Synthesis of 4,5-Benzotropone π-Complexes of Iron, Rhodium and Iridium and Their Potential Use in Catalytic Borrowing Hydrogen Reactions.

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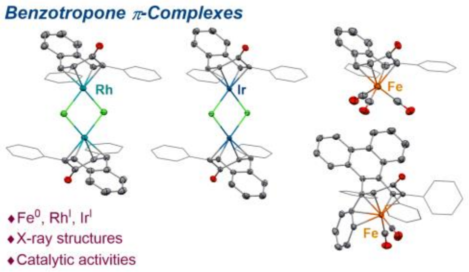
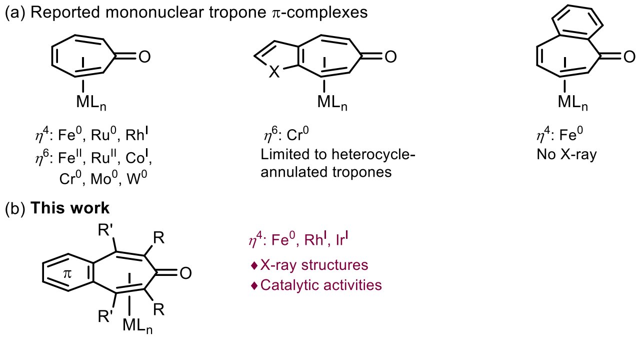
Abstract: The synthesis of rhodium, iridium, and iron π-complexes bearing 4,5-benzotropone ligands are reported. X-ray crystallographic analyses revealed that a tropone core coordinates to a metal center in a η^4 manner with a tub-form geometry. Some of the benzotropone π-complexes exhibited catalytic activity for the *N*-alkylation of aniline via borrowing hydrogen.



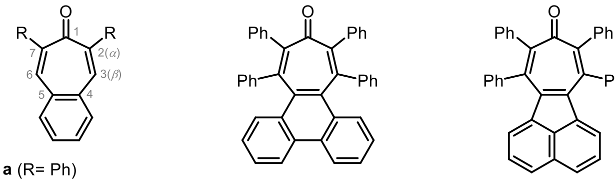
Since it was first synthesized in the early 1950s,[1] cyclohepta-2,4,6-trien-1-one, or tropone, has played a prominent role in the development of non-benzenoid aromatic compounds.[2] In the field of organometallic chemistry, the formation of metal complexes with tropones has been the subject of intense studies, and both σ- and π-complexes with various metals have been reported. For example, tropone forms a σ-type 1:1 complex with MCl_2 (M = Mn, Co, Ni, Cu, Cd, Hg, Cd),[3] whereas a 2:1 complex is generated with $ZnCl_2$.[3] Concerning π complexes, both η^4- and η^6-complexes have been reported depending on the central metal being employed (Chart 1). For example, tropone forms η^4-complexes with rhodium(I)[4] and group 8 metals such as iron(0)[5,6] and ruthenium(0),[7] whereas η^6-complexes are favored with iron(II),[8] ruthenium(II)[9] and group 6 metals, including chromium, molybdenum and tungsten.[10] Despite the significant advancements that have occurred in the coordination chemistry of tropones, metal complexes of π-extended tropones have not been reported, except for chromium complexes[11,12] of 4,5-[*b*]furanotropone and 4,5-[*b*]thienotropone and an iron complex[13] of 2,3-benzotropone. Embedding a fused aromatic ring into a π-ligand stabilizes a complex with a lower hapticity, as represented by indenyl ligands,[14] which frequently leads to an increase in catalytic activity by providing a vacant coordination site on demand.

Chart 1. π-Complexes of Tropones.



Herein we report on the synthesis and characterization of rhodium, iridium and iron complexes ligated with 7*H*-benzo[7]annulen-7-one (4,5-benzotropone)[15] derivatives, the molecular structures of which were determined by X-ray crystallography. Moreover, some of the tropone complexes were found to catalyze the *N*-alkylation of aniline with benzyl alcohol via a borrowing hydrogen mechanism.

Chart 2. Tropone Ligands Used in This Study.



1a (R= Ph)
1b (R = *p*-OMeC_6H_4)
1c (R = *p*-$CF_3C_6H_4$)
1d (R = CO_2Me)

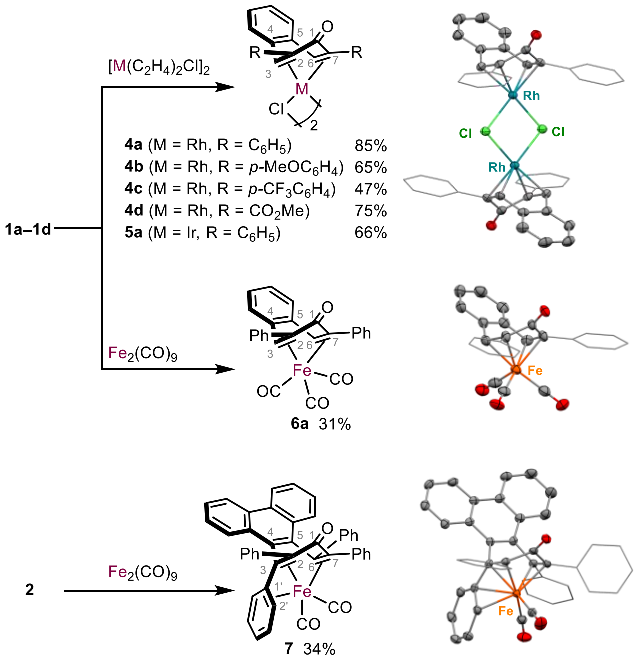
2

3

We focused on the use of multi-substituted 4,5-benzotropone derivatives **1**–**3** (Chart 2) as a ligand for transition metals to avoid undesired reactions at the tropone core[5*c*,10*c*,16] when such complexes are used in catalytic reactions. Compounds **1** can readily be synthesized via the Knoevenagel condensation of *o*-phthalaldehyde and the corresponding ketone.[17] More π-extended tropones **2** and **3** are accessible by Diels–Alder reactions of diphenylcyclopropenone and the corresponding cyclopentadienone derivative.[18,19]

Based on the synthetic procedure used for preparing a rhodium complex bearing a tetraphenylcyclopentadienone ligand,[20] the 2,7-disubstituted-4,5-benzotropone derivatives **1a**–**1d** were reacted with $[Rh(CH_2CH_2)_2Cl]_2$ in refluxing benzene to form the dimeric rhodium complexes **4a**–**4d** in 47–85% yields (Scheme 2). Complex **4a** could also be synthesized by reacting $RhCl_3$ and **1a** in methanol, although the product yield was slightly lower (55%, see electronic supplementary information (SI)). The iridium analogue **5a** was obtained by a ligand exchange reaction using $[Ir(CH_2CH_2)_2Cl]_2$ and **1a** in 66% yield. ^{1}H-NMR spectra of **4a** and **5a** in $CDCl_3$ displayed an up-field shift in *β*-protons compared to those in the parent **1a** from 7.73 ppm to 5.05 ppm for **4a** and to 5.47 ppm for **5a**, respectively, suggesting that the alkene moiety of **1a** is bound to the metal center. Single crystals of **4a** and **5a** suitable for X-ray crystallographic analysis were obtained by recrystallization from a $CHCl_3$/hexane solution. The ORTEP drawings of **4a**, and **5a** are shown in Scheme 1 (*cf.* Figure. S3 in the SI) and Fig. S5 in the SI, respectively, and selected structural parameters are summarized in Table 1. These data revealed that the 4,5-benzotropone coordinates to the metal center in a η^4 manner through the carbons at the 2,4,6 and 7 positions, resulting in the formation of a tub-form geometry. The seven-membered rings of the ligated **1a** in **4a** and **5a** were bent by 44–49 degrees (Table 1) whereas the conformation of the 4,5-benzotropone skeleton of the parent **1a** is planar.[21] Both **4a** and **5a** possess a C_{2h} symmetry in which two benzotropone cores are ligated in opposite directions. The distance for the C2–C3 and C6–C7 double bonds in the iridium complex **5a** were slightly longer than that of the rhodium analogue **4a**, indicating a stronger back donation from iridium than from rhodium.[22] In support of this conclusion, the calculated Wiberg bond indices (WBIs, Table 2)[23] for the C2–C3 and C6–C7 double bonds in **5a** (1.22) were smaller than that for the rhodium complex **4a** (1.30). Conversely, the WBIs for C2–Ir (0.515) and C3–Ir (0.598) of **5a** were larger than those for C2–Rh (0.409) and C3–Rh (0.491) in **4a**.

Scheme 2. Synthesis of Complexes 4–7.[a]



[a] ORTEP drawings of **4a**, **6a**, and **7** were plotted at the 50% probability levels. Hydrogen atoms were omitted for clarity. Phenyl groups that do not directly coordinate to the metals are depicted as wireframe forms.

Table 1. Selected Bond Lengths (Å) and Angles (deg.) for 4a, 5a, 6a, and 7.[a]

	4a	5a	6a	7
C2–C3	1.426(5)	1.446(6)	1.419(5)	1.464(4)
C6–C7	1.417(6)	1.433(6)	1.431(6)	1.429(4)
C1'–C2'				1.431(4)
C2–M	2.135(3)	2.108(6)	2.169(3)	2.086(3)
C3–M	2.130(3)	2.120(5)	2.135(3)	2.029(3)
C6–M	2.133(4)	2.115(4)	2.135(4)	2.228(3)
C7–M	2.124(3)	2.123(5)	2.181(3)	2.120(3)
C1'–M				2.137(3)
C2'–M				2.335(3)
θ	43.83	44.62	36.60	41.58
φ	45.15	49.00	49.81	57.23

[a] θ and φ are the bent angles between the meanplanes (C2–C3–C6–C7 and C1–C2–C7) and (C2–C3–C6–C7 and C3–C4–C5–C6), respectively.

Table 2. Wiberg Bond Indices.

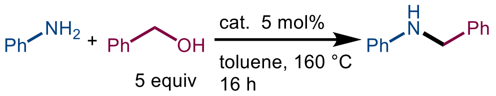
	4a	5a	6a	7
C2–C3	1.297	1.220	1.278	1.103
C6–C7	1.297	1.220	1.278	1.304
C1'–C2'				1.191
C2–M	0.409	0.515	0.321	0.450
C3–M	0.491	0.598	0.431	0.407
C6–M	0.491	0.598	0.431	0.335
C7–M	0.409	0.515	0.321	0.378
C1'–M				0.205
C2'–M				0.379

The benzotropone π-complex of iron was synthesized by following the synthetic method used to prepare the (tropone)Fe(CO)$_3$.[5] Thus, the treatment of **1a** with Fe$_2$(CO)$_9$ in benzene at 55 °C for 1.5 h afforded the iron tricarbonyl complex **6a** in 31% yield. ^{1}H-NMR spectra of **6a** in CDCl$_3$ also displayed a significant up-field shift of the β-protons to 4.61 ppm. Attempts to synthesize rhodium and iridium complexes of π-extended 4,5-benzotropone derivatives **2** and **3**, instead of **1**, using the identical protocol were unsuccessful. On the other hand, the reaction of tropone **2** and Fe$_2$(CO)$_9$ in benzene afforded the corresponding iron complex **7**. The structures of the iron complexes **6a** and **7** were unambiguously determined by X-ray crystallography (Scheme1). A (2,3,6,7-η^4)- coordination with a ligated seven-membered ring having a bent structure was observed for iron complexes **6a** and **7**, as in the cases for the corresponding rhodium and iridium complexes (i.e., **4a**, **4d** and **5a**). This type of (2,3,6,7-η^4)-coordination is different from that for the iron complex bearing a parent tropone as a ligand, which exclusively coordinates in a (2,3,4,5-η^4) manner.[4,5b] An interesting feature of complex **7** is that one of the carbonyl ligands is substituted by a phenyl group at the 3 position, which coordinates to the iron center in a η^2 manner (Scheme 1). The C2–C3 bond length of **7** (1.46 Å) is slightly longer than that of **6a** (1.42–1.43 Å), while the distances between C2–C3 and the iron center (1.92 Å, see Chart S1 and Table S1 in the SI) in **7** are shorter than those for **6a** (2.03 Å), likely due to the additional coordination of a phenyl group. The WBI for the C2–C3 bond (1.10) of **7** indicated a more single bond-like character compared to **6a** (WBI for C2–C3: 1.28). The relatively long distance between the C1'–C2' double bond and the iron center (2.07 Å) indicates that the phenyl group at the 3-position is weakly coordinating and could serve as a hemilabile ligand[24] that would generate a vacant coordination site for promoting catalysis.

Since the structural and coordination features of **4**–**7** are similar to those of cyclopentadienone ligands, such as Shvo type catalysts,[25] we hypothesized that the benzotropone complexes **4**–**7** could serve as a catalyst for borrowing hydrogen reactions.[26] Thus, we examined the reaction of benzyl alcohol and aniline in the presence of 5–10 mol% of **4**–**7** at 160 °C for 16 h. The use of the rhodium complex **4a** as a catalyst provided the desired *N*-benzylation product in 74% yield (Entry 1). Whereas no product was formed when methoxy groups were introduced at the *p*-positions of the pendant phenyl groups in **4b** (Entry 2), the electron deficient 4-trifluoromethyl analogue **4c** (Entry 3) and the ester derivative **4d** (Entry 4) afforded the desired product in comparable yield. The iridium analogue **5a** (Entry 5) also showed catalytic activity but the yield was only 15%. Iron complexes **6a** and **7** showed no catalytic activities for this reaction (Entries 6 and 7).

In conclusion, rhodium, iridium and iron complexes ligated with 4,5-benzotropone derivatives were synthesized and characterized. X-ray crystallographic analysis and the findings revealed that these complexes have a tub-shape conformation with (2,3,6,7-η^4)-coordination. Some of the rhodium complexes catalyzed *N*-alkylation reactions of aniline with benzyl alcohol via borrowing hydrogen. Further investigations of the reaction mechanism and applications to other catalytic transformation using benzotropone complexes are now underway in our laboratory.

Table 1. Application of Borrowing-Hydrogen Reactions.



entry	cat.	GC yields (%)
1	**4a**	74
2	**4b**	trace
3	**4c**	65
4	**4d**	79
5	**5a**	15
6[a]	**6a**	0
7[a]	**7**	0

[a] 10 mol% was used as a catalyst.

Supporting Information

Experimental procedures and supporting characterization data and spectra (PDF)
Compound **1d**, **2**, **4a**, **4d**, **5a**, **6a**, **7** crystal structure (CIF)

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Notes

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