Synthetic Methods

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Rhodium Dinaphthocyclooctatetraene Complexes: Synthesis, Characterization and Catalytic Activity in [5+2] Cycloadditions**

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New reactions provide new ways to think about bond construction and thus more, and often greener, options for achieving greater step,[1] atom[2] and time economical,[3] if not ideal, syntheses.[4] Guided by these considerations, we previously introduced a reaction for seven-membered ring synthesis involving metal-catalyzed [5+2] cycloadditions of vinylcyclopropanes (VCPs) and π systems.[5] While rhodium complexes have shown the greatest generality in catalyzing this process, working both intra- and intermolecularly and with absolute stereocontrol[6] and even in water,[7] ruthenium,[8] nickel,[9] and iron[10] catalysts have also been effective in many cases. We report herein the first studies of a new family of catalysts for [5+2] cycloadditions based on relatively little studied rhodium cyclooctatetraene (COT) complexes. We describe the synthesis and metal complexation of our dinaphtho[*a,e*]cyclooctatetraene (dnCOT) ligand **5** derived from a recently introduced [2+2+2+2] cycloaddition of diynes.[11] The resulting Rh–dnCOT catalyst provides [5+2] cycloadducts in high yields, often in minutes at room temperature, is compatible with a variety of functionalities, and exhibits enhanced or even reversed regiocontrol in selected cases, relative to known catalysts.

The [2+2+2+2] cycloaddition of diynes has proven to be an excellent reaction for the synthesis of highly substituted COTs.[11] In addition to the value of such COTs as synthetic building blocks and components of novel materials and devices,[12–16] a further motivation for our interest in this process was the potential use of COTs as ligands for catalysis. Due to their tub-shaped conformation, certain COTs can coordinate transition metals in a 1,2,5,6-η^4 manner analogous to dienes such as cyclooctadienes (CODs).[17] Interestingly, the distance and bite angle between the binding alkene moieties in metal complexes of both COD and COT are the same across a variety of crystal structures, with a distance of 2.8 Å and a bite angle of 86°.[18] While it is tempting to associate COD's generally superior binding ability to transition metals with pre-organization of the alkenes, the distance between alkenes in unbound COD (3.20 Å) is greater than that for unbound COT (3.09 Å).[18] Furthermore, COD's inherently greater flexibility (and thus entropic binding penalty) should bias metals in favor of COT entropically. Despite this, COD has been more commonly used than COT as a ligand in metal complexes.[17] The similarities between CODs and COTs and the ease of synthesis of substituted COTs using the recently introduced [2+2+2+2] cycloaddition methodology prompted our interest in determining whether judiciously modified COTs could be effective ligands for metal catalysis.

While many COTs are relatively labile metal ligands (1,2,5,6-η^4 coordination),[17,19] structural modifications to the COT scaffold, such as benzannulation, often enhance their ability to bind to transition metals.[20,21] Members of the dibenzo[*a,e*]cyclooctatetraene (dbCOT) subfamily have been complexed with a variety of transition metals (e.g., Pd, Pt, Rh, Ir, Co, Mo, Cr, Cu).[22] However, the catalytic activity of these complexes remains relatively underexplored. In fact, dbCOT has found use as an effective poison in tests for homogeneous catalysis.[23] Reports of catalytic activity of dbCOT–metal complexes are relatively rare,[24,25] and, significantly, no dbCOT complexes have been evaluated as catalysts for cycloadditions.

Based on anticipated beneficial properties of its complexes (e.g., crystallinity) and ease of synthesis, dnCOT **5** was targeted for this study. Treatment of commercially available 1,2-bis(bromomethyl)benzene (**1**) with copper trimethylsilyl acetylide followed by deprotection affords diyne **3** (Scheme 1) which upon Ni-catalyzed [2+2+2+2] cycloaddition provides cycloadduct **4** in excellent yield (up to 87% over 3 steps). Oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) at room temperature furnishes dnCOT **5** as a crystalline solid (see X-ray, Figure 1a). This step economical (4 steps) sequence is highly efficient (up to 70% overall yield) and has been carried out successfully on a multi-gram scale, offering advantages in yield, flexibility, and/or brevity relative to a previous synthesis of dnCOT (6 steps, 4.1% overall yield)[26] and notable syntheses of the related dbCOT (4 steps, 47% overall yield; 3 steps, 38% overall yield).[27]

Complexation of dnCOT **5** with rhodium was accomplished by treatment of the former with [{RhCl(CO)$_2$}$_2$] which proceeds with evolution of CO and the formation of a poorly soluble intermediate, putatively the [{RhCl(dnCOT)}$_2$] dimer **6** (Scheme 1). Treatment of this intermediate with silver hexafluoroantimonate in DCM/MeCN gives rise to Rh^I–

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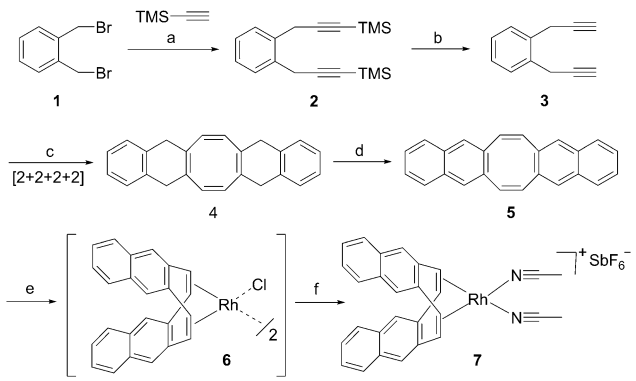
Supporting information for this article (full experimental details, characterization of new compounds, preparation and characterization of dnCOT and its rhodium and iridium metal complexes, and procedures for [5+2] cycloadditions) is available on the WWW under http://dx.doi.org/10.1002/anie.201108270.



Scheme 1. Synthesis of dnCOT (**5**) and $[Rh(dnCOT)(MeCN)_2]SbF_6$ (**7**): a) EtMgBr, CuI, THF, 0 °C to reflux, 14 h, 93–96%. b) $AgNO_3$, EtOH/H_2O, RT, 30 min, then NaCN, 1 h, 83–95%. c) $(DME)NiBr_2$ (20 mol%), Zn (40 mol%), H_2O (20 mol%), THF, 60 °C, 4 h, 80–95%. d) DDQ, PhMe, RT, 15 min, 86-90%. e) $[\{RhCl(CO)_2\}_2]$, DCM, RT, 20 h, 97%. f) $AgSbF_6$, DCM/MeCN, RT, 1 h, 92%. Yields with ranges represent variation of yields based on scale (see Supporting Information).

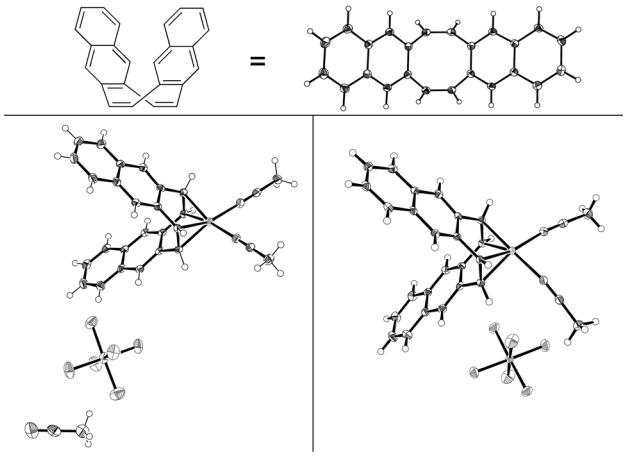
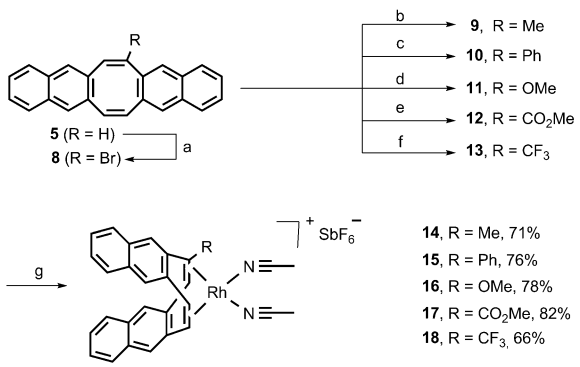


Figure 1. ORTEP representations of a) dnCOT ligand (**5**) and b, c) $[Rh(dnCOT)(MeCN)_2]SbF_6$ complex (**7**).

dnCOT complex **7** in high yield. Complex **7** was characterized by ^1H NMR and ^{13}C NMR spectroscopy as well as by X-ray crystallography (Figure 1). In going from unbound dnCOT **5** to metal complex **7**, a large upfield shift of the dnCOT alkene proton resonances (7.08 ppm to 5.59 ppm), characteristic of metal binding, was observed by ^1H NMR spectroscopy. Interestingly, the X-ray analysis yielded two crystal forms from the same batch of crystals: the first is the expected crystal structure (Figure 1c), while the second (Figure 1b) includes an additional molecule of acetonitrile. Complex **7** is bench-stable at room temperature for several months without attenuation of catalytic activity (see below). Following a similar complexation sequence, the corresponding Ir^I complex $[Ir(dnCOT)(MeCN)_2]SbF_6$ was also prepared from dnCOT **5** (see Supporting Information).

In addition to the parent dnCOT ligand (**5**), we were interested in exploring routes to functionalized dnCOT ligands, and whether such ligands might also form Rh^I complexes. Furthermore, we envisioned that the development of a facile method for tuning the dnCOT ligand would provide a valuable strategy for future evaluations of steric and electronic effects on catalytic reactions involving this ligand class. Brominated dnCOT (Br-dnCOT, **8**) was targeted as a convenient diversification point to access a wide variety of substituted systems; **8** is synthesized in 88% yield from **5** in a one-flask procedure (Scheme 2). Using a variety of coupling

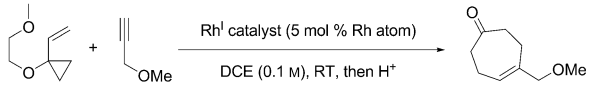


Scheme 2. Synthesis and elaboration of Br-dnCOT **8** into Rh^I complexes: Reagents and conditions: a) 1. Br_2, DCM; 2. DBU, PhH, 88%. b) $MeB(OH)_2$, $K_3PO_4{\cdot}nH_2O$, $Pd(OAc)_2$ (10 mol%), PPh_3 (40 mol%), THF, 16 h, 78%. c) $PhB(OH)_2$, $K_3PO_4{\cdot}nH_2O$, $Pd(OAc)_2$ (10 mol%), PPh_3 (40 mol%), THF, 20 h, 93%. d) CuBr (20 mol%), NaOMe (2 equiv), 1-methyl-2-pyrrolidone/MeOH, microwave 110 °C, 1 h, 74%. e) $Pd(OAc)_2$ (3 mol%), Xantphos (6 mol%), MeOH (10 equiv), CO (1 atm), NEt_3, 79%. f) CuI, $NaCO_2CF_3$, NMP, 110 °C, 34%. g) 1. $[\{RhCl(CO)_2\}_2]$ or $[\{RhCl(C_2H_4)_2\}_2]$, DCM, 24 h; 2. MeCN, $AgSbF_6$, 2 h (see Supporting Information for details).

strategies, we were able to access a number of different substituted dnCOTs **9**–**13** (R-dnCOT, R = Me, Ph, OMe, CO_2Me, and CF_3). Impressively, for all of these species, complexation with Rh^I proceeds as with the parent dnCOT ligand (**5**), affording the corresponding metal complexes (**14**–**18**) for each (Scheme 2).

Having demonstrated the tunability of the ligand core, we sought to evaluate the catalytic activity of $[Rh(dnCOT)(MeCN)_2]SbF_6$ (**7**) in an established Rh^I reaction. Recently, we reported that cationic Rh^I complexes (such as $[Rh(C_{10}H_8)(COD)]SbF_6$, **19**)[28] featuring a COD ligand are efficient catalysts for both inter-[5] and intramolecular[28] [5+2] cycloadditions with alkynes, in addition to the dimeric complex $[RhCl(CO)_2]_2$ (**20**). We therefore chose to further explore the use of Rh^I catalysts in this reaction with our dnCOT complex **7**. The data in Table 1 illustrate a direct comparison of dnCOT-based rhodium catalyst **7** against other rhodium(I) species (**19** and **20**) in a test [5+2] cycloaddition. Significantly, under these conditions, $[Rh(dnCOT)(MeCN)_2]SbF_6$ outperforms the best known catalysts for this process with respect to both yield and reaction time, producing cycloheptenone **23** from commercially available VCP **21** and alkyne **22** in 94% yield in 15 min at room temperature (Table 1, entry 1). While not optimized, the beneficial effect of dnCOT ligation can also be realized in situ (Table 1, entry 4 vs. entry 3) by titrating the otherwise sluggish $[\{RhCl(CO)_2\}_2]/AgSbF_6$ complex with dnCOT **5**, thereby producing a catalyst that turns over substrate in minutes rather than hours to days.

Table 1: Intermolecular [5+2] reactions using Rh^{I} complexes.



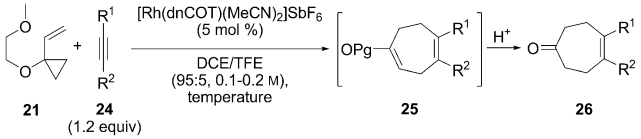
21 22 (1.2 equiv) 23

Entry	Rh^{I} catalyst (5 mol% [Rh])	*t*	Yield [%][a]
1	$[Rh(dnCOT)(MeCN)_2]SbF_6$ (**7**)	15 min	94
2	$[Rh(C_{10}H_8)(COD)]SbF_6$ (**19**)	15 min	87
3	$[\{RhCl(CO)_2\}_2]$ (**20**) + $AgSbF_6$[b]	24 h	8[c]
4	$[\{RhCl(CO)_2\}_2]$ (**20**) + dnCOT (**5**)[b] + $AgSbF_6$[b]	15 min	70

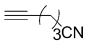
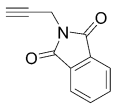
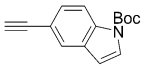
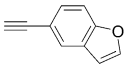
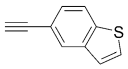
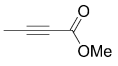
[a] Yield of isolated product. [b] Amount used: 5 mol%. [c] VCP **21** was not completely consumed.

Rh–dnCOT **7** was also found to be compatible with a variety of functionalities (Table 2). Significantly, **7** provides both excellent yields (>90%) of isolated cycloheptenone

Table 2: High-yielding intermolecular [5+2] cycloadditions of VCP **21** and alkynes for functionalized cycloheptenones.



21 24 (1.2 equiv) 25 26

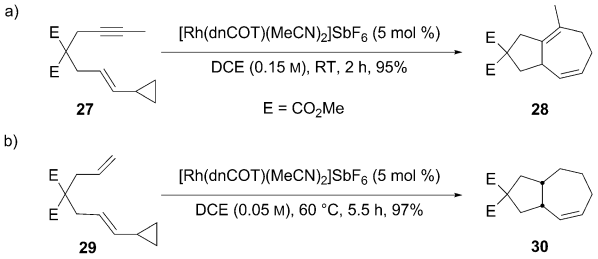
Entry	Alkyne		*T* [°C], *t*	Product	Yield [%][a]
1[b]		**24a**	60, 1 h	**26a**	94
2		**24b**	60, 1 h	**26b**	97
3		**24c**	25, <15 min	**26c**	98
4		**24d**	25, <15 min	**26d**	93
5		**24e**	25, <15 min	**26e**	96
6		**24f**	25, 35 min	**26f**	98
7[c]			25, 3.5 h	**26f**	98

[a] Yield of isolated product. [b] No TFE used. [c] Catalyst loading: 1 mol%.

products and short reaction times, often requiring only minutes at room temperature for complete conversion. A number of propargyl or ethynyl heterocycles, including a phthalimide (**24b**, entry 2), an indole (**24c**, entry 3), a benzofuran (**24d**, entry 4) and even a benzothiophene (**24e**, entry 5) undergo the [5+2] cycloaddition with VCP **21** in >90% yield.

The slightly longer reaction time for nitrile **24a** and phthalimide **24b** possibly reflects substrate or product coordination to the catalyst, which would reduce its effective availability. The disubstituted alkyne **24f** (entry 6) also reacts efficiently. A generally applicable catalyst loading was found to be 5 mole percent of **7**. However, this amount can be reduced to 1 mole percent (entry 7) without affecting the yield and only modestly increasing the reaction time.

Complex **7** is also highly effective in catalyzing the intramolecular [5+2] cycloadditions of VCPs tethered to alkynes or alkenes. The bicyclo[5.3.0]decane cycloadducts **28** and **30** are obtained in excellent yields (≥95%, Scheme 3).[29] Unlike Wilkinson's catalyst, **7** does not cause product alkene isomerization and reacts with VCP **29** to provide bicycle **30** with complete diastereoselectivity.



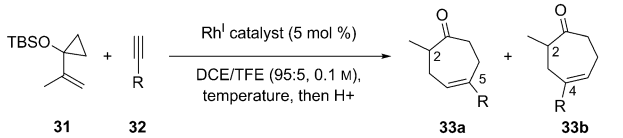
27 28 29 30

Scheme 3. Intramolecular [5+2] cycloadditions using $[Rh(dnCOT)(MeCN)_2]SbF_6$ (**7**).

In addition to improvements in reaction rates and efficiency, our original motivation for examining COT ligands was that they would provide a scaffold for control of cycloaddition selectivity relative to previously studied catalysts ($[\{RhCl(CO)_2\}_2]$ and the η^6 coordinated arene ligand in $[Rh(C_{10}H_8)(COD)]SbF_6$). Toward this end we examined the performance of catalyst **7** on cycloaddition regioselectivity. [5+2] Cycloadditions of terminal alkynes with VCP **31** can give rise to regioisomeric (2,5)- and (2,4)-substituted cycloadducts **33a** and **33b**, respectively (Table 3). Recently, we reported the first study of the regioselectivity of the [5+2] cycloaddition with $[\{RhCl(CO)_2\}_2]$ (**20**, literature values reproduced in Table 3).[30] Significantly, in several cases, the novel metal complex $[Rh(dnCOT)(MeCN)_2]SbF_6$ (**7**) was shown to enhance (entries 1, 4, 6, and 17) or even reverse (entry 8) the regioselectivity observed with $[\{RhCl(CO)_2\}_2]$ (**20**, Table 3).[31] It is noteworthy that in these representative reactions over a range of sterically and electronically diverse alkynes, $[Rh(dnCOT)(MeCN)_2]SbF_6$ (**7**) displays the best overall activity with respect to both reaction rate at room temperature and combined yields of **33a/b** (outperforming $[Rh(C_{10}H_8)(COD)]SbF_6$ (**19**) in some direct comparisons).

These data suggest encouraging potential for the development of catalyst-controlled chemo-, regio-, and stereoselective organometallic reaction systems using $[Rh(dnCOT)(MeCN)_2]SbF_6$ (**7**) and its derivatives. In additional preliminary studies, $[Rh(dnCOT)(MeCN)_2]SbF_6$ (**7**) was also shown to catalyze both an intermolecular [4+2] reaction[32] of diene **41** and alkyne **42** (Scheme 4a) and an intramolecular [2+2+2] cycloaddition[33] of tri-yne **44** (Scheme 4b), thereby demonstrating the potential Rh–dnCOT complexes have as general cycloaddition or cycloisomerization catalysts for reactions of VCPs, dienes, alkynes, and alkenes.

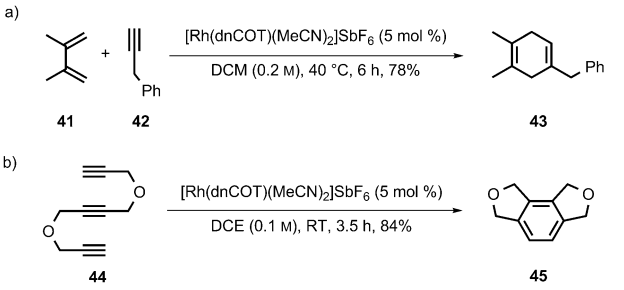
Table 3: Effect of catalysts on the regioselectivity of [5+2] cycloadditions between VCP **31** and terminal alkynes.



31 **32** **33a** **33b**

Entry	R	Cat.	*T* [°C], *t*	Yield [%][a]	Product	Ratio[b] **a**:**b**
1	Ph	**7**	23, 60 min	95	**34a/b**	>20:1
2	Ph	**20**	40, 7 h	78	**34a/b**	7.7:1
3	Ph	**19**	23, 30 min	68	**34a/b**	6.8:1
4	*p*-OMe-C_6H_4	**7**	23, 60 min	85	**35a/b**	>20:1
5	*p*-OMe-C_6H_4	**20**	40, 5.5 h	76	**35a/b**	5.9:1
6	*p*-COMe-C_6H_4	**7**	23, 60 min	87	**36a/b**	>20:1
7	*p*-COMe-C_6H_4	**20**	40, 9 h	66	**36a/b**	11:1
8	TMS	**7**	23, 1.5 h	92	**37a/b**	1:4.0
9	TMS	**20**	40, 18 h	85	**37a/b**	>20:1
10	TMS	**19**	23, 1.5 h	54	**37a/b**	1:>20
11	*n*Pr	**7**	23, 60 min	74	**38a/b**	5.4:1
12	*n*Pr	**20**	40, 48 h	76	**38a/b**	7.1:1
13	*n*Pr	**19**	23, 45 min	57	**38a/b**	1.1:1
14	CO_2Me	**7**	23, 15 min	95	**39a/b**	1.7:1
15	CO_2Me	**20**	40, 4.25 h	84	**39a/b**	3.0:1
16	CO_2Me	**19**	23, 15 min	73	**39a/b**	1.2:1
17	COMe	**7**	23, 15 min	96	**40a/b**	1:20
18	COMe	**20**	40, 2.75 h	91	**40a/b**	1:1.9
19	COMe	**19**	23, 15 min	65	**40a/b**	1:>20

[a] Combined yield of isolated **a** + **b**. [b] Ratio determined by ^{1}H NMR spectroscopy.



41 **42** **43** **44** **45**

Scheme 4. [4+2] and [2+2+2] cycloadditions catalyzed by [Rh(dnCOT)(MeCN)$_2$]SbF$_6$ (**7**).

In summary, a high-yielding and scalable synthesis of the parent dnCOT ligand **5** has been realized through the use of a newly introduced, scalable Ni^0-catalyzed [2+2+2+2] cycloaddition of a 1,7-diyne. Complexation of this ligand with rhodium affords the novel cationic Rh^I complex [Rh(dnCOT)(MeCN)$_2$]SbF$_6$ (**7**). Similarly, modification of **5** provides access to various dnCOT substituted complexes. Complex **7** is highly effective in catalyzing the intramolecular [5+2] cycloadditions of VCPs and alkyne and alkene components. It also catalyzes the intermolecular [5+2] cycloaddition of alkynes, often in minutes at room temperature, and is compatible with a wide range of commonly encountered S,N,O-heterocyclic functionality. In initial studies, complex **7** was often found to enhance or reverse the regioselectivity of intermolecular [5+2] cycloadditions when compared to previously reported catalysts. Complex **7** currently exhibits the best overall rates and yields in [5+2] cycloadditions. It also shows generality for other cycloadditions. Further studies on the design, preparation, and catalytic activities of related metal–COT complexes, including modified dnCOT derivatives such as **9**–**13** and topologically chiral COT catalysts, are being explored in connection with this and other cycloadditions and metal-catalyzed reactions.

Experimental Section

CCDC 854807, 854808, and 854809 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) P. A. Wender, B. L. Miller, *Nature* **2009**, *460*, 197–201; b) P. A. Wender, V. A. Verma, T. J. Paxton, T. H. Pillow, *Acc. Chem. Res.* **2008**, *41*, 40–49.
[2] a) B. M. Trost, *Science* **1991**, *254*, 1471–1477; b) B. M. Trost, *Angew. Chem.* **1995**, *107*, 285–307; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 259–281.
[3] P. A. Wender, B. A. Loy, A. J. Schrier, *Isr. J. Chem.* **2011**, *51*, 453–472.
[4] The "ideal synthesis" has been defined in various ways over the years: a) J. B. Hendrickson, *J. Am. Chem. Soc.* **1975**, *97*, 5784–5800; recently, increasing emphasis has been placed on step count, waste stream, safety, environmental, operational and time considerations: b) P. A. Wender, B. L. Miller, in *Organic Synthesis: Theory & Applications*, *Vol. 2* (Ed: T. Hudlicky), JAI, Greenwich, **1993**, pp. 27–66; c) R. A. Sheldon, *Chem. Commun.* **2008**, 3352–3365; d) P. T. Anastas, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, **1998**.
[5] For the first intramolecular and intermolecular examples, see: a) P. A. Wender, H. Takahashi, B. Witulski, *J. Am. Chem. Soc.* **1995**, *117*, 4720–4721; b) P. A. Wender, H. Rieck, M. Fuji, *J. Am. Chem. Soc.* **1998**, *120*, 10976–10977; for reviews, see: c) P. A. Wender, G. G. Gamber, T. J. Williams in *Modern Rhodium-Catalyzed Organic Reactions* (Ed.: P. A. Evans), Wiley-VCH, Weinheim, **2005**, pp. 263–299; for more recent intermolecular examples, see: d) P. A. Wender, L. E. Sirois, R. Stemmler, T. J. Williams, *Org. Lett.* **2010**, *12*, 1604–1607; e) X.-Z. Shu, S. Huang, D. Shu, I. A. Guzei, W. Tang, *Angew. Chem.* **2011**, *123*, 8303–8306; *Angew. Chem. Int. Ed.* **2011**, *50*, 8153–8156; for a recent review, see: f) H. Pellissier, *Adv. Synth. Catal.* **2011**, *353*, 189–218.
[6] a) P. A. Wender, L. O. Haustedt, J. Lim, J. A. Love, T. J. Williams, J.-Y. Yoon, *J. Am. Chem. Soc.* **2006**, *128*, 6302–6303; b) R. Shintani, H. Nakatsu, K. Takatsu, T. Hayashi, *Chem. Eur. J.* **2009**, *15*, 8692–8694.
[7] P. A. Wender, J. A. Love, T. J. Williams, *Synlett* **2003**, 1295–1298.
[8] B. M. Trost, H. C. Shen, D. B. Horne, E. D. Toste, B. G. Steinmetz, C. Koradin, *Chem. Eur. J.* **2005**, *11*, 2577–2590.
[9] G. Zuo, J. Louie, *J. Am. Chem. Soc.* **2005**, *127*, 5798–5799.
[10] A. Fürstner, K. Majima, R. Martin, H. Krause, E. Kattnig, R. Goddard, C. W. Lehmann, *J. Am. Chem. Soc.* **2008**, *130*, 1992–2004.

[11] a) P. A. Wender, J. P. Christy, *J. Am. Chem. Soc.* **2007**, *129*, 13402 – 13403; b) P. A. Wender, J. P. Christy, A. B. Lesser, M. T. Gieseler, *Angew. Chem.* **2009**, *121*, 7823 – 7826; *Angew. Chem. Int. Ed.* **2009**, *48*, 7687 – 7690; for the seminal report of the intermolecular Ni^0-catalyzed [2+2+2+2] reaction of mono-ynes, see: c) W. Reppe, O. Schlichting, K. Klager, T. Toepel, *Justus Liebigs Ann. Chem.* **1948**, *560*, 1 – 92.
[12] M. J. Marsella, R. J. Reid, *Macromolecules* **1999**, *32*, 5982 – 5984.
[13] a) O. Scherman, I. Rutenberg, R. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 8515 – 8522; b) M. Carnes, D. Buccella, J. Decatur, M. L. Steigerwald, C. Nuckolls, *Angew. Chem.* **2008**, *120*, 3024 – 3027; *Angew. Chem. Int. Ed.* **2008**, *47*, 2982 – 2985.
[14] P. Roesky, *Eur. J. Inorg. Chem.* **2001**, 1653 – 1660.
[15] For recent examples, see: a) A. Sygula, F. R. Fronczek, R. Sygula, P. W. Rabideau, M. M. Olmstead, *J. Am. Chem. Soc.* **2007**, *129*, 3842 – 3843; b) T. Nishiuchi, Y. Kuwatani, T. Nishinaga, V. Iyoda, *Chem. Eur. J.* **2009**, *15*, 6838 – 6847.
[16] For reviews on the properties of COTs, see: a) E. L. Spitler, C. a. J. Ii, M. M. Haley, *Chem. Rev.* **2006**, *106*, 5344 – 5386; b) L. A. Paquette, *Acc. Chem. Res.* **1993**, *26*, 57 – 62.
[17] For a review of chiral diene ligands, see: a) C. Defieber, H. Grützmacher, E. M. Carreira, *Angew. Chem.* **2008**, *120*, 4558 – 4579; *Angew. Chem. Int. Ed.* **2008**, *47*, 4482 – 4502; for a recent application to axially chiral ligands, see: b) S.-S. Zhang, Z.-Q. Wang, M.-H. Xu, G.-Q. Lin, *Org. Lett.* **2010**, *12*, 5546 – 5549.
[18] F. H. Allen, *Acta Crystallogr. Sect. B* **2002**, *58*, 380 – 388. See Supporting Information for specific distance value details.
[19] For selected examples, see: a) J. Davidson, G. Vasapollo, *J. Chem. Soc. Dalton Trans.* **1985**, 2231 – 2238; b) A. Pidcock, G. Roberts, *J. Chem. Soc. A* **1970**, 2922 – 2928; c) J. Schrenk, K. Mann, *Inorg. Chem.* **1986**, *25*, 1906 – 1908; d) P. Caddy, M. Green, E. Obrien, L. Smart, P. Woodward, *J. Chem. Soc. Dalton Trans.* **1980**, 962 – 972; e) K. Jensen, *Acta Chem. Scand.* **1953**, *7*, 868 – 870.
[20] A. Singh, P. Sharp, *Organometallics* **2006**, *25*, 678 – 683.
[21] D. Anton, R. Crabtree, *Organometallics* **1983**, *2*, 621 – 627.
[22] a) J. Müller, P. Göser, M. Elian, *Angew. Chem.* **1969**, *81*, 331 – 332; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 374 – 375; b) T. Mak, H. Wong, K. Sze, L. Book, *J. Organomet. Chem.* **1983**, *255*, 123 – 134; c) W. Geiger, T. Gennett, M. Grzeszczuk, G. Lane, J. Moraczewski, A. Salzer, D. Smith, *J. Am. Chem. Soc.* **1986**, *108*, 7454 – 7461; d) J. Degray, W. Geiger, G. Lane, P. Rieger, *Inorg. Chem.* **1991**, *30*, 4100 – 4102; e) A. Singh, P. Sharp, *Inorg. Chim. Acta* **2008**, *361*, 3159 – 3164.
[23] For the seminal work, see: a) D. Anton, R. Crabtree, *Organometallics* **1983**, *2*, 855 – 859; b) J. Widegren, R. Finke, *J. Mol. Catal. A* **2003**, *198*, 317 – 341; c) P. Nilsson, O. F. Wendt, *J. Organomet. Chem.* **2005**, *690*, 4197 – 4202; d) C. S. Consorti, F. R. Flores, F. Rominger, J. Dupont, *Adv. Synth. Catal.* **2006**, *348*, 133 – 141.
[24] Grützmacher et al. have shown that metal complexes of dbCOT catalyze transfer hydrogenations, hydroborations, and 1,4-additions to unsaturated ketones. F. Lang, F. Breher, D. Stein, H. Grützmacher, *Organometallics* **2005**, *24*, 2997 – 3007.
[25] Helmchen et al. demonstrated that $[\{Ir(dbCOT)Cl\}_2]$ modified with a chiral phosphoramidite ligand catalyzes asymmetric allylic substitutions and enantio/regioselective allylic hydroxylation: a) S. Spiess, C. Welter, G. Franck, J.-P. Taquet, G. Helmchen, *Angew. Chem.* **2008**, *120*, 7764 – 7767; *Angew. Chem. Int. Ed.* **2008**, *47*, 7652 – 7655; b) M. Gärtner, S. Mader, K. Seehafer, G. Helmchen, *J. Am. Chem. Soc.* **2011**, *133*, 2072 – 2075.
[26] Y. Man, T. Mak, H. Wong, *J. Org. Chem.* **1990**, *55*, 3214 – 3221.
[27] a) S. Chaffins, M. Brettreich, F. Wudl, *Synthesis* **2002**, 1191 – 1194; b) X. Wang, X. Hou, Z. Zhou, T. Mak, H. Wong, *J. Org. Chem.* **1993**, *58*, 7498 – 7506.
[28] P. A. Wender, T. J. Williams, *Angew. Chem.* **2002**, *114*, 4732 – 4735; *Angew. Chem. Int. Ed.* **2002**, *41*, 4550 – 4553.
[29] These results compare quite favorably to, for example, $[Rh(C_{10}H_8)(COD)]SbF_6$ (ref. [28]).
[30] P. Liu, L. E. Sirois, P. H.-Y. Cheong, Z.-X. Yu, I. V. Hartung, H. Rieck, P. A. Wender, K. N. Houk, *J. Am. Chem. Soc.* **2010**, *132*, 10127 – 10135.
[31] For both **34a/b** and **37a/b**, the regioselectivity is constant at VCP conversions ranging from 20–100% (see Supporting Information for details).
[32] S. Paik, S. U. Son, Y. K. Chung, *Org. Lett.* **1999**, *1*, 2045 – 2047.
[33] H. Kinoshita, H. Shinokubo, K. Oshima, *J. Am. Chem. Soc.* **2003**, *125*, 7784 – 7785.

