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TRANSITION METAL COMPLEXES OF TRÖGER'S BASE AND THEIR CATALYTIC ACTIVITY FOR THE HYDROSILYLATION OF ALKYNES

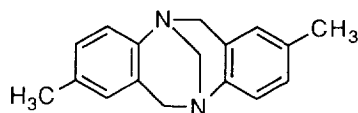
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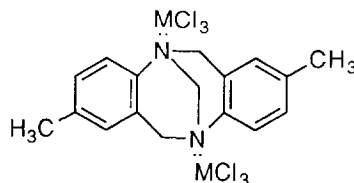
Abstract. Rhodium(III) and iridium(III) complexes of Tröger's base (TB), of structural type $TB \cdot 2MCl_3$ ($M = Rh, Ir$), were prepared by treatment of TB with MCl_3 . The rhodium complex readily catalyzed the hydrosilylation of alkynes with high regio- and stereoselectivity observed in some cases.

Tröger's base (TB),¹ one of the more fascinating molecules in organic chemistry,² has received a great deal of attention within the last decade. This V-shaped chiral amine, whose chirality is solely due to the presence of two stereogenic nitrogen atoms, is of interest as a unit in the construction of molecular receptors³ and as a chiral solvating agent.⁴ A number of recent reports deals with the synthesis and study of TB, its derivatives, analogues and their inclusion compounds.^{3,5}

We anticipated that transition metal complexes containing a rigid TB ligand may display interesting catalytic properties especially in terms of regio- and stereoselectivity. To our knowledge there are no examples of TB-containing metal complexes in the literature. Addition of an ethanolic solution of (\pm)-TB (1 equiv.) to a solution of rhodium(III) chloride hydrate (2 equiv.) in ethanol at room temperature results in the formation of a pink solid which was isolated in 84% yield. The same product is formed using a 1:1 or 2:1 ratio of TB to $RhCl_3$. The 1H NMR spectrum shows that the complex retains the symmetrical structure of TB, thus indicating that both nitrogen atoms are coordinated to rhodium atoms. The proton signals of the endo-methylene group, benzylic groups and aromatic rings are strongly affected by the coordination of TB to the rhodium centers (Fig. 1). Elemental analysis data are also in accord with the formula for $TB \cdot 2RhCl_3$.⁶ Enantiomerically pure TBs reacted similarly.⁶ The reaction of TB with iridium(III) chloride hydrate gives $TB \cdot 2IrCl_3$ in 85% yield.⁷



TB



$TB \cdot 2MCl_3$, $M = Rh$ or Ir

Both $\text{TB}\cdot\text{RhCl}_3$ and $\text{TB}\cdot\text{IrCl}_3$ are air stable and non-hygroscopic; they are miscible in DMF and DMSO and insoluble in common organic solvents such as EtOH, Me_2CO , ether, THF, CHCl_3 , CH_2Cl_2 , etc.

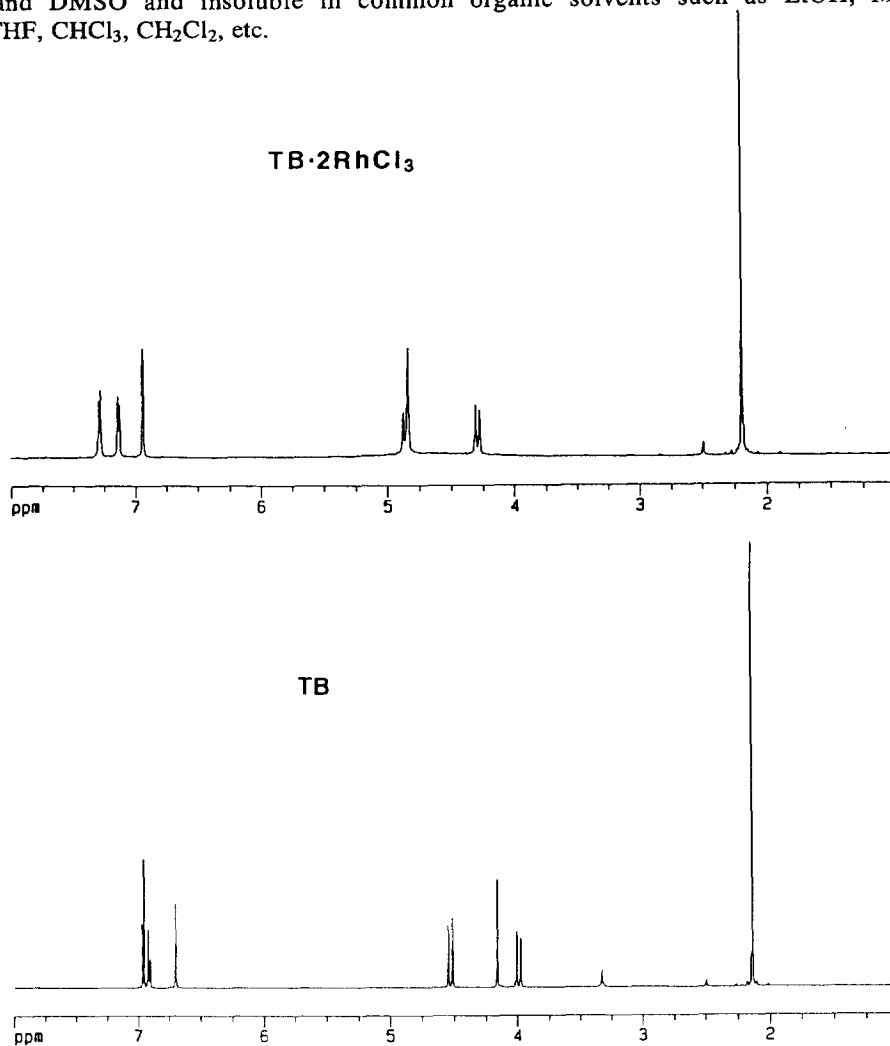
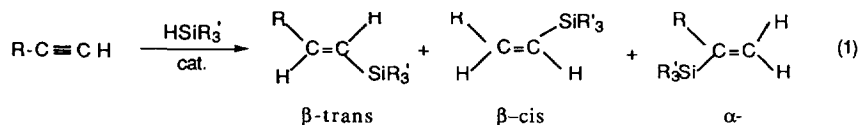


Fig. 1. 500 MHz ^1H -NMR spectra of Tröger's base (bottom) and $\text{TB}\cdot 2\text{RhCl}_3$ (top) in DMSO-d_6 .

The hydrosilylation of terminal alkynes was chosen as a model system to assess the catalytic activity of $\text{TB}\cdot 2\text{MCl}_3$. This reaction can afford the normal syn-addition product (β -trans-alkenylsilane), thermodynamically less stable anti-addition product (β -cis-alkenylsilane), as well as the α -isomer [eq. (1)].^{8,9}

The hydrosilylation reactions were effected without added solvent, using equimolar amounts of alkyne and silane and 0.1 mol.% of catalyst. The rhodium-containing



complex readily catalyzed the addition of various silanes to terminal alkynes (see Table 1) whereas its iridium counterpart was virtually inactive.

Table 1. Hydrosilylation of terminal alkynes catalyzed by TB-2RhCl₃^a

Alkyne	Silane	Conditions: temperature, time	Conversion, %	Products ratio ^b		
				β -trans	β -cis	α -
PhC≡CH	HSiCl ₃	r.t., 24 h	100	5	95	-
	HSiMe ₂ Cl	r.t., 48 h	100	23	77	-
	HSiMe ₂ Ph	r.t., 24 h	100	5	95	-
	HSiMe ₂ Bu-t	70°C, 24 h	100	80	-	20
	HSiEt ₃	r.t., 48 h	86	39	43	18
	HSi(Pr-i) ₃	100°C, 72 h	100	95	-	5
BuC≡CH	HSiMe ₂ Ph	r.t., 24 h	64	22	78	-
	HSiMe ₂ Cl	r.t., 24 h	37	59	29	12
Cl(CH ₂) ₃ C≡CH	HSiMe ₂ Ph	r.t., 24 h	100	23	77	-
	HSiMe ₂ Cl	r.t., 24 h	55	56	28	18
	HSiEt ₃	r.t., 48h	36	6	94	-

^aAlkyne (3 mmol), silane (3 mmol), catalyst (3·10⁻³mmol); ^bRatios were determined by NMR and GC.

Phenylacetylene reacted smoothly at room temperature with silanes, containing electron-withdrawing groups at silicon (HSiCl₃, HSiMe₂Cl, HSiMe₂Ph), affording the β -cis-vinylsilanes as the principal products. It should be pointed out that the β -cis-alkenylsilanes formed, did not undergo isomerization to the thermodynamically more stable trans-isomers.^{9,10} Trialkylsilanes, as anticipated, were less reactive than chloro- or phenylsilanes. While HSiMe₂Bu-t and HSi(Pr-i)₃ only reacted with PhC≡CH at elevated temperatures and gave mainly the trans-adducts, HSiEt₃ did react at room temperature but with lower regio- and stereoselectivity. Aliphatic alkynes are less reactive than phenylacetylene and under similar conditions their conversions were lower. Treatment of 1-hexyne and 5-chloro-1-pentyne with HSiMe₂Ph gave β -cis-alkenylsilanes as the major products. Addition of HSiMe₂Cl to the same alkynes was less selective with the β -trans-adduct predominating. Finally, triethylsilane slowly hydrosilylated 5-chloro-1-pentyne affording the corresponding β -cis-adduct in a highly stereoselective manner. It should be also emphasized that RhCl₃ did not catalyze the reaction of PhC≡CH with HSiMe₂Ph at room temperature (24 h); no hydrosilylation also occurred at 100°C, some polymerization of phenylacetylene took place under these conditions. Therefore, a TB-containing rhodium complex (rather than silane-stabilized colloidal metal formed by the dissociation of RhCl₃ from the complex followed by the reduction with the silane) is the catalytically active species. The homogeneity of the catalyst was confirmed by a mercury test.¹¹ The reaction of

phenylacetylene with HSiMe_2Ph , in the presence of a large excess of mercury ($\text{Hg}:\text{Rh}\approx 100:1$), gave the same products, with the same ratio, within the same period of time and under the same reaction conditions as the experiment effected in the absence of mercury.

In conclusion, TB readily forms complexes of type $\text{TB}\cdot 2\text{MCl}_3$ by reaction with MCl_3 ($\text{M} = \text{Rh}, \text{Ir}$). $\text{TB}\cdot 2\text{RhCl}_3$ smoothly catalyzes the hydrosilylation of terminal alkynes giving rise in some cases to anti-addition products, viz. cis-alkenylsilanes, with selectivity of up to 95%. Both Rh and Ir complexes derived from enantiomerically pure TB are potential catalysts for asymmetric transformations. These studies are currently in progress in this laboratory.

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6. **Synthesis of $\text{TB}\cdot 2\text{RhCl}_3$.** A solution of (\pm)-TB (250 mg, 1 mmol) in 95% ethanol (20 mL) was added dropwise to a solution of $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ (572 mg, 2 mmol) in ethanol (30 mL). The reaction mixture was stirred at room temperature for 6 h. The pink solid was filtered, washed thoroughly with ethanol (20 mL) and dried first in air and then in vacuo (0.5 mm Hg, 50-60°C, 12 hrs). Yield: 560 mg (84%). Anal. Found: C 30.15, H 3.10, N 4.38, Cl 32.11; Calcd.: C 30.53, H 2.71, N 4.19, Cl 31.80. $^1\text{H-NMR}$ ($\text{DMSO-d}_6/\text{TMS}$), δ (ppm) 2.22 (s, 6H), 4.29 and 4.85 (ABq, $J = 16$ Hz, 4H), 4.81 (s, 2H), 6.95 (s, 2H), 7.14 and 7.32 (ABq, $J = 8$ Hz, 4H). ($-$)- $\text{TB}\cdot 2\text{RhCl}_3$ and ($+$)- $\text{TB}\cdot 2\text{RhCl}_3$ were prepared similarly from the corresponding enantiomerically pure TBs in 87 and 84% yield, respectively.
7. **$\text{TB}\cdot 2\text{IrCl}_3$:** dark-violet powder, yield 80%; $^1\text{H NMR}$ ($\text{DMSO-d}_6/\text{TMS}$), δ (ppm): 2.22 (s, 6H), 4.31 and 4.89 (ABq, $J = 16$ Hz, 4H), 4.86 (s, 2H), 6.95 (s, 2H), 7.14 and 7.32 (ABq, $J = 8$ Hz, 4H); anal. Found: C 24.34, H 2.41, N 3.08, Cl 25.45; Calcd. C 24.09, H 2.14, N 3.31, Cl 25.10.
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10. No isomerization occurred when reaction mixture, obtained by the hydrosilylation of phenylacetylene with dimethylphenylsilane, was allowed to stand in the presence of $\text{TB}\cdot \text{RhCl}_3$ for two days at room temperature.
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