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The coordination chemistry and reactivity of amino-dithiaphospholanes with rhodium, iridium, and ruthenium

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ABSTRACT

Novel amino-dithiaphospholane complexes of ruthenium, iridium, and rhodium were synthesized, and their properties were studied. Reaction of the new amino-dithiaphospholane $(RS)_2PNR'_2$ (R = binaphthyl, R′ = CH_2Ph, (rac)-**4**) with $[RuCl_2(p\text{-cymene})]_2$ afforded $[RuCl_2(p\text{-cymene})((rac)\text{-}\mathbf{4})]$ in 67% isolated yield. Similarly, the new amino-dithiaphospholanes $(RS)_2PNR'_2$ (R = cyclohexyl, (rac)-**7**) and $(RS)_2PNR'_2$ (R = phenyl, **9**) gave upon reaction with $[RhCl(CO)_2]_2$ and $[IrCp^*Cl_2]_2$ the novel complexes $[RhCl(CO)(L)_2]$ and $[IrCp^*Cl_2(L)]$ (L = (rac)-**7**, **9**) in 61–96% yields. The ruthenium complex is catalytically active for the etherification of propargylic alcohols with methanol and ethanol (8–48 h, 90 °C, 40–85% isolated yields).

Phosphoramidites (**1**, Fig. 1) have recently attracted considerable interest as ligands in transition metal catalyzed organic transformations.[1] Phosphoramidites are a versatile ligand class, which can serve as two-, four-, six-, or eight-electron donors.[2] We have recently reported that phosphoramidite complexes of ruthenium are catalytically active for β-oxo ester formation from propargylic alcohols and carboxylic acids[3a] and in the Mukaiyama aldol reaction.[3b] During our investigations we found that steric properties of the phosphoramidites can influence the catalytic activity of the corresponding ruthenium complexes. However, thus far we have not observed the impact of electronic factors on the catalytic performance of our phosphoramidite complexes. Placing bromo substituents on the aromatic backbone of the phosphoramidites (**1c** in Fig. 1) as well as employment of ligands with partially hydrogenated naphthyl units (**1d** in Fig. 1) did not show significant impact on the catalytic activity of the corresponding ruthenium complexes in β-oxo ester formation.[3a]

We were interested in determining whether electronic tuning closer to the phosphorous atom (which coordinates directly to the metal) can influence the catalytic performance of the corresponding metal complexes. Replacement of the two oxygen atoms directly bonded to the phosphorous center by sulfur seemed to hold the greatest promise. Sulfur analogs of phosphoramidites (such as **2** in Fig. 1) are known in the literature and they have been referred to as amino-dithiaphospholanes.[4] However, to the best of our knowledge, amino-dithiaphospholanes have never been employed as ligands in transition metal complexes. Herein, we describe the first amino-dithiaphospholane complexes of ruthenium, iridium, and rhodium as well as a catalytic application of the ruthenium complex.

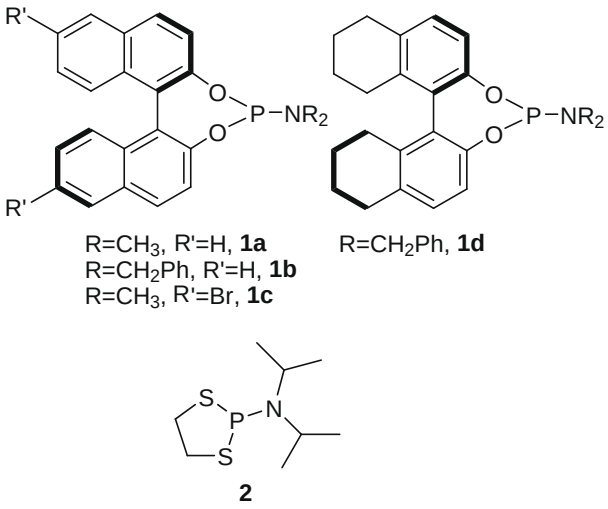

Figure 1. Phosphoramidite ligands and an amino-dithiaphospholane derivative (**2**).

First, we synthesized the BINOL-based amino-dithiaphospholane (rac)-**4** and a ruthenium complex thereof. According to

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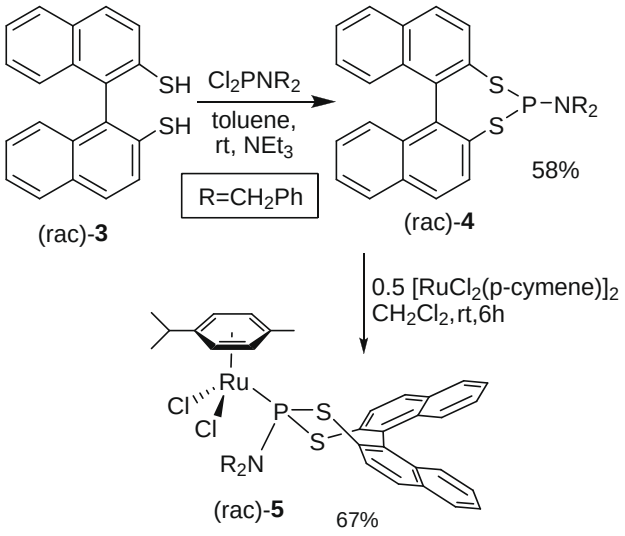
standard procedures previously applied in our laboratory,[3a] known racemic 1,1′-binaphthyl-2,2′-dithiol (rac)-**3**[5] was reacted with *N*,*N*-dibenzyl-1,1-dichlorophosphinamine ($Cl_2PN(CH_2Ph)_2$), which was generated in situ from PCl_3 and dibenzylamine (Scheme 1). The amino-dithiaphospholane (rac)-**4** was isolated in 58% yield as a white powder after flash chromatography. It is known that the commercial ruthenium precursor $[RuCl_2(p\text{-cymene})]_2$ forms ruthenium complexes with the general formula $[RuCl_2(p\text{-cymene})(L)]$ when treated with phosphoramidite ligands.[3a,6] Accordingly, the amino-dithiaphospholane ligand (rac)-**4** was reacted with $[RuCl_2(p\text{-cymene})]_2$ under standard conditions (CH_2Cl_2, room temperature, 6 h). After recrystallization, the corresponding amino-dithiaphospholane ruthenium complex (rac)-**5** was obtained as a tan solid in 67% yield.

Due to the lengthy, three-step synthesis of dithiol (rac)-**3**, we sought simpler dithiols for amino-dithiaphospholane syntheses. Accordingly, the known[7] racemic *trans*-cyclohexane-1,2-dithiol (rac)-**6** was treated with $Cl_2PN(CH_2Ph)_2$ to obtain the corresponding amino-dithiaphospholane (rac)-**7** as a white powder in 85% yield (Scheme 2).

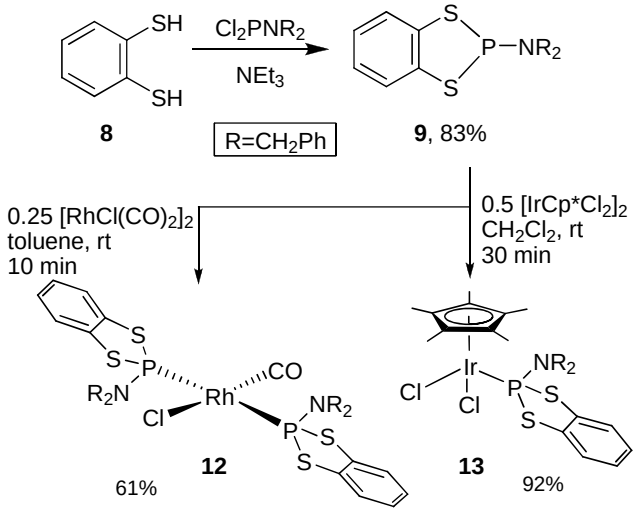
Similarly, commercial benzene-1,2-dithiol **8** was converted to the aromatic amino-dithiaphospholane **9**, which was isolated as a pale pink solid in 83% yield (Scheme 3).

It is known that the commercial rhodium precursor $[RhCl(CO)_2]_2$ forms complexes with the general formula $[RhCl(CO)(L)_2]$ when treated with monodendate phosphines L.[8] Similarly, iridium complexes of the general formula $[IrCp^*Cl_2(L)]$ (Cp^* = pentamethylcyclopentadienyl) can be obtained[9] from the known precursor $[IrCp^*Cl_2]_2$.[10] Accordingly, when the amino-dithiaphospholanes (rac)-**7** and **9** were reacted with $[RhCl(CO)_2]_2$, the corresponding rhodium complexes (rac)-**10** and **12** were obtained as tan powders in 88% and 61% yields after washing with pentane (Schemes 2 and 3). Employing similar protocols with $[IrCp^*Cl_2]_2$, the corresponding iridium complexes (rac)-**11** and **13** were synthesized in 96% and 92% yield, respectively (Schemes 2 and 3).

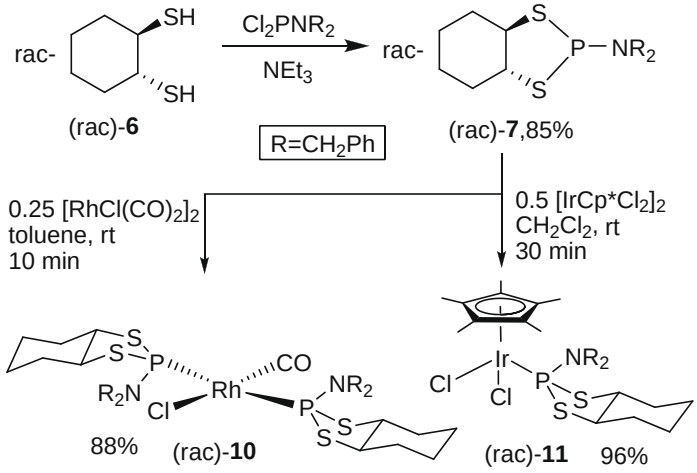
The novel amino-dithiaphospholanes (rac)-**4**, (rac)-**7**, and **9** and their metal complexes (rac)-**5** and **10**–**13** were analyzed by NMR (^1H, ^{13}C, ^{31}P), IR, and mass spectrometry (including HRMS). The FAB mass spectra showed a molecular ion peak for all ligands and metal complexes. For the complexes, a diagnostic fragmentation pattern due to loss of Cl and/or CO ligands was observed.[11]



Scheme 1. Synthesis of an amino-dithiaphospholane (rac)-**4** and its ruthenium complex (rac)-**5**.



Scheme 3. Synthesis of an aromatic amino-dithiaphospholane and rhodium and iridium complexes thereof.



Scheme 2. Synthesis of an aliphatic amino-dithiaphospholane and rhodium and iridium complexes thereof.

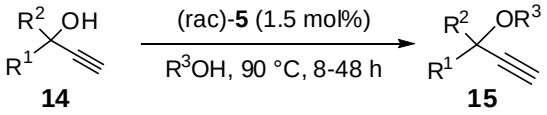
The coordination of the amino-dithiaphospholanes was best seen by a shift of their ^{31}P NMR signals in the spectra of their corresponding metal complexes. For example, the free amino-dithiaphospholane (rac)-**7** showed a ^{31}P NMR signal at 102.0 ppm, whereas its corresponding metal complexes (rac)-**10** and (rac)-**11** resonated around 121.5 and 90.5 ppm. In addition, the rhodium complexes (rac)-**10** and **12** exhibited rhodium-phosphorus couplings (J_{PRh} = 160.6–163.8 Hz), which are diagnostic of a square planar complex of composition [RhCl(CO)(L)$_2$].[8b] For complexes (rac)-**5**, (rac)-**11**, and **13**, diagnostic signals for coordinated *p*-cymene and Cp* were observed in the ^{13}C NMR. Six signals between 110.6 and 80.0 ppm indicated coordinated *p*-cymene for (rac)-**5,** and resonances between 95.0–93.3 and 9.5–9.1 ppm indicated coordinated Cp* for (rac)-**11** and **13**.

Finally, the IR spectra of the rhodium carbonyl complexes (rac)-**10** and **12** also supported the proposed structures. They exhibited a single, strong $\nu_{C\equiv O}$ signal at 1983 and 1984 cm^{-1}, respectively. These values are also typical for structurally related rhodium monocarbonyl complexes.[12] No IR signals for the dimeric [RhCl(CO)$_2$]$_2$ starting material were observed, which shows multiple $\nu_{C\equiv O}$ absorptions.

Next, we were interested in determining if the novel amino-dithiaphospholane complexes could be employed as catalysts. It is known that a number of ruthenium complexes activate propargylic alcohols catalytically.[13] The catalytic exchange of the OH of propargylic alcohols (**14** in Scheme 4) by nucleophiles appeared to be especially appealing. A multistep sequence to perform this transformation, referred to as the 'Nicholas reaction', is known,[14] and only a few metal complexes have been reported so far to catalyze the Nicholas reaction.[13b,d] Accordingly, the ruthenium complex (rac)-**5** was tested as a catalyst for the transformation of propargylic alcohols **14** to the corresponding propargylic methyl and ethyl ethers (**15**) employing methanol and ethanol as nucleophiles.

Indeed, it was observed that methanolic and ethanolic solutions of a number of tertiary propargylic alcohols with ruthenium complex (rac)-**5** as catalyst resulted in the formation of the corresponding methyl and ethyl ethers upon heating. The results of the catalytic experiments are compiled in Scheme 4, and the isolated yields ranged from 40% to 85%. Mechanistically, an allenylidene intermediate [Ru=C=C=CR$_2$] might be involved in the catalytic cycle,[13b,d] but that the ruthenium complex simply acts a Lewis acid cannot be excluded. Identification of the catalytically active species and mechanistic investigations for the reaction shown in Scheme 4 are currently underway.

All NMR spectra of the ligands and metal complexes described above showed baseline purity, and spectra for the rhodium and iridium complexes are given in the Supplementary data. When the rhodium and iridium complex syntheses were performed in deuterated solvents, ^1H and ^{31}P NMR spectra showed complete conversion within minutes. However, it was not possible to obtain correct elemental analyses for most of the ligands and complexes.



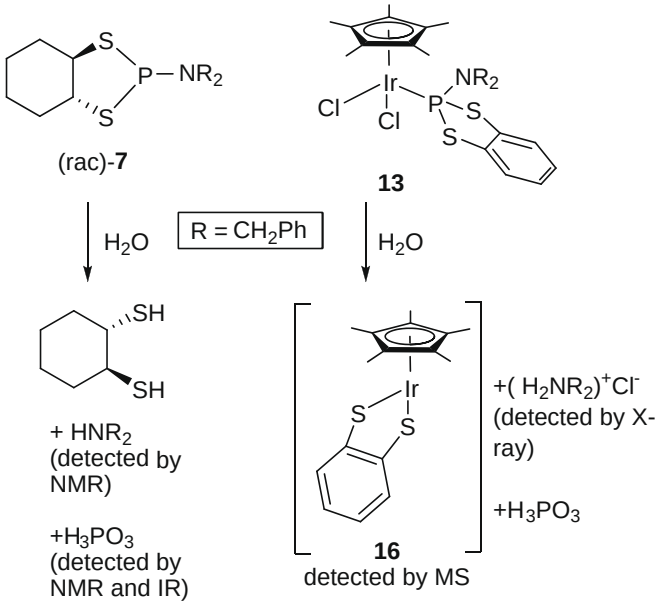
R^1 = Ph, R^2 = CH_3, R^3 = CH_2CH_3, **a**, 40%
R^1 = R^2 = Ph, R^3 = CH_3, **b**, 58%
R^1 = Ph, R^2 = R^3 = CH_3, **c**, 85%

Scheme 4. Application of (rac)-**5** in the etherification of propargylic alcohols **14**.

Attempts to obtain X-ray quality crystals of the iridium complex **13** resulted in needles, which turned out to be dibenzylammonium chloride. Further NMR tube experiments revealed that the ligands as well as the metal complexes appeared to be sensitive to hydrolysis, and some representative decomposition pathways are compiled in Scheme 5.

When NMR samples of the amino-dithiaphospholane (rac)-**7** and the metal complexes **12** and **13** were treated with one drop of water, ^1H and ^{31}P spectra showed the absence of starting material. Instead, for all samples ^1H NMR resonances around 3.9 ppm (NCH_2 group of dibenzylamine) and in some cases broad resonances around 5 ppm (tentatively assigned to –*SH*) were observed. The spectra of the hydrolyzed metal complexes exhibited broad signals around 11 ppm in the ^1H NMR. Their IR spectra showed a broad band around 950 cm^{-1}, and the NMR of the hydrolyzed (rac)-**7** exhibited a ^{31}P NMR signal around 0 ppm suggesting the presence of phosphorous acid. Species **16** could be identified by HRMS upon hydrolysis of **13**. The hydrolysis of ligand (rac)-**7** was much slower than that of the metal complexes and has literature precedent. The structurally related amino-dithiaphospholane **2** (Fig. 1) is known to phosphorylate alcohols with concomitant P-N bond cleavage. [4a] Accordingly, extensive workup attempts by chromatography and recrystallization did not result in purer compounds. The ruthenium complex (rac)-**5** might follow the same decomposition pathways in alcohols as shown in Scheme 5 for aqueous hydrolysis, when utilized as a catalyst for the reaction shown in Scheme 4. Detailed investigations of these processes are currently underway.

In conclusion, this work shows for the first time the coordination chemistry of amino-dithiaphospholanes with transition metals. Ruthenium, rhodium, and iridium complexes of amino-dithiaphospholanes were synthesized, which turned out to be sensitive to hydrolysis. The ruthenium amino-dithiaphospholane complex (rac)-**5** was shown to be catalytically active in the conversion of propargylic alcohols to their corresponding alkyl ethers. Further investigations of the coordination chemistry of amino-dithiaphospholanes and their potential application as catalysts in organic transformations are currently underway.



Scheme 5. Representative hydrolysis pathways of amino-dithiaphospholanes and their metal complexes.

Acknowledgments

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Supplementary data

Full experimental details and spectroscopic data of all new compounds, ^{1}H and ^{13}C NMR spectra of the catalysis products shown in Scheme 4 and of the rhodium and iridium complexes **10**–**13**.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.12.034.

References and notes

1. Key literature, recent examples and reviews: (a) Eberhardt, L.; Armspach, D.; Harrowfield, J.; Matt, D. *Chem. Soc. Rev.* **2008**, *37*, 839; (b) Toselli, N.; Martin, D.; Achard, M.; Tenaglia, A.; Bürgi, T.; Buono, G. *Adv. Synth. Catal.* **2008**, *350*, 280; (c) Kostas, I. D.; Vallianatou, K. A.; Holz, J.; Börner, A. *Tetrahedron Lett.* **2008**, *49*, 331; (d) Mršić, N.; Lefort, L.; Boogers, J. A. F.; Minnaard, A. J.; Feringa, B. L.; de Vries, J. G. *Adv. Synth. Catal.* **2008**, *350*, 1081; (e) Minnaard, A. J.; Feringa, B. L.; Lefort, L.; de Vries, J. G. *Acc. Chem. Res.* **2007**, *40*, 1267; (f) Zhang, W.; Zhang, X. *J. Org. Chem.* **2007**, *72*, 1020; (g) Shekar, S.; Trantow, B.; Leitner, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *128*, 11770; (h) Zhao, B.; Wang, Z.; Ding, K. *Adv. Synth. Catal.* **2006**, *348*, 1049; (i) Alexakis, A.; Albrow, V.; Biswas, K.; d'Augustin, M.; Prietob, O.; Woodward, S. *Chem. Commun.* **2005**, 2843; (k) van den Berg, M.; Minnaard, A. J.; Haak, R. M.; Leeman, M.; Schudde, E. P.; Meetsma, A.; Feringa, B. L.; de Vries, A. H. M.; Maljaars, C. E. P.; Willans, C. E.; Hyett, D.; Boogers, J. A. F.; Henderickx, H. J. W.; de Vries, J. G. *Adv. Synth. Catal.* **2003**, *345*, 308; (l) de Vries, A. H. M.; Meetsma, A.; Feringa, B. L. *Angew. Chem., Int. Ed.* **1996**, *35*, 2375.
2. Mikhel, I. S.; Rüegger, H.; Butti, P.; Camponovo, F.; Huber, D.; Mezzetti, A. *Organometallics* **2008**, *27*, 2937.
3. (a) Costin, S.; Rath, N. P.; Bauer, E. B. *Adv. Synth. Catal.* **2008**, *350*, 2414; (b) Costin, S.; Rath, N. P.; Bauer, E. B. *Inorg. Chim. Acta* **2008**. doi:10.1016/j.ica.2008.09.003.
4. (a) Miller, G. P.; Silverman, A. P.; Kool, E. T. *Bioorg. Med. Chem.* **2008**, *16*, 56; (b) Okruszek, A.; Sierzchała, A.; Fearon, K. L.; Stec, W. J. *J. Org. Chem.* **1995**, *60*, 6998; (c) Okruszeck, A.; Sierzchała, A.; Sochacki, M.; Stec, W. J. *Tetrahedron Lett.* **1992**, *33*, 7585; (d) Farschtschi, N.; Gorenstein, D. G. *Tetrahedron Lett.* **1988**, *29*, 6843.
5. Cram, D. J.; Helgeson, R. C.; Koga, K.; Kyba, E. P.; Madan, K.; Sousa, L. R.; Siegel, M. G.; Moreau, P.; Gokel, G. W.; Timio, J. M.; Sogah, G. D. Y. *J. Org. Chem.* **1978**, *43*, 2758.
6. Huber, D.; Anil Kumar, P. G.; Pregosin, P. S.; Mikhel, I. S.; Mezzetti, A. *Helv. Chim. Acta* **2006**, *89*, 1696.
7. Iqbal, S. M.; Owen, L. N. *J. Chem. Soc.* **1960**, 1030.
8. (a) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 214; (b) Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc. A* **1971**, 1104.
9. (a) Durran, S. E.; Smith, M. B.; Dale, S. H.; Coles, S. J.; Hursthouse, M. B.; Light, M. E. *Inorg. Chim. Acta* **2006**, *359*, 2980; (b) Yamamoto, Y.; Sugawara, K.; Kakeya, M. *Inorg. Chim. Acta* **2002**, *340*, 21.
10. White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, 228.
11. Branan, D. M.; Hoffman, N. W.; McElroy, E. A.; Ramage, D. L.; Robbins, M. J.; Eyler, J. R.; Watson, C. H.; DeFur, P.; Leary, J. A. *Inorg. Chem.* **1990**, *29*, 1915.
12. Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 597.
13. (a) Bustelo, E.; Dixneuf, P. H. *Adv. Synth. Catal.* **2007**, *349*, 933; (b) Cadierno, V.; Diez, J.; Garcia-Garrido, S. E.; Gimeno, J. *Chem. Commun.* **2004**, 2716; (c) Cadierno, V.; Gimeno, J.; Nebra, N. *Adv. Synth. Catal.* **2007**, *349*, 382; (d) Inada, Y.; Yoshikawa, M.; Milton, M. D.; Nishibayashi, Y.; Uemura, S. *Eur. J. Org. Chem.* **2006**, 881. and literature cited therein.
14. Nicholas, K. M. *Acc. Chem. Res.* **1987**, *20*, 207.