Stereoisomerism of *bis*(σ-Zincane) Complexes: Evidence for an Intramolecular Pathway

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Dedication ((optional))

Abstract: *The first bis(σ-zincane) complexes, heterotrimetallic species [M(CO)$_4$(η^2-HZnBDI)$_2$], have been prepared (BDI = κ^2-{2,6-i-Pr$_2$C$_6$H$_3$NCMe}$_2$CH). For M = Cr a single stereoisomer is observed in solution and the solid-state. For M = Mo and W, cis and trans isomers where found to reversibly interconvert at 297 K. Despite the huge steric demands of the ligand on zinc, in all cases the cis isomer was found to be the most thermodynamically stable. The activation parameters for the isomerization when M = Mo are ΔH‡ = 20.8 kcal mol^{-1} and ΔS‡ = –12.8 cal K^{-1} mol^{-1}. In combination with DFT calculations, the negative activation entropy suggests an intramolecular rotation mechanism for isomerization.*

Analysis of the solution chemistry of metal carbonyl complexes has shed light on the mechanisms of ligand exchange at octahedral transition metals. For example, *cis* to *trans* isomerization of [M(CO)$_4$L$_2$] complexes has been shown to be dependent on the nature of the ligand, L.[1-5] For sterically demanding phosphines (L = PPh$_3$, PPhCy$_2$, P(O-*o*-tolyl)$_3$), ligand dissociation to form a coordinatively unsaturated 16-electron intermediate is the dominant pathway, while for smaller phosphines (L = P(OMe)$_3$, PMe$_3$, PEt$_3$, P^{n}Bu$_3$) an intramolecular process has been postulated.[6-8] One possible mechanism for the latter pathway is a 120° rotation of the ligands about a C_3-axis of the octahedron *via* a trigonal prismatic intermediate or transition state.[9] The switch between mechanisms has been rationalized in terms of the *cis*-labilizing effect of ligands with a greater steric influence. The data gained from these studies has informed analysis of countless catalytic processes with transition metal complexes.

Little is known about the stereoisomerism of *bis*(σ-complexes) in which two E–H bonds are coordinated to a transition metal (E = H, CR$_3$, SiR$_3$, BR$_2$).[10-13] Both the geometric relation of heavy atoms and the relative position of the hydrides needs to be considered (Figure 1).

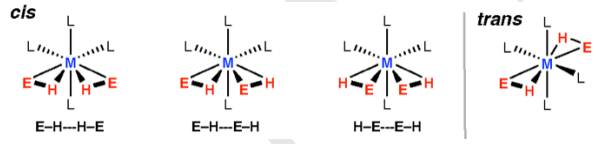

Figure 1. Stereoisomers of an octahedral [ML$_4$(η^2-H–E)$_2$] complex, E = H, CR$_3$, SiR$_3$ or BR$_2$.

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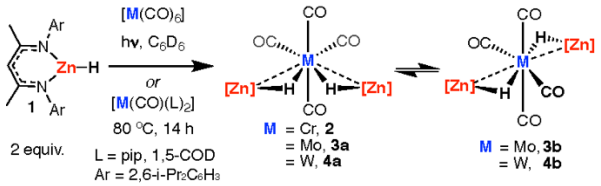
Due to the paucity of suitable systems for study, it is not yet clear if our textbook descriptions of isomerization can be extended to *bis*(σ-complexes). For the handful of *bis*(σ-complexes) that have been isolated,[14-18] either bond activation competes with isomerization,[19,20] the E–H bonds are incorporated within a chelating ligand that biases the system to certain geometries,[21-26] or rates of ligand exchange are too fast to permit a detailed study of the reaction mechanism.[27-29] Insight into isomerization mechanisms may have direct relevance to catalytic processes involving σ-complex assisted metathesis,[10,30] for which dynamic processes involving E–H bonds adjacent to reactive hydrides are well understood.[31,32]

In the past few years we,[33-38] and others,[39-43] have investigated the coordination of Al–H, Ga–H, Zn–H, and Mg–H bonds to transition metals.[44,45] Herein we report stereoisomerism in *bis*(σ-zincane) complexes of the group 6 carbonyls: fluxional heterotrimetallics. Through a combined experimental and computational approach, we conclude that isomerization occurs by an intramolecular mechanism that directly parallels classic examples.[6-8] The photochemical reaction of **1** with [M(CO)$_6$] in a 2:1 ratio yielded a single product **2** in the case of M = Cr. Isolated samples of **2** display a single bridging hydride resonance at δ = – 8.08 ppm in C$_6$D$_6$. X-ray diffraction studies allowed the positions of the hydrides to be resolved in the difference map and assignment of **2** as a *bis*(σ-zincane) complex with a *cis*-geometry and a Zn–H---H–Zn arrangement (*vide infra*). Infrared data on **2** revealed carbonyl stretches consistent with a predicted approximate C_{2v}-symmetry.[1]



Scheme 1. Synthesis and isomerization of Zn–M–Zn heterotrimetallics. [Zn] = Zn*BDI* (*BDI* = {2,6-i-Pr$_2$C$_6$H$_3$NCMe}$_2$CH).

In contrast, a mixture was observed when **1** reacts with either of the heavier group 6 carbonyls, M = Mo or W, under photochemical conditions (Scheme 1). Two bridging hydride resonances are observed for both the Mo and W analogues (**3a**, δ = – 5.63 ppm; **3b**, δ = – 7.01 ppm; **4a**, δ = – 6.18 ppm, $^1J_{W–H}$ = 51.6 Hz; **4b**, δ = – 7.23 ppm, $^1J_{W–H}$ = 63.6 Hz). The ratio of products is not under kinetic control and identical mixtures were obtained by reaction of **1** with either [*cis*-W(CO)$_4$(1,5-COD)] or [*cis*-Mo(CO)$_4$(pip)$_2$] (pip = piperidine) under thermal conditions. A weight of evidence supports the formation of geometric isomers.

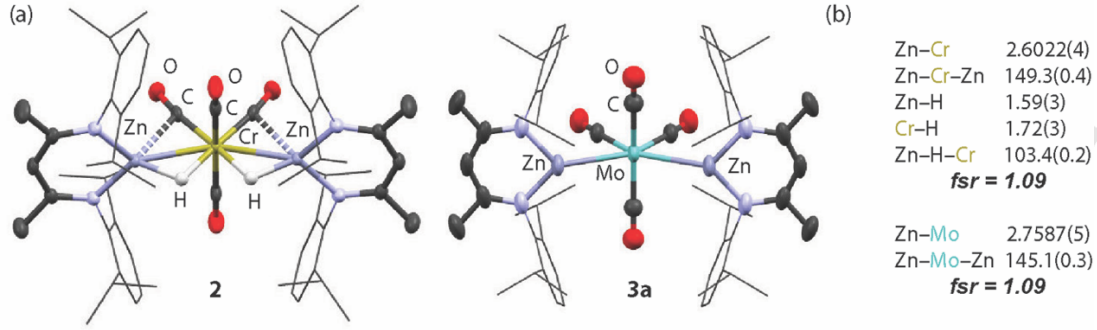


Figure 2. (a) The crystal structures of **2** and **3a**. The disorder of each structure over two sites is not represented. (b) Experimental data bond lengths (Å) and angles (°); *fsr* is the formal shortness ratio.[46]

Crystallographic analysis on four independent samples of **3-4** repeatedly returned near identical structures bearing a *cis*-relation of the main group metals. The Zn–M–Zn angle ranges from 145 - 150° (Figure 2). ^{1}H–^{13}C HMBC experiments elucidated the $^{2}J_{C-H}$ coupling between the hydride and carbonyl ligands in **3-4.** These experiments showed two carbonyl resonances for the major *cis*-isomers (**2**, δ = 215.2, 220.0 ppm; **3a**, δ = 203.8, 212.7 ppm; **4a**, δ = 194.5, 202.2 ppm). The minor isomers have only a single carbonyl resonance (**3b**, δ = 206.5 ppm; **4b,** 196.0 ppm) and hence the time-averaged D_{4h}-symmetry expected for a *trans bis*(σ-zincane).

Due to the close proximity of the hydrogen atoms in the solid-state data of **2**, an equilibrium between a metal dihydrogen complex and *bis*(σ-zincane) complex was considered as an alternative explanation for the data. Formation of an H–H bond was ruled out conclusively, however, by a series of NMR experiments. Complexes **3-4** show long T_1 relaxation times (0.7 to 1.3 s) across 188 to 298 K, and are well beyond those established for enhanced relaxation rates in dihydrogen complexes. Furthermore, a partially deuterated (~50% H, ~50 % D) analogue of **4a/b**, prepared by addition of a 1:1 mixture of **1** and **1-D** to [W(CO)$_6$], showed no significant $^{1}J_{H-D}$ coupling ruling out formation of a H–D bond.

A variable temperature NMR study on **4a/4b** across a 193 – 353 K range revealled only small changes in the ratio of the isomers and effectively no change in $^{1}J_{W-H}$ values as the temperature was varied. Nevertheless, EXSY NMR experiments showed, in all cases, that the geometric isomers are in chemical exchange at 297 K. Hence, tungsten-based heterotrimetallics **4a** and **4b** are in equilibrium with one another, as are the molybdenum analogues **3a** and **3b**. In all cases the *cis*-isomer is the most stable. For the chromium complex **2** there is no evidence for the formation of the *trans*-isomer or a solution equilibrium.

Careful and repeated analysis of mixtures of **3a** and **3b** by ^{1}H NMR spectroscopy revealed that the position of equilibrium at 297 K could be perturbed by photolysis with a 400 W Hg lamp.[47,48] The first order rate constants (k_1 + k_{-1}) for the conversion of **3b** to **3a** (Figure 3a) were obtained by photolyzing a sample of **3a/b** in C_6D_6, freezing the reaction mixture immediately after the lamp was removed, transferring to an NMR spectrometer, warming to 298K and recording the ^{1}H NMR spectrum as a function of time.

Eyring analysis (Figure 3b) using this approach allowed complete characterization of the equilibrium for **3a/3b** (Figure 3c). If photolysis perturbs the ratio of a mixture **4a/4b** then the kinetics to reestablish the thermodynamic position of equilibrium are too fast to be measured by the approach outlined above. Activation parameters for the isomerization are displayed in Figure 3c and the negative entropy of activation is consistent with an intramolecular pathway. For comparison, intramolecular *trans*- to *cis*-isomerization of [Mo(CO)$_4$(P^{n}Bu$_3$)$_2$] has been shown to proceed with $\Delta H^{\ddagger}$ = 24.2 ± 1.6 kcal mol^{-1} and $\Delta S^{\ddagger}$ = – 9.8 ± 4.0 cal K^{-1} mol^{-1}.[8] Intermolecular phosphine dissociation from [Mo(CO)$_4$(PPh$_3$)$_2$] results in positive values of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ ≈ 30 kcal mol^{-1}.[49,50]

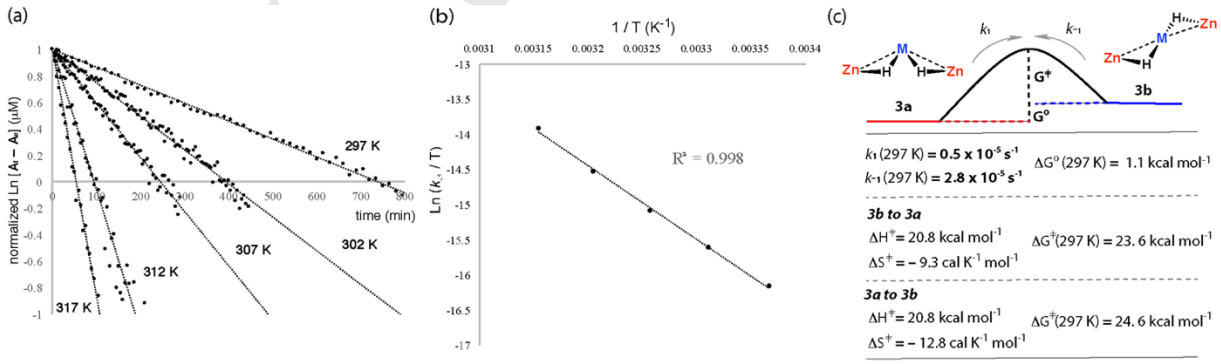


Figure 3. (a) Rates of reaction for conversion of **3b** to **3a**. (b) Eyring analysis for the conversion of **3b** to **3a**. (c) Quantitative data for the solution dynamics of **3a**/**3b**.

Monitoring the isomerization of **3a**/**3b** in the presence of an external ligand, HBpin, revealed no incorporation of the borane in to the product (HBpin = catecholborane).

The isomerization mechanism was approached by first considering the parent *bis*(dihydrogen) complexes as models for **2-4**. spectroscopic evidence has been presented for $[M(CO)_5(\eta^2\text{-}H_2)]$ (M = Cr, Mo, W),[51-54] while complexes for the form $[Cr(CO)_4(\eta^2\text{-}H_2)_2]$ have been generated in dihydrogen containing matrices or in liquid xenon solution.[55,56] DFT calculations revealed three minima, ***trans***, ***cis-1*** *and* ***cis-2*** (Figure 4). Both ***cis-1*** and ***cis-2*** are lower in energy than ***trans*** due to the *trans*-influence of the CO ligands.[32,57] The structure of ***trans*** contains perpendicular dihydrogen ligands, and allows both H_2 ligands to be stabilized by backdonation from orthogonal d_{xz} and d_{yz} orbitals.[21,58] C_3-rotations from ***trans*** interconvert the isomers through degenerate trigonal prismatic transition states and depending on the direction of rotation (C_3^1 or C_3^{-1}) yield either ***cis-1*** or ***cis-2*** (Figure 4).

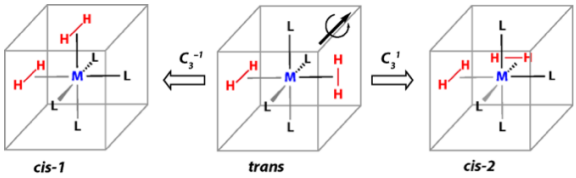
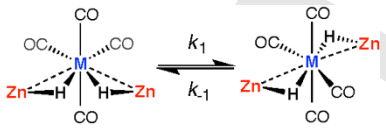


Figure 4. Theoretical $[M(CO)_4(\eta^2\text{-}H_2)_2]$ complexes and their interconversion by C_3^n rotations. M = Cr, Mo, W; L = CO.

For **2-4**, the crystallographically characterized geometry also present in ***cis-2*** is the global minimum regardless of whether long-range dispersion forces were modelling in the optimization (ωB97X or ωB97X-D functional). Of the remaining isomers, only the analogue of ***trans*** with perpendicular σ-(Zn–H) ligands was within a modest energy range of the *cis*-isomer (supporting information, Figure S13).

The experimental relative Gibbs free energies of the *bis*(σ-zincane) complexes could be estimated by the equilibrium constant ($K = k_1/k_{-1}$) recorded in toluene-d_8 at 297 K. Given the small energy differences involved, calculated values of *K* match well with experiment. DFT also correctly predicts that the *trans*-isomer of **2** is too high in energy to be observed experimentally by NMR spectroscopy at 297 K (Figure 5).



M = Cr	M = Mo	M = W
K_{exp} >100	K_{exp} = 6.0	K_{exp} = 1.9
$K_{calc(1)}$ >25,000	$K_{calc(1)}$ = 3.8	$K_{calc(1)}$ = 22.3
$K_{calc(2)}$ >10,000	$K_{calc(3)}$ = 80	$K_{calc(3)}$ = 30
$K_{calc(3)}$ > 2500	$K_{calc(3)}$ = 9.8	$K_{calc(3)}$ = 4.4

Figure 5. Experimental and calculated values of *K* for **2-4**. Gibbs energies in kcal mol^{-1}. Calc(1) = ωB97X / 6-31G / LanL2DZ. Calc(2) = ωB97X / 6-31G / SDD. Calc(3) = ωB97X / 6-31G / SDD - single point correction for dispersion (ωB97X-D) and solvent (benzene).

The favourable planar Zn–H---H–Zn arrangement within the *cis* isomers of **2-4** can be explained by a combination of: *(i)* the *trans*-influence of the CO ligands, *(ii)* disfavoured approach of the two Zn atoms due the sterically demanding ligands, and *(iii)* a stabilizing electrostatic interaction between the Zn atoms and the carbonyl ligands in the equatorial plane. For example, the Zn---C distance of 2.505(3) Å in **2** compares favourably with that in a heterobimetallic Zn---$Cr(CO)_5$ complex,[38] and along with the bending of the Cr–C–O angle to 172.3(3)° suggestes the carbonyl-ligands are semi-bridging (α = 0.35).[59]

The activation parameters for isomerisatization of **3a/b** are nearly identical to those measured for $[Mo(CO)_4(P^nBu_3)_2]$.[1] Furthermore, the dissociation of *BDI*ZnH from **3a** to form a square-based pyramidal intermediate is calculated to be significantly higher in energy, ΔG° = 33.7 kcal mol^{-1}, than the experimentally determined activation energy, $\Delta\Delta G$ ~ 9 kcal mol^{-1}. Ligand dissociation incorporates a heavy enthalpic penalty not just from breaking the Mo–H–Zn bond but also from the loss of dispersion interactions between the two β-diketiminate ligands.[60] In combination with calculations on the model *bis*(dihydrogen) sysem (Figure 4 & S11-12), these data provide a weigh of evidence for an isomerization pathway involving an intramolecular rotation (Figure 6).

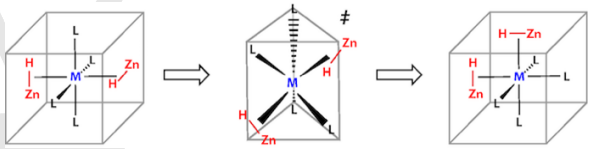


Figure 6. Proposed isomerization mechanism of bis(s-zincane) complexes.

In summary, the first examples of *bis*(σ-zincane) complexes, rare heterotrimetallics containing multiple 3-center 2-electron bonds, have been isolated and structurally characterized. A combination of theory and experiment provides a compelling weight of evidence for an intramolecular isomerization mechanism that interconverts *cis*- and *trans*-isomers. Given the increasing appreciation of σ-complex assisted metathesis in catalysis, a deep understanding of the solution dynamics of *bis*(σ-complexes) may become important for the design and mechanistic rationalization of catalytic reactions.

Acknowledgements

We are grateful to the European Research Council for provision of a Marie Curie Fellowship, MSCA IF action (OE) and starting grant (FluoroFix:677367). MRC is grateful to the Royal Society for a University Research Fellowship. Dr. Bryan Ward is thanked for helpful discussions.

Keywords: σ-complexes • *bis*(σ-complexes) • zinc hydride • isomerization • mechanism

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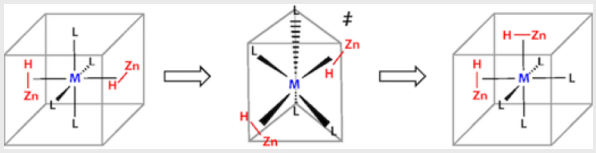
COMMUNICATION



The first octahedral bis(σ-zincane) complexes have been isolated and shown to undergo reversible isomerisation by an intramolecular pathway $\Delta H^{\ddagger}$ = 20.8 kcal mol^{-1} and $\Delta S^{\ddagger}$ = –12.8 cal K^{-1} mol^{-1}.

Olga Ekkert, Andrew J. P. White, Mark R. Crimmin

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Stereoisomerism of *bis*(σ-Zincane) Complexes: Evidence for an Intramolecular Pathway

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