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Catalytic amination reactions mediated by Co(II) Schiff base complexes

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Abstract

Co(acacen), **1**, (acacen = 2,11-dihydroxy-4,9-dimethyl-5,8-diaza-2,4,8,10-dodecatetraene dianion) was found to be a highly efficient catalyst for the allylic amination of non activated alkenes, using *N*-(*p*-toluensulfonyl)iminophenyliodinane (PhI=NTs) as nitrene precursor. This reactivity has been extended to the less reactive C–H bond of toluene. The effect of reaction times and of added cosolvent on yields and selectivities was investigated. Under the best conditions, allylic amines were obtained in a 40–70% isolated yield. A complex derived from the stoichiometric reaction of Co(acacen), **1**, with PhI=NTs has been isolated and spectroscopically characterized. Such a complex, although not able to transfer its NTs moiety to alkenes, is still active in catalyzing allylic amination of cyclohexene.

Keywords: Cobalt; Schiff bases; *N*-(*p*-toluensulfonyl)iminophenyliodinane; Amination reactions; Allylic amines

1. Introduction

The development of new methods for the direct and selective synthesis of organonitrogen compounds from hydrocarbons represents one of the great challenges in both academy and industry. In contrast to hydrocarbon oxidation, which has been developed into several important industrial and laboratory processes for the production of oxygenated compounds [1–6], the metal catalyzed intermolecular nitrogen-atom transfer reaction is an attractive goal that remains largely elusive [7,8]. Commercially important examples are few, i.e., the Mo–Bi catalyzed ammoxidation of propylene to acrylonitrile [9] and the Ni catalyzed hydrocyanation of butadiene to adiponitrile [10]. During the last decade, laboratory methods for the *N*-functionalization of alkenes have received increasing attention. Stoichiometric allylic amination of olefins has been performed with sulfur [11,12] and selenium [13] imido compounds and proceeds with retention of the double bond position. On the other hand several indirect routes mostly based on *ene* reactions of organonitrogen compounds, including azo- [14–16], nitroso- [17–20], and *N*-sulfinylcarbamate derivatives [21], exhibit high regioselectivities with double bond transposition, but require additional N–N or N–O reduction steps to produce allyl amines. The metal-catalyzed direct electrophilic amination of alkenes represents an attractive way for the synthesis of allylic amines. A stoichiometric allylic amination employing molybdenum oxaziridines has been introduced by Sharpless [22] and in 1992 Nicholas reported the first catalytic version of this reaction using phenylhydroxylamine as nitrogen-containing reagent and a dioxomolybdenum(VI) complex as catalyst [23]. Since then some molybdenum- [24], iron- [25–29] or more recently copper-catalyzed [30,31] processes employing arylhydr-

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oxylamines have been reported. These reactions proceed regioselectively with *N*-functionalization at the less substituted olefinic carbon. Another approach employs an amine in the presence of an oxidant as the aminating agent, thus avoiding the preliminary synthesis of the hydroxylamine [32]. We recently introduced a new synthetic way to produce allyl amines, using the more readily available nitroarenes as aminating agents, under reducing conditions (CO pressure) and in the presence of $Ru_3(CO)_{12}$/diimine as catalyst [33–36]. Subsequently, the use of $[Cp(*)Fe(CO)_2]_2$ as catalyst [37], the photoassisted version of this reaction [38] and the use of nitrosoarenes as aminating agents [39] have been reported. On the other hand it has long been established that nitrenes or nitrene precursors, such as *N*-(*p*-toluensulfonyl)iminophenyliodinane (PhI=NTs) can add to an alkene, forming an aziridine, or insert into the allylic C–H bond, forming an allylamine [40]. Despite the fact that the aziridination reaction has been recently developed and quite efficient systems are now available for the enantioselective addition of the tosyl nitrenoid species to alkenes [8,41–48], the selective insertion of nitrenoids into the allylic C–H bond has been explored only to a low extent [49,50].

In our ongoing study on amination reactions catalyzed by transition metals, we have recently reported that porphyrin complexes of cobalt(II) are able to activate aromatic azides for the amination under mild condition of allylic C–H bonds [51] and for the even more difficult activation of the C–H bonds of saturated organic compounds, to give secondary amines and imines [52,53] (Scheme 1).

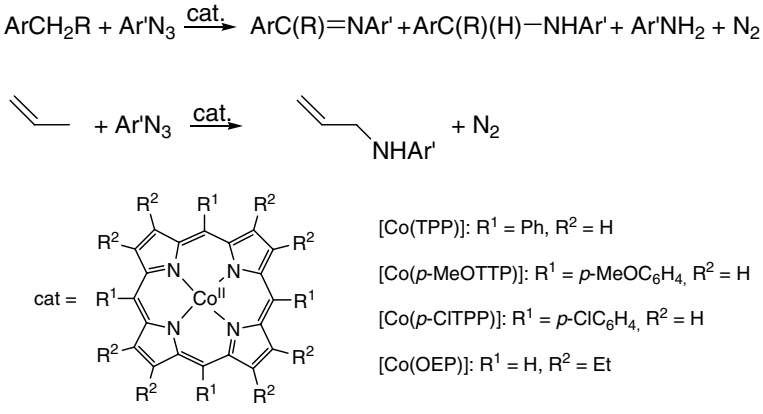
When cyclohexene was employed as the substrate, the Co(II) porphyrin complexes tested showed a remarkable selectivity for the allylic amine (53–61%) production [51]. Diazo compounds are isoelectronic with aromatic azides and recently we have shown for the first time that Co(II) porphyrin complexes may also act as catalysts for the cyclopropanation reactions [54]. Although cobalt(II) Schiff bases complexes are excellent catalysts for the cyclopropanation of olefins [55–58], to the best of our knowledge their use has never been extended to the amination reactions. Tailored tetradentate Schiff base complexes with two axial sites open to ancillary ligands, are very much like porphyrins, but more easily prepared and their use is gaining an increasing attention [59]. Nowadays active and well designed Schiff base ligands are considered ''privileged ligands'' [60] because they are easily prepared by the condensation between aldehydes and amines and are able to stabilize different metals in various oxidation states. We report here the results obtained using simple Schiff base complexes of Co(II) as catalysts in the amination reactions of alkenes employing PhI=NTs as nitrene precursor.

2. Results and discussion

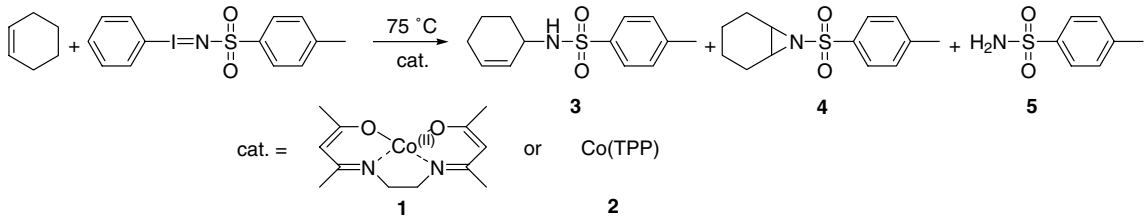
2.1. Catalytic reactions with cyclohexene

To evaluate the efficiency of Co(acacen), **1**, (acacen = 2,11-dihydroxy-4,9-dimethyl-5,8-diaza-2,4,8,10-dodecatetraene dianion) as catalyst for the intermolecular nitrogen-atom insertion into unactivated C–H bonds, the reaction of cyclohexene with *N*-(*p*-toluensulfonyl)iminophenyliodinane (PhI=NTs) was studied (Scheme 2). The same reaction was repeated in the presence of Co(TPP), **2**, (TPP = tetraphenylporphyrin dianion) as catalysts and the results obtained with the two systems were compared.

The results obtained employing different experimental conditions are reported in Table 1. The best results were obtained with a catalyst/PhI=NTs molar ratio 1:15, employing a mixture of cyclohexene/C_6H_6 4:1 as solvent. Under these conditions the reaction was complete in 8 h (the reaction can be followed by the dissolution of PhI=NTs and monitored by TLC), yielding the allylic amine **3** as the sole cyclohexene derived aminated product (67% isolated yield based on the starting *N*-(*p*-toluensulfonyl)iminophenyliodinane; Entry 4, Table 1).



Scheme 1.



Scheme 2.

Table 1
Amination of cyclohexene by PhI=NTs in the absence or in the presence of Co(II) catalysts[a]

Entry	Catalyst	*t* (h)	Cosolvent	Allylic amine (**3**) (%)[b]	Aziridine (**4**) (%)[b]	Sulfonamide (**5**) (%)[b]
1	None	8	C_6H_6	4.4	3.9	90.5
2	**1**	3	C_6H_6	14.3	8.7	77.7
3[c]	**1**	3	C_6H_6	24.1	26.5	47.2
4[c]	**1**	8	C_6H_6	66.9	–	29.8
5[d]	**1**	8	C_6H_6	61.9	–[d]	28.9
6	**1**	3	CH_2Cl_2	8.8	8.8	79.0
7[e]	**1**	3	C_6H_6	14.5	8.8	45.5
8	**1**	8	H_2O	–	–	85.0
9[e]	**2**	3	CH_2Cl_2	9.0	8.7	79.7
10	**2**	8	C_6H_6	64.5	–	30.1

[a] Typical experimental conditions: catalyst = 8.7 mg, mol ratio PhI=NTs/catalyst = 20, in 8 ml of cyclohexene plus 2 ml of cosolvent, at 75 °C.
[b] Isolated yields with respect to starting PhI=NTs.
[c] Mol ratio PhI=NTs/catalyst = 15.
[d] In the presence of added **4** (12.9 mol% with respect to PhI=NTs), mol ratio PhI=NTs/catalyst = 15. The added aziridine, **4**, (97.8%) was recovered unchanged at the end of the reaction.
[e] In the presence of 4 Å molecular sieves.

The only observed byproduct of the reaction is the corresponding *p*-toluensulfonamide, **5**, (30%), which can be formed either during the reaction or during the work-up (see later).

Interestingly when the reaction is stopped after 3 h (Entry 3), not only the yield of the isolated allylic amine **3** decreases, as expected, but an equal amount of the corresponding aziridine **4** is obtained as well. The lack of selectivity on a shorter time scale could apparently seem odd, but can be rationalized taking into account the following considerations. The uncatalyzed reaction proceeds slowly to give equimolar amounts of aziridine **4** and allylic amine **3** (Entry 1). Two different mechanisms should be operating with similar rates. Apparently the catalyst can accelerate both processes (Entries 2 and 3). It may be supposed that at longer reaction times the formed aziridine should be converted into the allylic amine. To check whether or not the aziridine is an intermediate in the formation of the allylic amine we run two different experiments. First, we treated the isolated aziridine **4** with **1** under the same reaction conditions used for the catalytic reactions. No reaction occurred. After 8 h no trace of the allylic amine could be detected and only the unreacted aziridine **4** was recovered. Second, we added a known amount of the isolated aziridine **4** (2 moles per mol of the catalyst) to the reaction mixture (Entry 5). After 8 h we obtained the expected amount of allylic amine **3** (61% with respect to the starting *N*-(*p*-toluensulfonyl)iminophenyliodinane only) and an amount of the aziridine **4** corresponding exactly to the added one (97.8%). At this stage, the reason for the different selectivities observed after 3 and 8 h is unclear, but the experimental data collected allows us to exclude that aziridine is an intermediate in the formation of the allylic amine. More probably the formation of the allylic amine can occur through two independent mechanisms and in one of this two mechanisms one sufficiently stable intermediate is formed which can evolve into the aziridine and the sulfonamide during the work up when the reaction is quenched before completeness. In the presence of the catalyst, this intermediate is instead slowly transformed into the allylic amine. It should be noted that, when the reaction is stopped before completion (undissolved PhI=NTs still present), the starting *N*-(*p*-toluensulfonyl)iminophenyliodinane is recovered as sulfonamide after column chromatography. This explains the high yield of sulfonamide at short reaction times.

The added benzene plays a relevant role: under these conditions both the catalyst and the aminating agent are soluble in the reaction medium. Iminoiodinanes are relatively strong oxidants, with very limited solubility in most solvents [61]. The use of CH_2Cl_2 as a cosolvent causes a significant drop in the selectivity of the reaction (Entry 6). To investigate the possible role of adventitious traces of water on the reaction mixture in the formation of the *p*-toluensulfonamide we run the reaction in the presence of molecular sieves. The beneficial effect of molecular sieves in decreasing the amount of the amide formed in similar reactions has already been reported in the literature [42]. Unfortunately in our case we did not observe any positive effect upon the addition of molecular sieves (Entry 7). Anyway when water was added as a cosolvent (Co(acacen), **1**, displays a remarkable solubility in neutral aqueous solutions) *p*-toluensulfonamide was recovered as the only product and no trace of the allylic amine was detected (Entry 8).

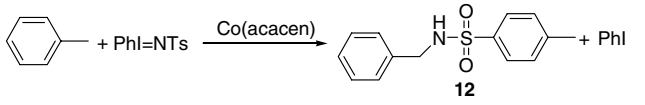
The reaction of cyclohexene with PhI=NTs was also run in the presence of Co(TPP), **2**, that, as already mentioned in the introduction, has been successfully applied by us as a catalyst for the allylic amination of non-activated double bonds [51] and the amination of benzylic hydrocarbons [52,53] by arylazides. The results are similar to those observed for the reactions catalyzed by **1** (Entries 9 and 10). It should be mentioned that PhI=NTs failed to give benzilic amination when the reaction was conducted in presence of **2** as catalyst [52,53].

2.2. Catalytic reactions with other alkenes and with toluene

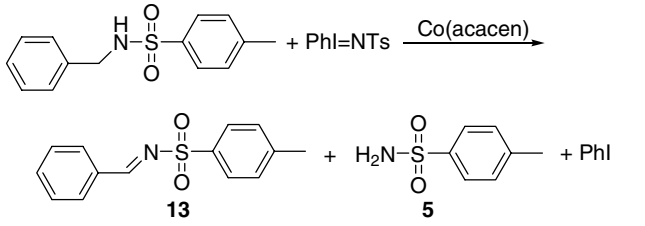
We next examined the allylic amination of different alkenes under the optimized conditions. The results are summarized in Table 2 (see Chart 1).

As expected the reaction of cyclopentene gave the allylic amine **6** in high isolated yield (63%, Entry 2). Only a 4% of the aziridination product **7** could be detected after 8 h. The reaction failed to give the allylic amination when a linear alkene like 1-octene was used (Entry 3). Moreover, only traces of the aziridine **8** could be detected. It should be noted that a drop in yields of the aziridination of linear alkenes by aryliminophenyliodinanes catalyzed by rhodium complexes has already been reported and that no allylic amination was observed [50]. We obtained fairly good results with α-methylstyrene. The allylic amine **9** was obtained in 40% yield after 8 h (Entry 5), while stopping the reaction after 3 h yielded equal amounts of the aziridine **10** (14.5%) and the allylic amine **9** (14.7%) (Entry 4). Styrene, which cannot give the allylic amine, failed to give a clean reaction and only *p*-toluensulfonamide, **5**, was recovered along with traces of the aziridine **11** (Entries 6 and 7). In this case, products recovery from the crude was complicated by the formation of polystyrenic byproducts in large amounts.

We have reported thus far the efficiency of **1** in activating PhI=NTs for the amination under mild conditions of allylic C–H bonds. The same catalytic system can also perform the more difficult activation of the C–H bond of the methyl group of toluene. The reaction does not stop to the formation of the secondary amine **12** (Eq. (1)) but proceeds further, at least in part, to give the imine **13** according to Eq. (2):



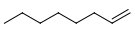
(1)



(2)

When a toluene (10 ml) solution of Co(acacen), **1**, was treated with PhI=NTs (catalyst/substrate molar ratio 1:14) the reaction proceeded in 3 h to give 4-methyl-*N*-[1-phenyl-meth-(*E*)-ylidene]-benzenesulfonamide, **13**, in a 45.4% isolated yield, along with *N*-benzyl-4-methyl-benzenesulfonamide, **12**, (4.2%) and *p*-toluen-

Table 2
Amination of different alkenes by PhI=NTs catalyzed by **1**[a]

Entry	Substrate	*t* (h)	Allylic amine (%)[b]	Aziridine (%)[b]	Sulfonamide (**5**) (%)[b]
1[c]		3	10.6 (**6**)	11.7 (**7**)	74.6
2		8	63.6 (**6**)	4.3(**7**)	29.0
3[c]		3	-	Traces (**8**)	69.3
4[c]		3	14.5 (**9**)	14.7 (**10**)	65.2
5		8	40.0 (**9**)	-	44.8
6[c]		3	-	Traces (**11**)	45.7
7		8	-	Traces (**11**)	35.5

[a] Catalyst = 8.7 mg, mol ratio PhI=NTs/catalyst 1:15, in 8 ml of alkene plus 2 ml of C_6H_6, at 75 °C.
[b] Isolated yields with respect to starting PhI=NTs.
[c] 5 ml of alkene plus 5 ml of C_6H_6.

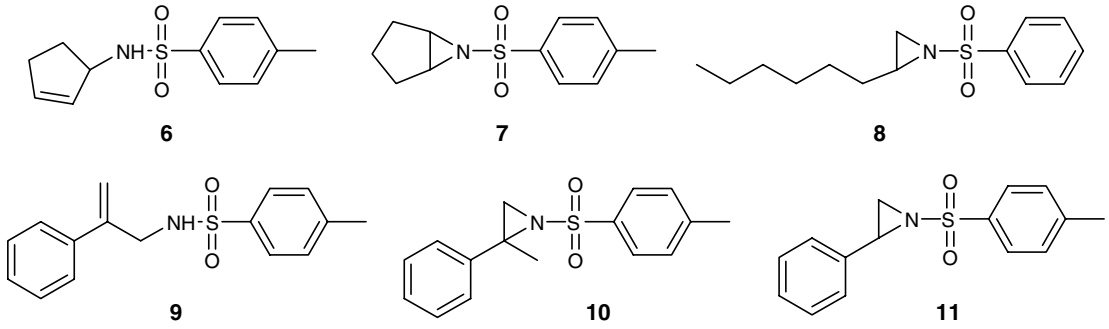


Chart 1.

sulfon- amide, **5**, (47.8%). It should be noted that the stoichio- metry in the reactions in Eqs. (1) and (2) implies that a maximum yield of 50% can be obtained with respect to the tosyliminophenyliodinane when the imine **13** is the main reaction product [52,53]. Sulfonimines are one of the few types of electron-deficient imines that are stable enough to be isolated but reactive enough to undergo addition reactions [62] and new simple metodologies for their synthesis are of great importance.

2.3. Stoichiometric reactions of PhI=NTs with Co(acacen)

The reaction of complex **1** with a stoichiometric amount of PhI=NTs in benzene at 75 °C proceeds smoothly to give a new compound **14** which has been isolated in a 35% yield. This complex is paramagnetic. Its mass spectrum shows a M + 1 peak at $m/z = 451$ and a major fragment $m/z = 281$ corresponding, respectively, to Co(acacen)(NTs) and Co(acacen). Elemental analysis is in agreement with such a formulation. For the first row metals Fe, Co, Ni and Cu, isolable complexes with a terminal imido functionality bonded to a single metal center, M=NR, are extremely rare [63]. In 1988 Mansuy reported the crystal structure of an iron–nitrene–porphyrin complex with a tosylnitrene inserted into an Fe–N bond [64] (Fig. 1(a)). This complex was obtained from the reaction of Fe(III)(TPP)(Cl) with 4 equiv. of PhI=NTs and its IR spectrum (KBr) was very similar to that of the starting complex. However, it exhibited two additional bands at 1154 ($\nu_{as}(SO_2)$) and 1095 ($\nu_s(SO_2)$) cm^{-1}, due to the tosyl group. Coordination of the nitrene to Fe(TPP)(Cl) thus resulted in a sensible lowering of the ($\nu_{as}(SO_2)$) and ($\nu_s(SO_2)$) frequencies, which were located, respectively, at 1235 and 1135 cm^{-1} in the spectrum of PhI=NTs and at 1305 and 1155 cm^{-1} in that of *p*-toluensulfonamide [65]. The IR spectrum (KBr) of complex **14** exhibited two intense bands characteristic of the tosyl substituent of the nitrene ligand at 1160 and 1098 cm^{-1}. Thus, on the basis of the elemental analysis and the spectral properties, we propose for complex **14** a bridged Co–NTs–N structure (Fig. 1(b)).

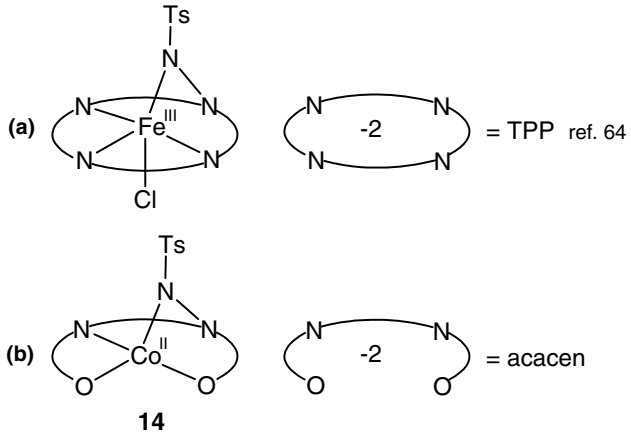


Fig. 1.

At this stage we cannot exclude the insertion into the Co–O bond of complex **1**, but we consider this possibility less likely due to the higher anionic character of the oxygen atoms with respect to the nitrogens of the ancillary ligand [66]. Since complex **14**, which derives from the insertion of the N–Ts moiety into a Co–N bond of Co(acacen) (**1**), was formed from the reaction with PhI=NTs under the same experimental conditions used during the catalysis, it was of interest to determine whether **14** was able to transfer its NTs moiety to an alkene or to catalyze aziridination by PhI=NTs. Complex **14** alone in C_6H_6 containing 175 equiv. of cyclohexene gave no allylic amine after 2 h at 75 °C. However, when used in place of Co(acacen) (**1**) under the conditions previously described for cyclohexene allylic amination by PhI=NTs, it acted as a catalyst leading to a similar yield of allylic amine (57%). From the aforementioned results, we consider that it is likely that the active intermediate formed during alkene allylic amination either transfers its NTs moiety to the alkene or undergoes an intramolecular isomerization leading to **14**. Even though

complex **14** does not transfer its NTs moiety to alkenes, it is clearly still able to reenter the catalytic cycle.

3. Conclusions

In this paper, we have reported on a new catalytic system for the selective allylic amination of unfunctionalized alkenes by PhI=NTs. Moreover, this catalytic activity could be extended to the less reactive C–H bond of a saturated hydrocarbon like toluene. Yields are in most cases only moderate to good. However, whereas several selective catalysts for the aziridination reaction have been recently reported, the selective insertion of nitrenoids into the allylic C–H bond has been explored only to a lower extent. Much work is needed to understand the mechanism of the alkene activation and the possible formation of a cobalt–nitrene active intermediate during the catalysis can not be excluded. The isolation of a complex derived from the insertion of a NTs moiety into a Co–N bond of Co(acacen) and the discovery that such a complex, although not able to transfer its NTs moiety to alkenes, is still active in catalyzing allylic amination of cyclohexene allowed us to shed some light over the reaction mechanism.

4. Experimental

4.1. General procedures

Unless otherwise specified, all reactions and manipulations were performed under an N_2 atmosphere by using standard Schlenk apparatus, cannula techniques, and magnetic stirring. CH_2Cl_2 (CaH_2) and cyclohexene, cyclopentene, 1-octene, *n*-hexane, α-methylstirene, benzene and toluene (sodium) were dried, distilled and stored under dinitrogen. Tetraphenylporphyrin [67], Co(TPP) [68,69], acacenH_2 [70], and PhI=NTs [65], were prepared according to literature procedures. Concerning the products, *p*-toluensulfonamide, **5**, is commercially available. The following products have been previously reported in the literature and have been characterized by comparison of their analytical data with the one reported in the literature: **3**, **4**, **6**, **7**[71], **8**[72], **9**[11], **10**, **11**[73], **12**[74], **13**[75]. ^{1}H NMR spectra were recorded on Advanced 300-DRX or AC 300 Bruker instruments. Infrared spectra were recorded on a BIO-RAD FTS-7 spectrophotometer. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University.

4.2. Synthesis of Co(acacen) *1*

A modification of the procedure by Mestroni [76] was used. AcacenH_2 (5.717 g, 25.5 mmol) was added to a solution of $CoCl_2 \cdot 6\,H_2O$ (6.140 g, 25.9 mmol) in degassed water (20 ml). An aqueous solution of NaOH (10.1 ml, 5 N) was added and the resulting suspension was refluxed for 1 h. An orange precipitated formed, which was collected by filtration and suspended in C_6H_6 (50 ml). After Dean-Stark removal of adsorbed water, the suspension was filtered on a Soxlet filter and extracted in continuous. The solution was then concentrated to half of its original volume and, after cooling at room temperature, orange crystals of Co(acacen) precipitated out from the solution and were collected by filtration and washed with *n*-hexane (3×10 ml) (1.633 g, 23%). The solid product can be stored without significative degradation over prolonged standing. IR (Nujol): $\nu = 1515$ (s, C=N) cm^{-1}; elemental analysis calc. (%) for $C_{12}H_{18}CoN_2O_2$ (281): C 51.25, H 6.45, N 9.96; found: C 51.17, H 6.24, N 9.59. MS (ESI): *m*/*z* 282.4 [$M^+ + 1$].

4.3. Catalytic reactions

A two-necked flask equipped with a side port and a reflux condenser with a nitrogen inlet on the top and kept under N_2 was charged with the solid reagents in a N_2 stream and then the liquid reagents and, if required the additional solvent were added at RT. The flask was then heated to 75 °C by a preheated oil bath. The reaction was monitored by TLC (*n*-hexane/CH_2Cl_2 1:9). The solution was then evaporated to dryness *in vacuo* and the product separated by flash chromatography on silica (*n*-hexane/CH_2Cl_2 1:9). Reagent amounts and reaction times are given in the tables.

4.4. Stoichiometric reaction of Co(acacen), *1*, with PhI=NTs

PhI=NTs (0.349 g, 0.942 mmol) was added in one portion to an orange solution of Co(acacen), **1**, (0.265 g, 0.942 mmol) in freshly distilled C_6H_6 (60 ml). The resulting suspension was stirred at RT for 24 h. The reaction mixture was then filtered trough a sintered glass filter to remove traces of *p*-toluensulfonamide and volatiles were removed in vacuo. The resulting brownish solid was then treated with *n*-hexane (30 ml), filtered, washed with additional *n*-hexane (3×6 ml) and collected (0.156 g, 35%). IR (KBr): $\nu = 1160$ (s, $\nu_{as}(SO_2)$), 1098 (s, $\nu_s(SO_2)$) cm^{-1}; elemental analysis calc. (%) for $C_{19}H_{25}CoN_3O_4S$ (450): C 50.67, H 5.59, N 9.33; found: C 50.30, H 5.23, N 9.41. MS (ESI): *m*/*z* 451 [$M^+ + 1$], 281.

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