CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201102427

A New Dirhodium Catalyst with Hemilabile Tropolonato Ligands for C–H Bond Functionalization

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Most organic synthetic methods are based on functional groups and involve the transformation of a bond either at the groups themselves or in their vicinity. Methods for the functionalization of unactivated C–H bonds render complementary synthetic strategies possible, since these bonds are inert to the reaction conditions of standard transformations.[1] Metal-bound carbenes,[2] nitrenes,[3] or oxygen[4] have been shown to be efficient catalytically generated species for the functionalization of C–H bonds. Catalysts derived from dirhodium tetraacetate (**1**, $[Rh_2(OAc)_4]$) are particularly effective in the decomposition of diazo compounds to form carbenes.[5] The most successful catalysts comprise proline-derived systems from the groups of McKervey[6] and Davies,[7] *tert*-leucine-derived systems of Hashimoto and Ikegami,[8] carboxamidates of Doyle[9] and tethered carboxylates of DuBois et al.[10] Yet many problems regarding the inherent reactivity of Rh carbenoids, particularly in synthetically most relevant intermolecular C–H insertion reactions, remain unsolved: reactions are often found to be highly substrate specific leading to low yields in unfavorable cases, high catalyst loadings of 6 mol% rhodium (i.e., 3 mol% $[Rh_2(L)_4]$) are typically required and high enantiomeric excesses can be accompanied by poor or no diastereoselectivity at all. These limitations can be attributed to a lack of structural diversity in the currently applied catalysts. With only a few exceptions,[11] the development of new dimeric Rh-catalysts focuses on structures bearing four bridging ligands.

We report here on 1) the preparation of a novel dirhodium catalyst (**2** Scheme 1), in which two bridging carboxylates are replaced by chelating tropolonato ligands, and its X-ray crystal structure; 2) investigations on its solution behavior that demonstrate the stability of the Rh_2^{4+} core and the hemilabile nature of the tropolonato ligands, and 3) examples of intra- and intermolecular C–H insertion reactions, which document the good catalytic activity of our new catalyst system.

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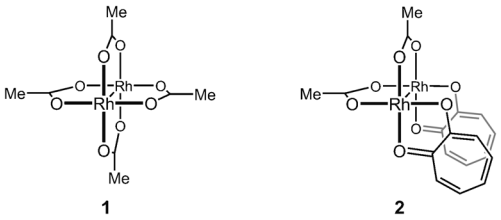
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201102427.



Scheme 1. Paddle-wheel structure of the parent compound dirhodium tetraacetate (**1**). Structure of our novel dirhodium catalyst (**2**) with chelating tropolonato ligands.

Our approach to expand the chemical space of dirhodium catalysts was guided by the idea that four bridging ligands, as in the currently applied dirhodium catalysts, might not be necessary to ensure the stability and catalytic activity of the Rh_2^{4+} core. Dirhodium compounds containing only two bridging ligands have been described in the literature.[12] We wanted to use this concept to alter the reactivity of dirhodium catalysts more fundamentally than through exploiting substituent effects on acetate derivatives and to put the currently accepted mechanisms of rhodium carbenoid chemistry to a test. In particular, we wanted to scrutinize the mechanistic paradigm that carbenoid transformations with dimeric rhodium catalysts exclusively involve substrate binding to the axial positions.[13] These positions can be readily occupied by weak donor species, for example, solvent molecules,[14] whereas the stronger equatorial rhodium spectator-ligand bonds are considered to remain intact. This implies that equatorial sites are inaccessible for substrate binding throughout the catalytic cycle. In 2005, Corey and co-workers put forward the hypothesis that the mechanism of cyclopropenation of alkynes with $[Rh_2(OAc)(dpti)_3]$ (dpti = diphenyltriflylimidazolidinone) involves a vacancy in an equatorial position on the rhodium dimer.[15] This suggestion was later questioned by Nowlan and Singleton on the basis of kinetic isotope effects and theoretical calculations.[16]

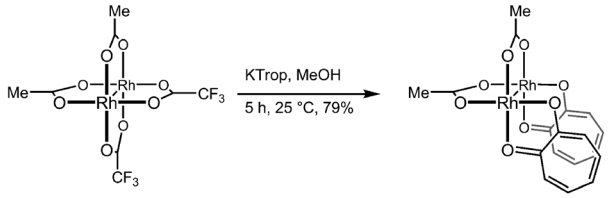
The concept, which we followed in designing new catalyst structures, is based on the notion that an equatorial coordination site could be deliberately offered, if a chelating non-bridging ligand was introduced. Bipyridyl (bpy) and related ligands are known to chelate dinuclear Rh^{II}-complexes either in an equatorial–equatorial or an equatorial–axial manner and have been tested for their antitumor activity.[17] We sought for a less basic chelating *O*,*O*-ligand that would behave similarly and thus potentially provide an equatorial

3 4

Scheme 2. Two alternative binding modes for an *O*,*O*-chelating ligand on a Rh_2^{4+} core. A vacant coordination site is indicated by a square. ax = axial, eq = equatorial.

coordination site for substrate binding (**4** Scheme 2), but would resemble carboxylates more closely in terms of its pK_a value and electron density. We turned to the tropolonato ligand as a vinylogous carboxylic acid, bearing in mind that it forms more stable complexes than for example, the acetylacetonato, maltol or quinolinol ligands.[18] Whereas mononuclear Rh^I-tropolonato complexes are known,[19] a dinuclear complex with tropolonato ligands has not yet been described.

Initial attempts to prepare a dirhodium tropolonato complex using the standard procedure, heating dirhodium tetraacetate in chlorobenzene in the presence of tropolone in a Soxhlet apparatus equipped with sodium carbonate, were not successful. By using the potassium salt of tropolone and turning to the *cis*-$[Rh_2(OAc)_2(tfa)_2]$ (tfa = trifluoroacetate) complex **5** as a starting material, we were finally able to prepare the complex $[Rh_2(OAc)_2(trop)_2]$ (**2**) in good yield (79 %, Scheme 3). Interestingly, the same product was ob-



5 2

Scheme 3. Preparation of complex **2** by selective substitution of tfa ligands.

tained using the *trans*-$[Rh_2(OAc)_2(tfa)_2]$ complex as a starting material, even though with other ligands, substitution of the tfa ligands occurs with retention of stereochemistry.[20] The formation of a tropolonato complex containing trifluoroacetate ligands, for example $[Rh_2(tfa)_2(trop)_2]$ or $[Rh_2(OAc)(tfa)(trop)_2]$, is not observed.

Since the NMR spectra of the title compound in standard NMR solvents contained limited information due to the high symmetry of the complex (cf. Figure 2a), we turned to X-ray crystallography to establish the structure. Suitable single crystals were grown by diffusion of *n*-hexane vapor into a saturated solution of the complex in CH_2Cl_2 at 4 °C. The complex crystallizes in the monoclinic space group *C*2/*c* and exhibits a ribbon superstructure with an alternating orientation of the molecules in which the rhodium atoms coordinate to an oxygen atom of a neighboring molecule

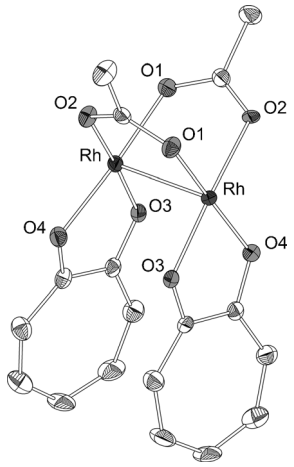


Figure 1. ORTEP representation of complex **2**. Two molecules of CH_2Cl_2 within the unit cell and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh–Rh 2.4963(8), Rh–O1 2.054(3), Rh–O2 2.032(3), Rh–O3 1.997(3), Rh–O4 1.995(3); O1-Rh-O2 86.9(9), O3-Rh-O4 81.2(2), O1-Rh-O3 95.9(3), O2-Rh-O4 95.7(9).

through their axial sites. The Rh–Rh distance of 2.4963(8) Å is consistent with the expected bond order of one (Figure 1). The tropolone moieties are held in an eclipsed conformation about the Rh–Rh single bond due to the two bridging acetate ligands. The O3-Rh-Rh-O4 torsion angle is negligibly small (0.1°) and the bite angle of the tropolonato ligands of 81.2(2)° is comparable to that of a mononuclear Rh^I tropolonato complex (79.4(2)°).[19b] Another noteworthy feature of the complex structure is the observation that contacts considerably closer than acceptable for π-stacking (ca. 3.3–3.5 Å) between the tropolone moieties are avoided by a 15.4° divergence of the O(1), O(2), O(3), O(4) least-squares planes. This is consistent with data of a $[Rh_2(OAc)_2(bpy)_2]$ bis-chelate complex.[17b]

We recorded the ^{1}H NMR spectra of $[Rh_2(OAc)_2(trop)_2]$ (**2**) in solvents with increasing donor capacity ($CDCl_3$, [D_8]THF, [D_6]acetone, CD_3OD and CD_3CN) to investigate the feasibility of displacing a tropolonato ligand from its equatorial position. The ^{1}H NMR spectrum of $[Rh_2(OAc)_2(trop)_2]$ (**2**) in [D_8]THF solution shows a typical *AA′BB′C* spin system for two identical tropolone rings located in a symmetric surrounding as it is found in the solid state (Figure 2a). Similar spectra are obtained in $CDCl_3$, [D_6]acetone, and CD_3OD. In CD_3CN, which is a more strongly coordinating solvent, the formation of a new tropolone species is observed at room temperature and more complex NMR spectra are obtained (Figure 2b). In the ^{1}H NMR spectrum, signals of two different tropolone moieties appear: one in symmetrical surrounding giving rise to the familiar *AA′BB′C* spin system, the other giving rise to a subspectrum with five well separated resonances, indicated by arrows in Figure 2b.

This observation might be interpreted in terms of a structure comprising a monodentate tropolonato ligand as depicted in Figure 3. The liberated equatorial position is most likely to be occupied by a CH_3CN molecule.[21] The NMR resonances of the monodentate tropolonato ligand resemble

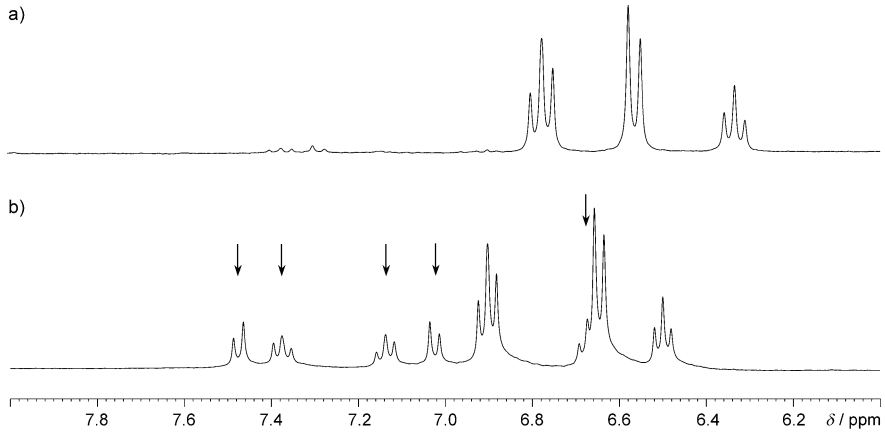


Figure 2. ^{1}H NMR resonances of complex **2** in different solvents: a) [D_8]THF, RT, 400 MHz; b) CD_3CN, RT, 500 MHz.

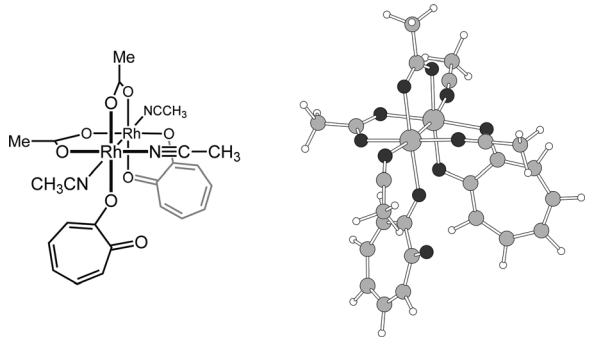


Figure 3. Suggested structure of the tropolonato dirhodium complex in acetonitrile solution based on DFT calculations using the B3LYP functional.

those of a tropolone ether with more localized double bonds, rather than a symmetrical bidentate tropolonato ligand with highly delocalized π-bonds as in free tropolone. The fact that no free tropolone is observed even after several hours at room temperature indicates that the monodentate tropolonato ligand is not bound to an easily substituted axial coordination site. After evaporation of the solvent (CD_3CN), the starting material is retrieved as determined by NMR spectroscopy in $CDCl_3$. Thus, the tropolonato ligand behaves like a hemilabile ligand under these conditions.[22]

To substantiate our findings from NMR spectroscopy and to prove the persistency of the Rh–Rh core in solution when it is held together by only two bridging acetate ligands, we used cyclic voltammetry as a sensitive tool to characterize redox-active intermediates. Indeed, the cyclic voltammogram of $[Rh_2(OAc)_2(trop)_2]$ (**2**) displays a single redox couple even in the strongly coordinating solvent acetonitrile, which is interpreted as a quasireversible one-electron oxidation of Rh_2^{4+} to Rh_2^{5+} (Figure 4b). The potential of $E_{1/2}=$ 0.471 V of complex **2** is shifted to lower potential by 336 mV relative to the parent compound $[Rh_2(OAc)_4]$ (**5**) in acetonitrile as a solvent (Figure 4a). As expected, this fact can be explained by a more pronounced electron-donor effect of the tropolonato ligands, that is, complex **2** is more easily oxidized. Interestingly, in THF solution a significantly lower potential of $E_{1/2}=0.164$ V was observed for the title compound (Figure 4c). For comparison, a related $[Rh_2(OAc)_2(bpy)_2]$ complex with two chelating bpy ligands, exhibits a reversible one-electron reduction at −0.89 V.[17b]

We were pleased to find that $[Rh_2(OAc)_2(trop)_2]$ (**2**), as a new type of dirhodium complex, is catalytically active in C–H bond insertion reactions. We investigated the chemoselectivity of **2** as a catalyst by performing intramolecular competition experiments (Tables 1 and 2). Due to the irreversibility of the C–H insertion reactions, the product ratios of the competition experiments are characteristic for the reactive intermediates involved. Applying diazoketone (*rac*)-**6** as a starting material for an aliphatic C–H bond insertion furnished a good combined yield of 83% with this unoptimized catalyst (Table 1, entry 1). The observed chemoselectivity, reflecting a preference for insertion into a tertiary C–H bond (→ (*rac*)-**7**) over insertion into a secondary C–H bond (→ (*rac*)-**8**) is slightly higher than the selectivities reported by Lahuerta and Pérez-Prieto for dirhodium catalysts bearing chiral phosphine ligands (Table 1, entries 2–4)[23] and dirhodium catalysts containing electron-withdrawing tfa ligands (Table 1, entries 5 and 6).

By using (*rac*)-**9** as a starting material, we wanted to probe the selectivity of our catalyst for aliphatic C–H bond

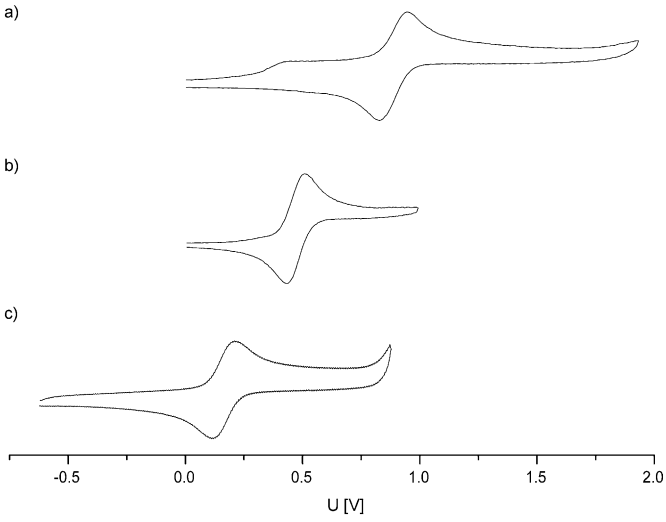
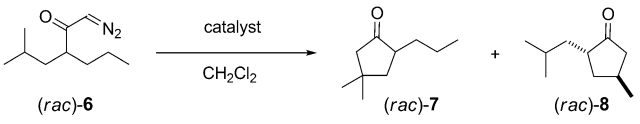


Figure 4. Cyclic voltammograms of a) **5** in MeCN, scan rate 20 mVs^{-1}; b) **2** in MeCN, scan rate 10 mVs^{-1} c) **2** in THF, scan rate 400 mVs^{-1}. Tetrabutylammonium hexafluorophosphate (0.01 M) was used as supporting electrolyte.

Table 1. Intramolecular competition between tertiary and secondary C–H bond insertion.

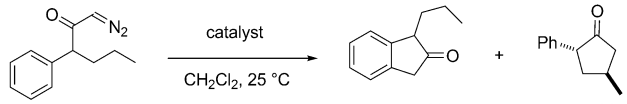


Entry	Catalyst [(mol%)]	T [°C]	t [h]	**7/8**	Yield [%]
1	$[Rh_2(OAc)_2(trop)_2]$ (2)	25	1	88:12	83
2[a]	$[Rh_2(OAc)_4]$ (1)	100	–[b]	79:21	84
3[a]	$[Rh_2(\mu\text{-}OAc)_2(\eta^1\text{-}OAc)_2(\eta^2\text{-}PPh_2(CH\text{-}R^*\text{-}OH)]$[c] (1)	100	–[b]	73:27	85
4[a]	$[Rh_2(\mu\text{-}tfa)_2(\eta^1\text{-}tfa)_2(\eta^2\text{-}PPh_2(CH\text{-}R^*\text{-}OH)]$[c] (1)	100	–[b]	76:24	80
5	*cis*-$[Rh_2(OAc)_2(tfa)_2]$ (2)	25	1	74:26	60
6	$[Rh_2(tfa)_4]$ (2)	25	1	71:29	74

[a] Data taken from ref. [23]. [b] Reaction times not indicated. [c] PPh_2(CH-R*-OH) = (1*S*,2*S*,5*R*)-(2-hydroxy-5-isopropenyl-2-methylcyclohexanyl)-(diphenyl)phosphane.

insertion versus aromatic substitution by means of an electrophilic addition/hydride migration process. In this reaction, the catalyst performed well, too, giving a combined yield of 72% with a selectivity of 87:13 ((*rac*)-**10**/(*rac*)-**11**) in favor of the aromatic substitution product (Table 2, entry 1). Although this selectivity is higher than what has been reported for dirhodium tetraacetate (Table 2, entry 2),[24] with $[Rh_2(tpa)_4]$[25] (tpa = triphenylacetate) and catalysts containing tfa ligands (Table 2, entries 3–5), almost complete selectivity for the formation of the indanone (*rac*)-**10** is observed.

Table 2. Intramolecular competition between insertion into a secondary C–H bond and aromatic substitution.



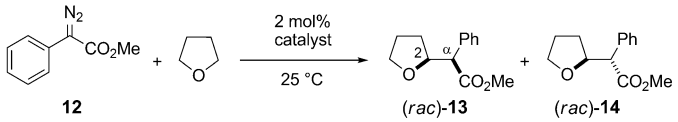
Entry	Catalyst [(mol%)]	T [°C]	t [h]	**10/11**	Yield [%]
1	$[Rh_2(OAc)_2(trop)_2]$ (2)	25	1	87:13	72
2[a]	$[Rh_2(OAc)_4]$ (5)	25	–[b]	78:22	83
3[c]	$[Rh_2(tpa)_4]$ (2)	0	0.25	>99:1	80
4	*cis*-$[Rh_2(OAc)_2(tfa)_2]$ (2)	25	1	96:4	84
5	$[Rh_2(tfa)_4]$ (2)	25	1	>99:1	88

[a] Data taken from ref. [24]. [b] Reaction times not indicated. [c] Data taken from ref. [25].

Intermolecular C–H insertions into cycloalkenes and saturated heterocycles are more challenging than the corresponding intramolecular reactions, but have been shown to be feasible with aryldiazoacetates.[2c–e] Tetrahydrofurans are synthetically most relevant, but diastereoselectivities are low in these reactions.[26] A highly effective catalyst for enantioselective C–H bond insertions, $[Rh_2((s)\text{-}DOSP)_4]$ (DOSP = *N*(*p*-dodecylphenylsulfonyl)prolinato), for example, furnishes a diastereoselectivity of 2.5:1 to 2.8:1.[27] In the reaction of methyl phenyldiazoacetate (**12**) using 2 mol% of our catalyst (**2**) in tetrahydrofuran at ambient temperature a diastereoselectivity of 7:1 in favor of the (2*R**,α*S**) diastereoisomer (*rac*)-**13** can be achieved (Table 3, entry 1). Rhodium tetraacetate and *cis*-$[Rh_2(OAc)_2(tfa)_2]$ (Table 3, entries 2 and 3) give similar yields but slightly lower diastereoselectivities, whereas $[Rh_2(tfa)_4]$ and $[Rh_2(piv)_4]$ give better yields but a significantly lower diastereoselectivity or no selectivity at all (Table 3, entries 4 and 5). Using $[Rh_2(tpa)_4]$ as a catalyst leads primarily to the formation of the (2*R**,α*R**) diastereoisomer (*rac*)-**14** (Table 3, entry 6).

In summary, we report on the first example of a dirhodium catalyst for C–H bond functionalization with chelating tropolonato ligands containing only two carboxylate bridges. Whereas other dirhodium compounds containing only two carboxylate bridges are known,[12,17] the incorporation of hemilabile tropolonato ligands broadens the chemical space of available dirhodium catalysts and offers opportunities for further improvements in catalyst design. We have demonstrated the catalytic activity of $[Rh_2(OAc)_2(trop)_2]$ (**2**) in two competition experiments and an intermolecular C–H bond insertion reaction. By using NMR spectroscopy, we were able to show that the chelating tropolonato ligands are hemilabile in a coordinating solvent (acetonitrile). This experiment serves as proof of our design concept, which was to make an equatorial coordination site accessible for substrate binding. Whereas we are not certain whether an equatorial coordination site is occupied by a substrate in the catalytic reactions we examined, such a mechanism would be fully plausible with our catalyst. The new catalyst we describe could be valuable for improving the mechanistic understanding of C–H functionalization reactions with dimeric rhodium catalysts.

Table 3. C–H insertion reaction of methyl phenyldiazoacetate and tetrahydrofuran.



Entry	Catalyst	t [h]	**13/14**[a]	Yield [%]
1	$[Rh_2(OAc)_2(trop)_2]$	12	7:1	45[b]
2	*cis*-$[Rh_2(OAc)_2(tfa)_2]$	3	4:1	46[b]
3	$[Rh_2(OAc)_4]$	3	4:1	46[b]
4	$[Rh_2(tfa)_4]$	1	3:1	69[b]
5	$[Rh_2(piv)_4]$	1	1:1	67[c]
6	$[Rh_2(tpa)_4]$	1	1:2	71[c]

[a] Diastereoselectivity was determined by ^{1}H NMR spectroscopy. [b] Yields were determined by GC-MS with *n*-dodecane as internal standard. [c] Isolated product yields.

Acknowledgements

The authors wish to thank Dr. Elisabeth Irran for X-ray structural analysis. Financial support from the Fonds der Chemischen Industrie and gen-

erous gifts of chemicals from Umicore and BASF are gratefully acknowledged.

Keywords: carbenes · C–H activation · chelates · homogeneous catalysis · rhodium

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Received: August 4, 2011
Published online: March 19, 2012

