Synthesis of bis(benzotriazol-1-yl)methane derivatives by cobalt-catalyzed formation of C-C bonds

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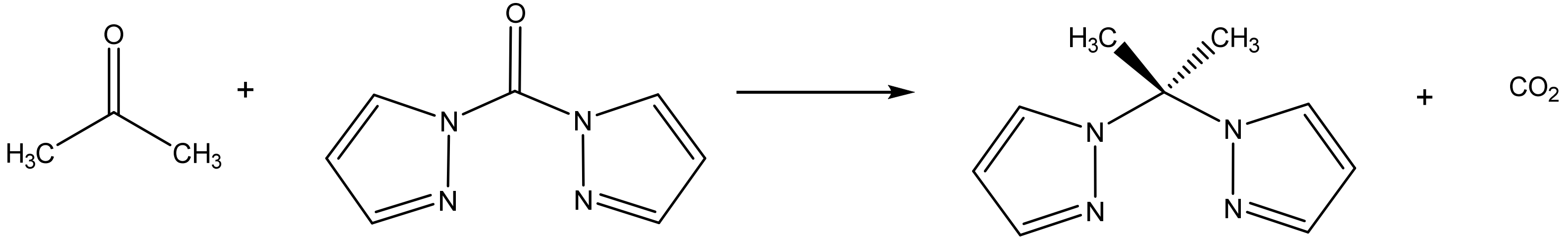
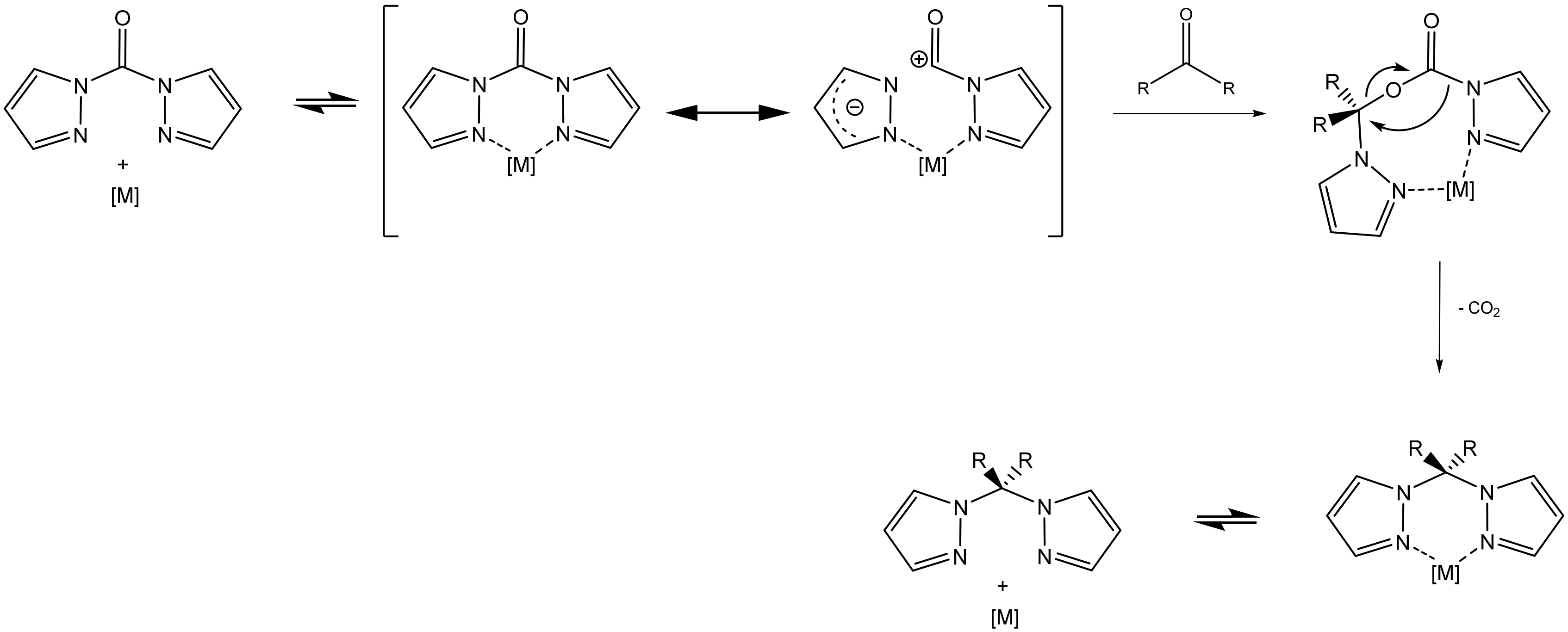
Introduction

Thé and Peterson reported the first example of $CoCl_2$-catalyzed reaction between 1,1'-carbonyldiazoles and carbonyl compounds in 1973. By elimination of CO_2, 2,2-bis(pirazol-1-yl)propane was obtained from bis(pyrazol-1-yl)methanone and acetone.



K. I. Thé, L. K. Peterson, *Can. J. Chem.* **51** (1973) 422-426.

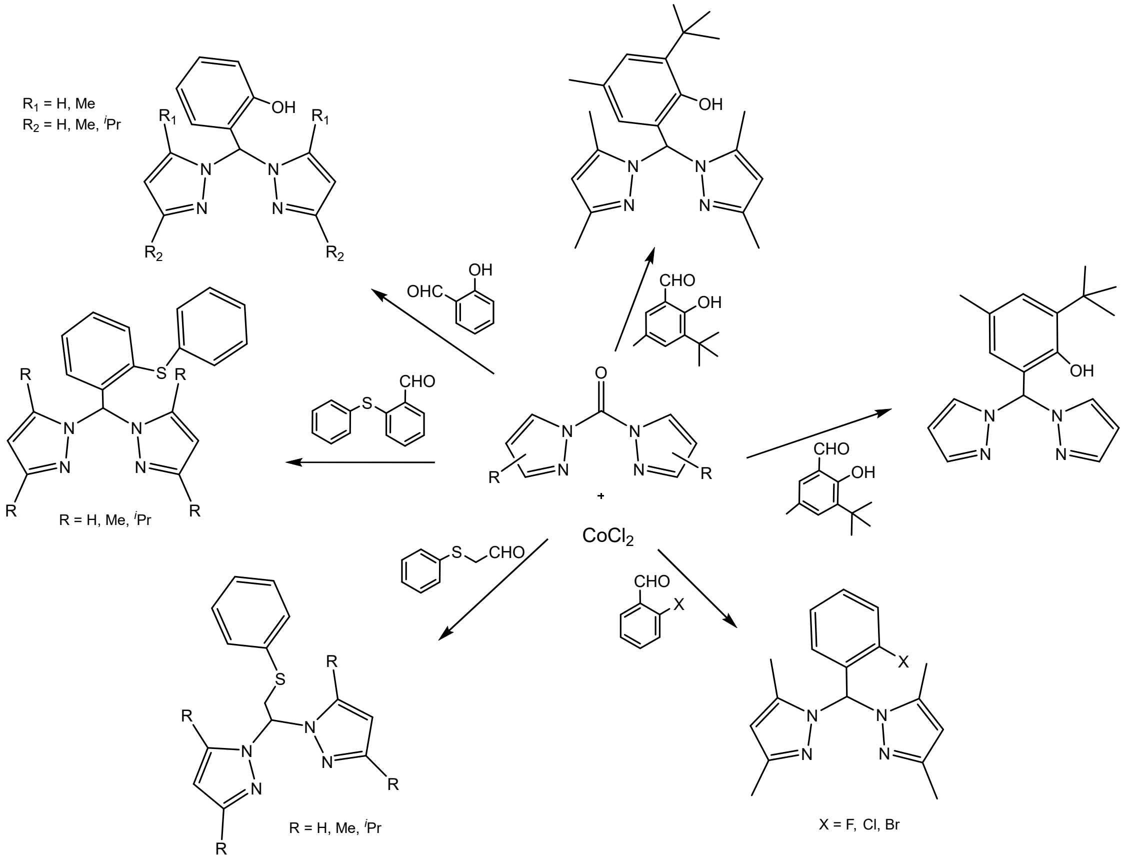
The following mechanism was later proposed:



K. I. Thé et al., *Can. J. Chem.* **51** (1973) 2448-2451.
L. K. Peterson et al., *Can. J. Chem.* **52** (1974) 2367-2374.

Further developments

The same synthetic approach was extended to aldehydes:



T. C. Higgs, C. J. Carrano, *Inorg. Chem.* **36** (1997) 291-297.
B. S. Hammes, C. J. Carrano *Inorg. Chem.* **38** (1999) 3562-3568.
T. C. Higgs, C. J. Carrano, *Eur. J. Org. Chem.* (2002) 3632-3645.

D.-W. Zhao et al., *J. Organomet. Chem.* **718** (2012) 89-95.
S. Tardito et al., *J. Am. Chem. Soc.* **133** (2011) 6325-6242.

The versatility of the synthesis allowed to obtain derivatives applicable in different areas of research.

Fields of application

Coordination chemistry

T. C. Higgs, C. J. Carrano, *Inorg. Chem.* **36** (1997) 298-306.

T. C. Higgs et al., *Inorg. Chem.* **37** (1998) 1473-1482.

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M. Strianese et al., *Inorg. Chem.* **50** (2011) 900-910.

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I. Bassanetti et al., *J. Am. Chem. Soc.* **136** (2014) 14883-14895.

I. Bassanetti et al., *Cryst. Growth Des.* **16** (2016) 3543-3552.

Bioinorganic chemistry

B. S. Hammes, C. J. Carrano, *Chem. Commun.* (2000) 1635-1636.

A. Beck et al., *Eur. J. Inorg. Chem.* (2001) 521-527.

C. R. Warthen et al., *J. Biol. Inorg. Chem.* **6** (2001) 82-90.

B. Kail et al., *Inorg. Chem.* **41** (2002) 1281-1291.

Organometallic chemistry and homogeneous catalysis

S. Milione et al., *Chem. Commun.* (2003) 1176-1177.

S. Milione et al., *Organometallics* **24** (2005) 4915-4925.

S. Milione et al., *Organometallics* **25** (2006) 266-274.

G.Paolucci et al., *Inorg. Chim. Acta* **362** (2009) 4353-4347.

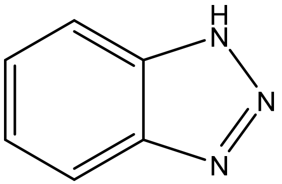
A. F. R. Kilpatrick et al., *Dalton Trans.* **39** (2010) 3653-3664.

A. Silvestri et al., *J. Polym. Sci. Part A* **48** (2010) 3632-3639.

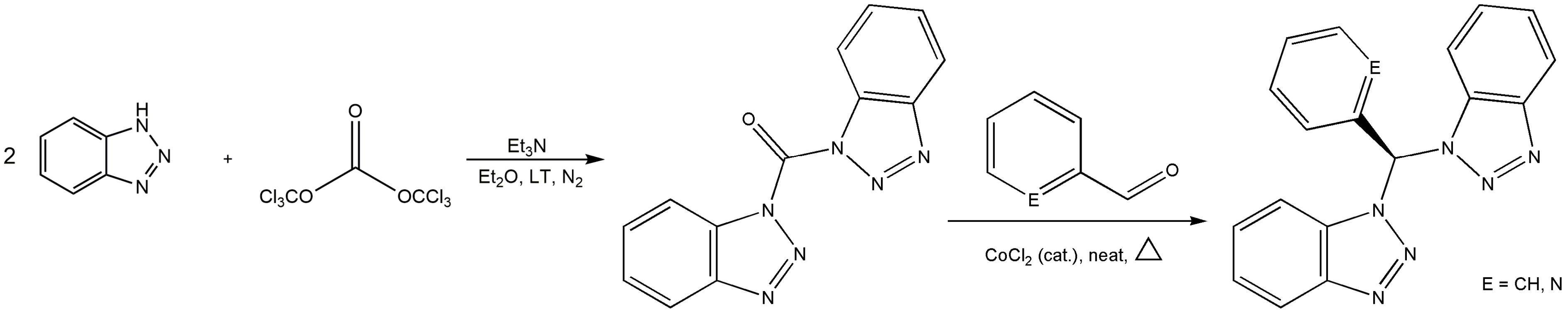
K. Ding et al., *J. Organomet. Chem.* **696** (2011) 3662-3667.

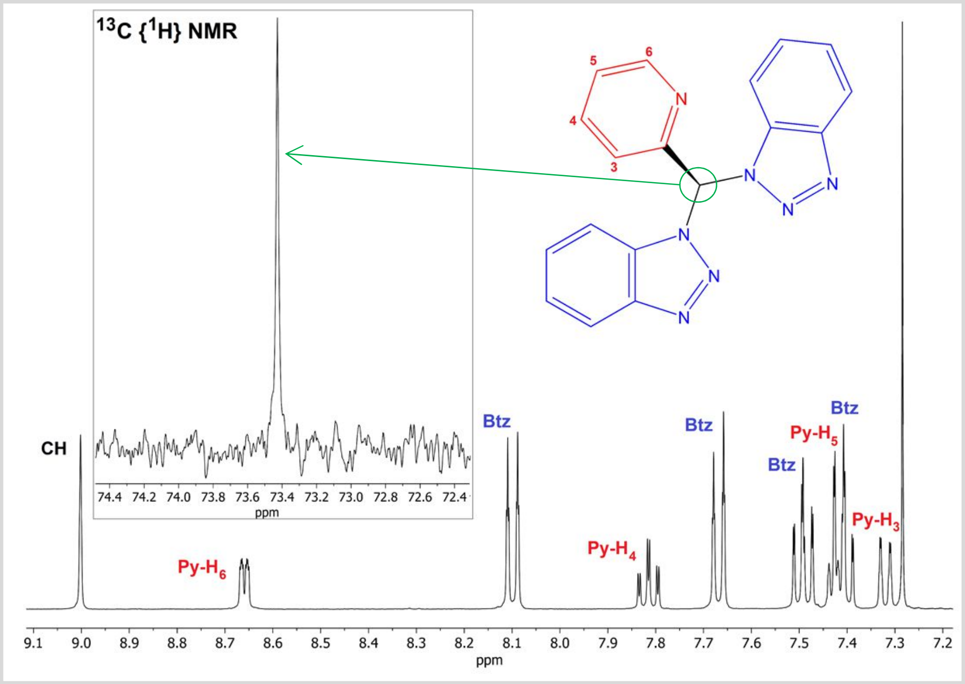
Benzotriazole

Benzotriazole appears to be both an ideal synthetic auxiliary in organic chemistry and a N-donor moiety in heteroscopionate ligands. However, to our knowledge, the synthetic approach presented was never applied to this heterocycle. These reasons led us to investigate bis(benzotriazol-1-yl)methanone to prepare directly bis(benzotriazol-1-yl)phenylmethane and bis(benzotriazol-1-yl)pyridin-2-ylmethane using the proper aldehyde and $CoCl_2$ as catalyst.

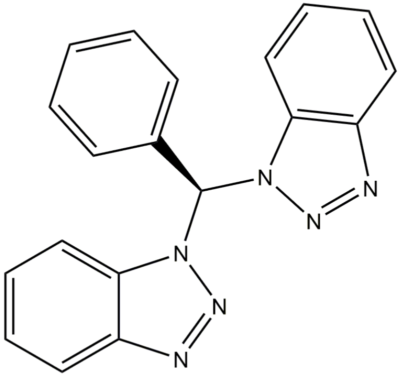


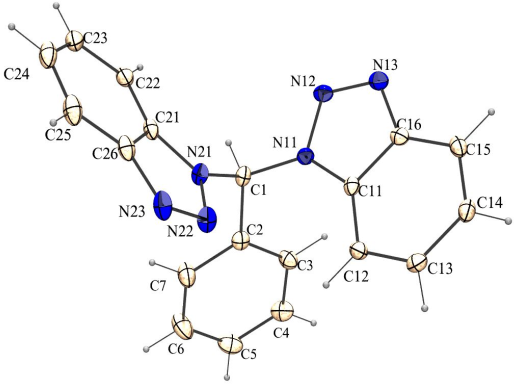
Results and Discussion



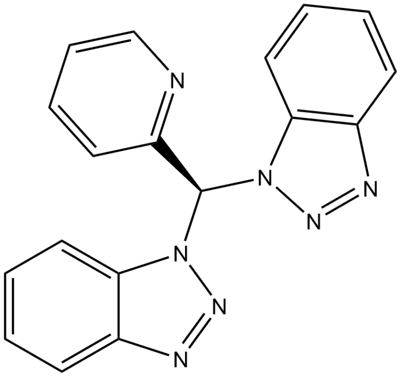


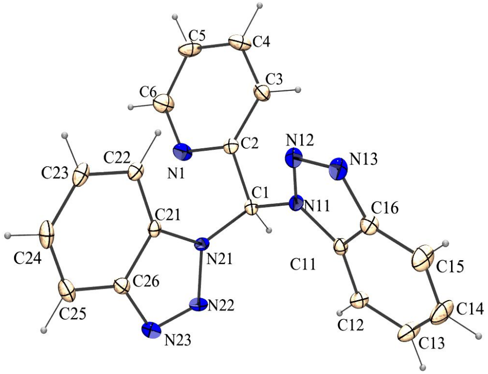
XRD characterization





Bis(benzotriazol-1-yl)phenylmethane	
C(1)-N(11)	1.4511(16) Å
C(1)-N(21)	1.4595(16) Å
C(1)-C(2)	1.5199(17) Å
N(11)-C(1)-N(21)	110.45(10)°
N(11)-C(1)-C(2)	114.23(10)°
N(21)-C(1)-C(2)	112.20(10)°



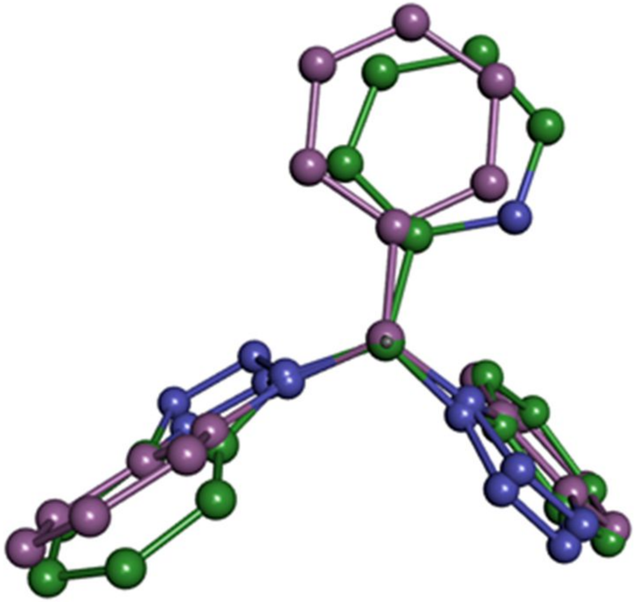


Bis(benzotriazol-1-yl)phenylmethane	
C(1)-N(11)	1.4548(14) Å
C(1)-N(21)	1.4542(14) Å
C(1)-C(2)	1.5285(16) Å
N(11)-C(1)-N(21)	109.86(9)°
N(11)-C(1)-C(2)	115.05(9)°
N(21)-C(1)-C(2)	110.72(9)°

Bond lengths and angles around C(1) are in line with a sp^3 configuration of the carbon atom.

XRD characterization

The three cycles adopt a helical conformation and nitrogen atoms (if present) are, as far as possible, in an anti- or pseudo trans conformation.



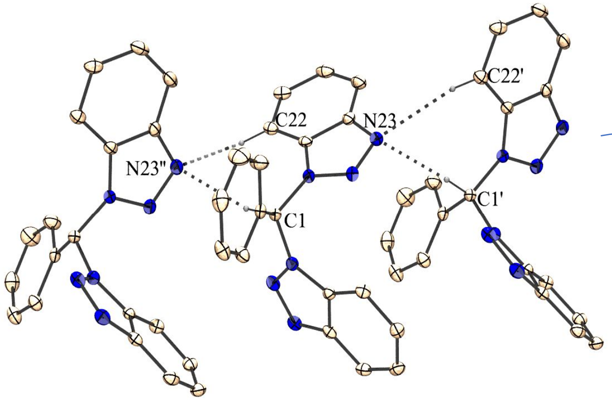
Selected torsion angles with H(1)-C(1) bond:

Bis(benzotriazol-1-yl)phenylmethane	
H(1)-C(1)-N(11)-N(12)	13.26°
H(1)-C(1)-N(11)-C(11)	-175.55°
H(1)-C(1)-N(21)-C(21)	-7.32°
H(1)-C(1)-N(21)-N(22)	177.74°
H(1)-C(1)-C(2)-C(3)	86.94°
H(1)-C(1)-C(2)-C(7)	-85.02°

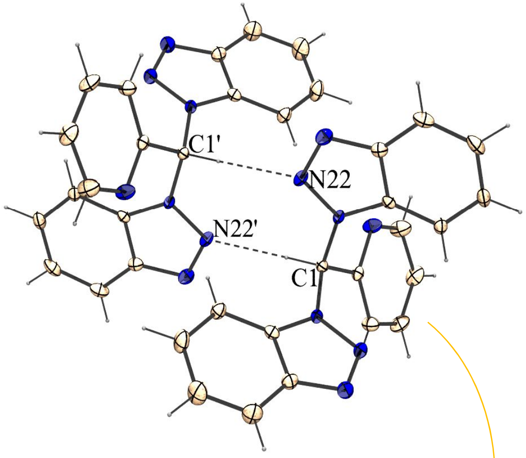
Bis(benzotriazol-1-yl)pyridin-2-ylmethane	
H(1)-C(1)-N(11)-N(12)	161.34°
H(1)-C(1)-N(11)-C(11)	31.40°
H(1)-C(1)-N(21)-N(22)	16.51°
H(1)-C(1)-N(21)-C(21)	165.86°
H(1)-C(1)-C(2)-N(1)	78.87°
H(1)-C(1)-C(2)-C(3)	97.81°

XRD characterization

The supramolecular structure does not contain the classical *π,π*-stacking between the rings but non-classical C-H···N hydrogen bond can be found.



The interactions grow in the *b*-direction.



Only dimeric structures are generated.

D-H...A	**d(D-H)**	**d(H...A)**	**d(D...A)**	**<(DHA)**
bis(benzotriazol-1-yl)phenylmethane				
C(1)-H(1)...N(23^{i})	1.00 Å	2.27 Å	3.1285(17) Å	143.6°
C(22)-H(22)...N(23^{i})	0.95 Å	2.61 Å	3.3776(17) Å	138.1°
bis(benzotriazol-1-yl)pyridin-2-ylmethane				
C(1)-H(1)...N(22^{ii})	1.00 Å	2.36 Å	3.3625(15) Å	175.6°

Symmetry transformations used to generate equivalent atoms: i: x, 1.5-y, z-0.5; ii: 1-x,1-y, -z.

Future outlook

The $CoCl_2$-catalyzed reaction can be easily extended to other aldehydes and ketones to afford homo- and heteroscopionates that can be applied in coordination chemistry as bi- or tridentate ligands.

The new bis(benzotriazol-1-yl)pyridin-2-ylmethane is currently under investigation as an example of homoscorpionate ligand in coordination chemistry.