type of reaction [5], to give tripm in 65% yield. Both dipm and tripm were isolated by chromatography as white crystalline solids. Their identities have been confirmed by ^{1}H NMR, GC–MS, and elemental analyses (see Section 7).

3. Donor strength of dipyrimidylamine

Tolman [6] has compared the electronic effects of various monodentate ligands by using the A_1 ν(CO) IR vibration of $LNi(CO)_3$ as an indicator. Chelating ligands cannot readily be studied with $LNi(CO)_3$, so Anton and Crabtree [7] suggested using the A_1 ν(CO) band of a more suitable system: *cis*-$Mo(CO)_4L_2$. These are easily made, air-stable, and nontoxic complexes, and both chelating and monodentate ligands can be studied [8]. A very good correlation between the data for $LNi(CO)_3$ and *cis*-$Mo(CO)_4L_2$ systems validates the approach and allows the Tolman electronic parameters to be correlated and so estimated for bidentate ligands [6,7]. The normal mode associated with the A_1 vibration mainly involves the pair of trans CO groups, and the bands are always strong enough to be easily observed and assigned.

We therefore made $Mo(CO)_4$(dipm) by a modification of a known type of method [8] involving the reaction of $Mo(CO)_6$ and dipm in refluxing toluene, and measured its IR spectrum in $CHCl_3$. The A_1 frequency was located at 2023 cm^{-1}, and comparison with other values found for *cis*-$[L_2Mo(CO)_4]$ complexes in the literature [7–9] gives the following order of donor strength:

PCl_3 (2072) < dibenzocyclooctatetraene (dct) (2052)
< $P(OPh)_3$ (2046) < cod (2038)
< $P(OMe)_3$ (2037) < dipm (**1**) (2023)
< PPh_3 (2022) < bpy (2010)

The IR data indicate that dipm is indeed substantially different electronically from 2,2′-bipyridine.

Pyrimidine is indeed a weaker base than pyridine, so we cannot be certain whether to interpret the difference in electronic effect as indicating simply weaker σ donation or enhanced π back donation as well. This may mean that dipm should behave more nearly like two PPh_3 groups than like 2,2′-bipyridine, at least as far as the electronic effects are concerned. Tripm did not give a clean $Mo(CO)_4$ or $Mo(CO)_3$ derivative, and so we have not been able to extend this work to tripm itself, but the electronic effect is not expected to change very much between dipm and tripm.

4. Synthesis of [RuCl(*p*-cymene)(κ^2-tripm)][SbF_6]

For comparison with the previously prepared tripyridylamine analogue **2b**, [RuCl(*p*-cymene)(κ^2-tripm)][SbF_6], we treated $[RuCl_2(p\text{-cymene})]_2$ with 2 equiv. of tripm, and 2 equiv. of $AgSbF_6$ in CH_2Cl_2. The product was found to be [RuCl(*p*-cymene)(κ^2-tripm)][SbF_6] (**3**).

The ^{1}H NMR spectroscopic data show six different tripm resonances in the integral ratio 2:2:2:1:1:1 consistent with κ^2-binding rather than three resonances in 3:3:3 ratio, which would be consistent with the alternative $[Ru(p\text{-cymene})(\kappa^3\text{-tripm})]^{2+}$ structure. The uncoordinated ring shows diasterotopic resonances for the 3 and 5 protons.

The κ^2-tripm binding mode was found for **3** even though sufficient Ag^+ ion had been provided to remove both chlorides from the metal. Attempts to remove the remaining chloride with excess $AgSbF_6$ or $TlPF_6$ under more vigorous conditions (THF, reflux) were uniformly unsuccessful, suggesting that the κ^3-tripm binding mode may be unfavorable.

5. Crystal structure of [RuCl(*p*-cymene)(κ^2-tripm)][SbF_6]

To verify the structure of **3** and binding mode of tripm, an arene ruthenium complex. [RuCl(*p*-cymene)(κ^2-tripm)][SbF_6] (**3**) was synthesized in 80% yield by reaction of $[RuCl_2(p\text{-cymene})]_2$ with 2 equiv. of tripm, and 2 equiv. of $AgSbF_6$ in CH_2Cl_2. Crystals of **3** were obtained and the X-ray structure solved. The distances and bond angles established in this molecule are very similar to those identified in the tripyridylamine ana-

logue, [RuCl(*p*-cymene)(κ²-tripyam)][SbF_6] **2b** (Tables 1 and 2; Fig. 1).

A surprise was the fact that the third, uncoordinated pyrimidine is orthogonal to the central –NAr_2 system, unlike the near-coplanar arrangement in the κ²-tripyridylamine analogue. A coplanar arrangement favors resonance stabilization of the central N lone pair but militates against κ³-binding to the metal; an orthogonal arrangement prevents resonance but permits κ³-binding because the pyrimidine N of the third ring now points towards the metal. This suggests that the earlier proposal 2b, that κ²-binding of tripyam and tripm is inhibited by resonance stabilization of the coplanar arrangement for the third ring, is over-simple. In the new structure (**3**) we now see that the central N lone pair can be resonance-stabilized by the two coordinated rings with the result that in **3** the coordinated –NAr_2 system is much closer to coplanar than in the tripyam analogue. Nevertheless, the resonance stabilization of the N lone pair, whatever its source, still keeps the three N–Ar bonds near coplanar and in that way disfavors κ³-binding because this requires a pyramidal sp^3 central N.

Table 1
Crystal data of [RuCl(*p*-cymene)(κ²-tripm)][SbF_6] (**3**)

Empirical formula	$C_{22}H_{23}N_7ClRuSbF_6$
Formula weight	757.73
Crystal color/habit	orange prisms
Crystal dimensions (mm)	$0.097 \times 0.17 \times 0.31$
Crystal system	monoclinic
No. reflections used for unit cell determination	25 (10.6–18.0°)
Lattice parameters	
a (Å)	9.814(4)
b (Å)	19.469(7)
c (Å)	13.936(6)
β (°)	105.07(3)
V (Å³)	2571(3)
Space group	$P2_1/a$ (# 14)
Z value	4
D_{calc} (g cm^{-3})	1.957
*F*000	1480
μ(Mo Kα) (cm^{-1})	18.07

Table 2
Selected bond lengths (Å) and angles (°) for [RuCl(*p*-cymene)(κ²-tripm)][SbF_6] (**3**)

Bond angles	
Cl–Ru–N2	87.3(1)
Cl–Ru–N6	87.4(1)
N2–Ru–N6	79.6(2)
Ru–N2–C1	118.9(3)
Ru–N2–C2	123.3(4)
C1–N2–C2	116.1(5)
Ru–N6–C9	120.6(3)
Ru–N6–C10	122.3(3)
C6–N9–C10	116.4(4)
Bond lengths	
Ru–Cl	2.388(2)
Ru–N2	2.111(4)
Ru–N6	2.109(4)
Ru–C13	2.225(5)
Ru–C14	2.201(5)
Ru–C15	2.198(5)
Ru–C16	2.213(5)
Ru–C17	2.184(5)
Ru–C18	2.161(5)
N1–C1	1.370(6)
N1–C5	1.449(6)
N1–C9	1.403(6)

The Ru–N distances in **3**, 2.111(4) and 2.109(4) Å, are somewhat longer than in the tripyridylamine analogue (2.106(8) and 2.097(8) Å 2b). Although this difference is not very meaningful, it is at least consistent with pyrimidines binding less well than pyridines, in line with the lower pK_a of pyrimidine controlling the outcome and not in agreement with the idea that pyrimidines accept π back-bonding more effectively.

The abnormal orthogonal conformation for the uncoordinated pyrimidine ring seen in the crystal structure led us to look for factors that might be responsible. The endo-nitrogen of the ring, N(5), seemed to be abnormally close (3.56 Å) to C(17) of the arene ring. Assuming a planar arene allows us to place H(17) 1.09 Å away from C(17), this leads to parameters for the C(17)–H(17)···N(5) system (N···H, 2.70 Å; C–H···N, 135.4°) that are in the range (N···H, 2.52-2.72 Å; C–H···N, $>125°$) noted by Taylor and Kennard [10] in their classic study of C–H···X hydrogen bonds.

We conclude that this unusual sort of intermolecular C–H···N hydrogen bond may be favored because the C–H proton is expected to be abnormally acidic, both by binding to Ru(II) and by the net positive charge on the complex. The tripyridylamine complex **2b** does not show this C–H···N structure, so the energy of the hydrogen bond favoring an orthogonal ring may be comparable to the resonance energy favoring a coplanar ring and the outcome may be determined by packing effects.

6. Preferential κ² conformation of tripm

It has been reported that tripyridylamine can function either as a bidentate or a tridentate ligand, when coordinated to a transition metal [11]. Mosny et al. [2b,12] have also reported the conversion from a κ²-tripyridylamine to a κ³-tripyridylamine form in one case [12]. Several tripm complexes have now been synthesized, in all of which tripm apparently functions as a bidentate ligand, even though some of the corresponding tripyridylamine complexes have a tridentate structure. For example, we have reported [2] that

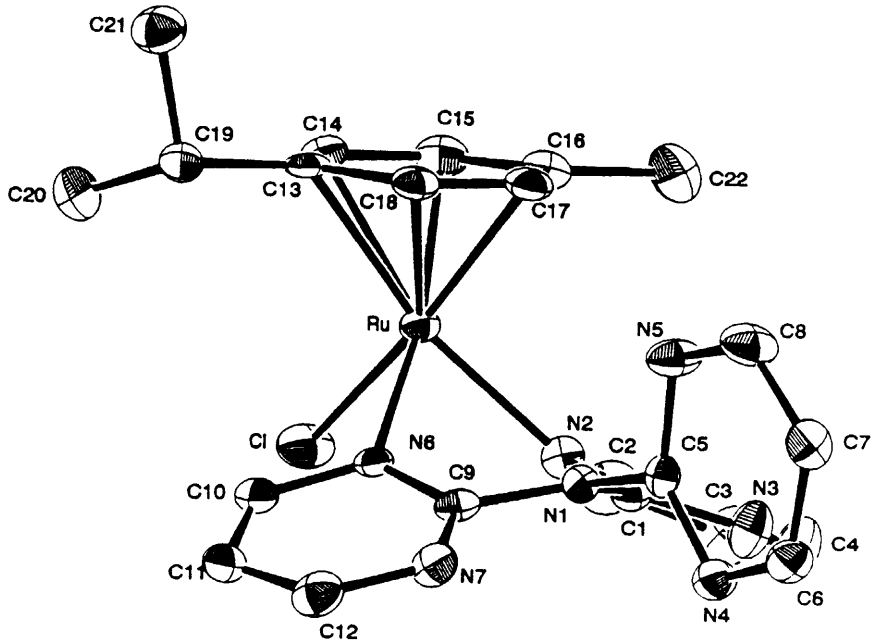

Fig. 1. ORTEP drawing of $[Ru(\eta^6\text{-cymene})(\kappa^2\text{-trpm})Cl]SbF_6$ (**3**).

$RuCl_2(PPh_3)_3$ reacts with tripyridylamine in refluxing methanol for 24 h to give $[RuCl_2(PPh_3)(\kappa^3\text{-tripyam})]$ [2], but exactly the same synthetic procedure applied totripm [12] gives $[RuCl_2(PPh_3)_2(\kappa^2\text{-tripm})]$. The κ^2-tripm structure is evident from the close analogy between the ^1H NMR spectrum of this complex with that of the crystallographically characterized species, **3**. This shows the higher tendency of tripm over tripyridylamine to adopt a κ^2-binding mode.

7. Experimental section

7.1. General

All manipulations were carried out in a dry Ar atmosphere using standard Schlenk techniques. Chemicals were used as received (Aldrich). ^1H NMR spectra were recorded on a GE Omega 300 spectrometer. Microanalyses were performed by Atlantic Microlab. $[RuCl_2(p\text{-cymene})]_2$ was synthesized according to the literature procedure [13].

7.2. Synthesis of dipm

A mixture of 2-aminopyrimidine (1.0 g, 1.1×10^{-2} mol), 2-chloropyrimidine (1.2 g, 1.1×10^{-2} mol), and K_2CO_3 (3.0 g, excess) was heated at 160°C for 1 h. Cold water (200 ml) was added, and the mixture was filtered to obtain an aqueous layer, which was further extracted with CH_2Cl_2 (2×200 ml). The organic layer was dried over $MgSO_4$ for 0.5 h, and then was reduced to afford an off-white product. Yield: 0.55 g (30%). ^1H NMR (CD_2Cl_2): δ 10.21 (s br, 1H), 8.68 (d, $^3J_{HH} = 4.8$ Hz, 4H), 6.94 (t, $^3J_{HH} = 4.8$ Hz, 2H). *Anal.* Calc. for $C_8H_7N_5$: C, 55.48; H, 4.07; N, 40.44. Found: C, 55.41; H, 4.12; N, 40.28%. GC–MS: 173 m/z.

7.3. Synthesis of tripm

Tripm was prepared by a modification of the method reported by Faller and Gundersen for making tripyam [5]. A mixture of dipm (400 mg, 2.30 mmol), 2-bromopyrimidine (2.8 g, 18 mmol), copper (0.2 g), KI (0.1 g), and K_2CO_3 (1.0 g) was refluxed at 160°C for 24 h in mesitylene (20 ml). The mixtures were then filtered through Celite, and to the filtrate were added hexanes (50 ml) to precipitate a brown solid. This was then dissolved in CH_2Cl_2 (40 ml) and eluted through a basic alumina column to obtain a colorless filtrate, which was then reduced in volume to afford a white solid product. Yield: 370 mg (65%). ^1H NMR (CD_2Cl_2): δ 8.63 (d, $^3J_{HH} = 4.9$ Hz, 6H), 7.11 (t, $^3J_{HH} = 4.9$ Hz, 3H). *Anal.* Calc. for $C_{12}H_9N_7$: C, 57.37; H, 3.61; N, 39.02. Found: C, 57.35; H, 3.59; N, 39.03%. GC–MS: 251 m/z.

7.4. Synthesis of $Mo(CO)_4(\kappa^2\text{-dipm})$

A mixture of $Mo(CO)_6$ (0.15 g, 0.57 mmol) and dipm (0.11 g, 0.64 mmol) was refluxed in toluene (20 ml) for 5 h. The resulting yellow–orange precipitate was filtered and washed with hexanes. Recrystallization from CH_2Cl_2–Et_2O afforded a yellow–orange solid. Yield: 105 mg (0.28 mmol, 49%). ^1H NMR (CD_2Cl_2): δ 9.10 (s br 1H, N–H), 8.65 (d, $J = 4.5$ Hz, 2H), 8.96 (d,

$J = 5.4$ Hz, 2H), 6.96 (dd, $J = 4.5$, 5.4 Hz, 2H). *Anal.* Calc. for $C_{12}H_7N_5MoO_4$: C, 37.86; H, 4.86; N, 18.38. Found: C, 37.49; H, 4.69; N, 18.15%.

7.5. Synthesis of [RuCl(p-cymene)(κ²-tripm)][SbF₆]

To a solution of $[RuCl_2(p\text{-cymene})]_2$ (30 mg, 0.050 mmol), tripm (25 mg, 0.10 mmol), and freshly distilled CH_2Cl_2 (20 ml) was added $AgSbF_6$ (34 mg, 0.10 mmol). The solution was stirred at room temperature in the absence of light for 30 min. It was then filtered through Celite to yield a clear bright yellow solution. The solvent was reduced in vacuo and hexanes were added. A precipitate formed and was filtered and washed with hexanes and dried in vacuo to yield a yellow solid, which was recrystallized from CH_2Cl_2–hexanes. Yield: 61 mg (80%). ^{1}H NMR (CD_2Cl_2): δ (tripm) 8.97 (d, $J = 4.8$ Hz, 2H), 8.95 (complex, 2H), 8.59 (d, $J = 4.5$ Hz, 1H), 8.57 (d, $J = 4.8$ Hz, 1H), 7.52 (t, $J = 5.0$ Hz, 1H), 7.37 (dd, $J = 4.8$, 4.5 Hz, 2H); (cymene C–*H*): 5.62 (d, $J = 6.0$ Hz, 2H), 5.51 (d, $J = 6.0$ Hz, 2H); [C*H*$(CH_3)_2$]: 2.94 (m, 1H); [C–C*H*$_3$]: 2.10 (s, 3H); [CH(C*H*$_3)_2$]: 1.31 (d, $J = 7.2$ Hz, 6H). *Anal.* Calc. for $C_{22}H_{23}N_7ClF_6RuSb$: C, 34.87; H, 3.04; N, 12.94. Found: C, 34.59; H, 2.99; N, 12.75%.

7.6. Synthesis of [RuCl₂(PPh₃)₂(κ²-tripm)]

To a solution of $RuCl_2(PPh_3)_3$ (1.6 g, 1.68 mmol) in dry degassed methanol (30 ml) was added tripm (0.58 g, 2.5 mmol). The stirred solution was refluxed for 15 h. After cooling, the resulting orange precipitate was filtered, washed with MeOH (10 ml), and ether (10 ml) and dried in vacuo. Recrystallization from CH_2Cl_2–hexanes gave the product (80%, 1.4 g, 1.3 mmol). ^{1}H NMR (CD_2Cl_2): δ (tripm) 9.0 (d, $J = 4.8$ Hz, 2H), 8.95 (multiplet, 2H), 8.65 (d, $J = 4.5$ Hz, 1H), 8.55 (d, $J = 5$ Hz, 1H), 7.0–8.0 (tripm, PPh_3 broad, 32H). *Anal.* Calc. for $C_{48}H_{39}N_7Cl_2P_2Ru$: C, 60.85; H, 4.12; N, 10.34. Found: C, 60.69; H, 3.99; N, 10.24%.

7.7. X-ray study on [RuCl(p-cymene)(κ²-tripm)][SbF₆]

The crystal data are reported in Table 1. A crystal of **3** was mounted on a glass fiber and data collected at $-90°$ on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation and the ω–2θ scan technique. The space group was based on the systematic absences and the successful refinement. Of the 5701 reflections collected, 5387 were unique ($R_{int} = 0.181$). The intensities of three representative reflections were measured after every 60 min and remained constant. The linear absorbtion correction was 18.1 cm^{-1}, but azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. The structure was solved by the Patterson method using 4089 observed ($I > 3\sigma(I)$) reflections and 343 variable parameters. The standard deviation of an observation of unit weight was 1.85. Calculations were performed using TEXSAN crystallographic software of Molecular Structure Corp.

8. Conclusions

Dipm (**1**) and tripm (**2**) can be successfully synthesized in moderate yield. The crystal structure of [RuCl(η⁶-*p*-cymene)(κ²-tripm)]SbF_6 (**3**) suggests the presence of an unusual intramolecular C–H···N hydrogen bond between the cymene C–H and pyrimidine N. IR data for $Mo(CO)_4$(dipm) suggest that dipm has a Tolman electronic effect close to that of a pair of PPh_3 ligands. The M–L bonding may not be as strong as in tripyridylamine because the κ²-form of tripm is apparently the common binding mode, as in $[RuCl_2(PPh_3)_2$-(κ²-tripm)], unlike the tripyridylamine analogue 2b, $[RuCl_2(PPh_3)$(κ³-tripyam)], which is κ³-bound. Resonance stabilization of the κ²-form, together with the weaker σ-donor character of tripm versus tripyridylamine, is thought to be responsible.

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