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[18] When the crystallizations are performed on *p*-sulfanylphenol SAMs on gold/glass substrates rather than on colloids, no modification other than calcite is observed. However, when the pH value is lowered to about 10.5, the aragonite:calcite ratio of crystals deposited on *p*-sulfanylphenol SAMs on gold/glass is about 40:60 at 22 °C and 85:15 at 45 °C, as determined from the Rietveld refinement of powder X-ray profiles. These are the highest aragonite weight fractions that we have been able to obtain at 22 °C on SAMs of simple thiols. We are now attempting to prepare colloids coated with thiols that permit dissolution of the colloids in water at neutral pH values in the hope of inducing aragonite.
[19] On the other hand, the use of (flat) SAM/gold templates with a well-defined hexagonal 2D crystal structure, such as SAMs of hexadecanethiol, result in calcite crystallizing with the [001] direction nearly always perpendicular to the substrate, suggesting the role of epitaxy.[9]
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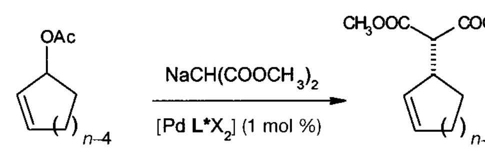
Enantioselective Allylic Substitution of Cyclic Substrates by Catalysis with Palladium Complexes of P,N-Chelate Ligands with a Cymantrene Unit[**]

Steffen Kudis and Günter Helmchen[*]

Palladium complex catalyzed asymmetric C–C bond forming reactions with allylic compounds are being investigated with great intensity.[1] As ligands, modular C_2 diphosphanes[2] and phosphanylcarboxylic acids[3] gave good results, particularly with small cyclic substrates. For acyclic substrates, chiral phosphanyldihydrooxazoles were successfully used as ligands,[4] and enantioselectivities of up to more than 99:1 were achieved. However, cyclic substrates **1** (Scheme 1) furnished low enantioselectivities with these ligands. Because of the favorable properties of phosphanyldihydrooxazoles, such as ease of synthesis and high turnover numbers in catalysis, it was of interest to develop ligands of this type that are suitable for cyclic substrates. We found such compounds on the basis of mechanistic considerations.

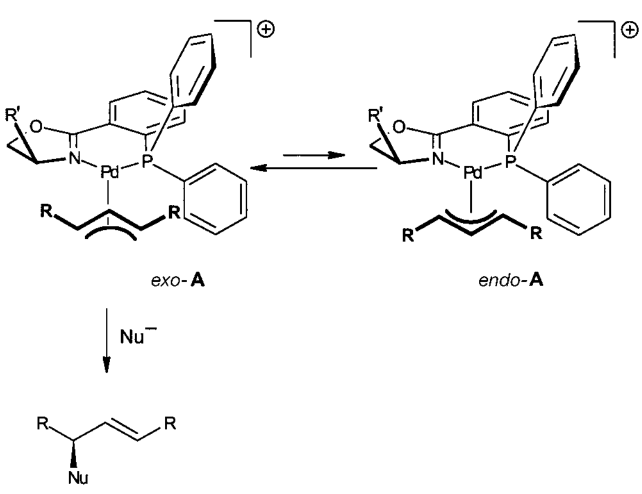


1 **2**

a: $n = 5$, **b**: $n = 6$, **c**: $n = 7$

Scheme 1. Palladium complex catalyzed allylic substitution of cyclic allyl acetates.

Key concepts of the reactions with dihydrooxazoles and other P,N ligands[5] are a) the assumption of preferred attack of the nucleophile at the carbon atom of the allyl group in the position *trans* to the phosphorus atom and b) the postulate that of the diastereomeric *exo*- and *endo*-π-allyl complexes **A** (Scheme 2), the *exo* isomer reacts faster. As the relative reactivities of these diastereomers are nearly equal, the ratio of their concentrations mainly determines the enantioselectivity of the substitution. The reason for the low selectivity with cyclic substrates is insufficient differentiation, that is, equal populations of *exo* and *endo* isomers.



Scheme 2. The *exo*–*endo* isomerism of π-allylpalladium complexes with phosphanyldihydrooxazole ligands (R' = *i*Pr, *t*Bu).

With second-generation ligands, the enantioselectivity for cyclic substrates was increased significantly by substituting the pseudoaxial phenyl group by a 2-biphenylyl group;[6] *ee* values of 50–80 % were obtained. The higher enantioselectivity had been anticipated, since the crystal structure of complex **B** with R = *i*Pr and $n = 6$ displayed only the conformer in which the terminal phenyl group is directly above the allyl system. This conformer is the most favorable for achieving high selectivity. According to ^{1}H NMR NOE measurements,[7] conformer **B** is in equilibrium with conformer **C**, in which the 2-biphenylyl group is rotated away from the palladium center and does not interact with the allyl group. To restrict rotational freedom of

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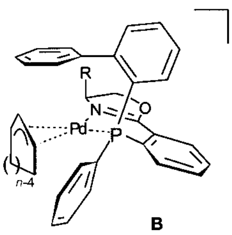
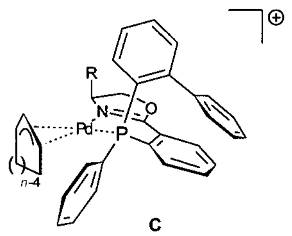
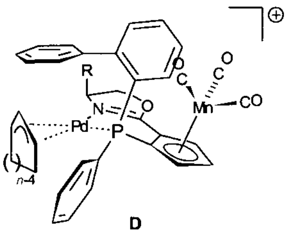


B



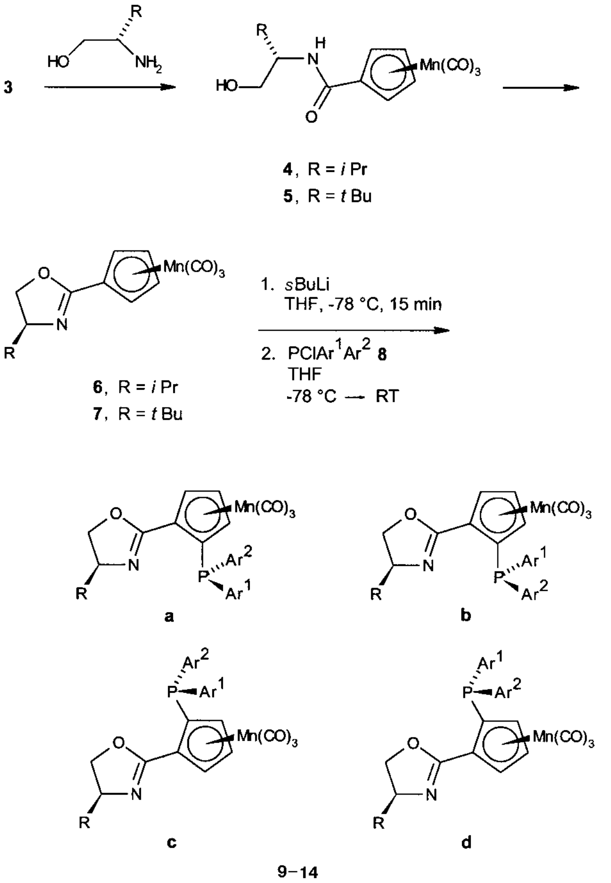
C



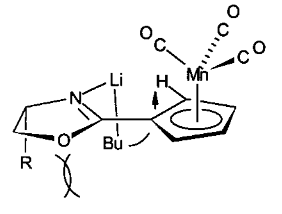
D

the 2-biphenylyl group, we replaced the "flat" benzene ring with a sterically demanding tricarbonylcyclopentadienylmanganese (cymantrene) unit (**D**).

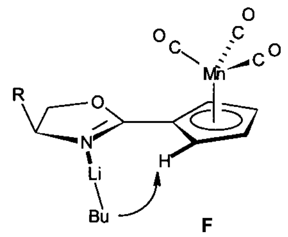
To synthesize the new ligands, cymantrenecarbonyl chloride[8] (**3**) was treated with (*S*)-valinol and (*S*)-*tert*-leucinol to give the amides **4** (94%) and **5** (90%), which were transformed into the dihydrooxazoles **6** (81%) and **7** (80%) by established procedures[9] (Scheme 3). Like the analogous ferrocene derivatives,[10] the new dihydrooxazoles can be diastereoselectively lithiated and then treated with chlorophosphanes. In contrast to the ferrocene derivatives, lithiocymantrenes slowly equilibrate, so that the time period between metalation and addition of the chlorophosphane should be kept as short as possible. For example, at −78 °C with 2 h between addition of *s*BuLi and chlorodiphenylphosphane, we obtained **9a** and **9c** (ratio 85:15) from **6**, and **10a** and **10c** (ratio 88:12) from **7**. The minor epimers **9c** and **10c** were not formed when an interval of 15 min was employed. The relative configurations of the new compounds were assigned by assuming reactions via the transition states **E** and **F** (preferred) in analogy to corresponding ferrocene derivatives.



Scheme 3. Synthesis of the cymantrene-containing phosphanyldihydrooxazoles **9**–**14**: **9a**, **9c**: R = *i*Pr, $Ar^1 = Ar^2 = Ph$; **10a**, **10c**: R = *t*Bu, $Ar^1 = Ar^2 = Ph$; **11a**, **11b**: R = *t*Bu, $Ar^1 = Ph$, $Ar^2 = 2\text{-Bp}$; **12a**, **12b**: R = *t*Bu, $Ar^1 = 3,5\text{-}(CH_3)_2C_6H_3$, $Ar^2 = 2\text{-Bp}$; **13a**, **13b**: R = *t*Bu, $Ar^1 = 3,5\text{-}(CF_3)_2C_6H_3$, $Ar^2 = 2\text{-Bp}$; **14a**: R = *t*Bu, $Ar^1 = Ar^2 = 2\text{-Bp}$ (2-Bp = 2-biphenylyl).



E



F

Phosphorus was introduced as an additional stereogenic center by reaction of the lithio derivatives with (2-biphenylyl)(chloro)phenylphosphane. Epimers **11a** and **11b** were obtained in 64% yield in the ratio 6:5; **11c** and **11d** were not observed. Crystallization from *n*-hexane/ether gave **11b** with greater than 99.9% purity in 26% yield. The configuration was determined by X-ray structural analysis (see below). The pure epimer **11a** was obtained as an oil from the mother liquor in 31% yield by chromatography. Heating a mixture of the diastereomers to above 90 °C caused epimerization at the phosphorus atom and furnished **11a** with high selectivity (**11a**:**11b** = 9:1). The analogous phosphanes **12b** (32%), **13b** (31%), and **14a** (28%) were prepared in order to further assess electronic and steric effects.

The new ligands were tested in substitution reactions according to Scheme 1 (Table 1). Catalysts prepared in situ from these ligands were considerably more active than complexes of type **A** or **B** (approximate sixfold increase in reaction rate). As anticipated, the influence of the cymantrene unit was small for ligands **9a**, **9c**, and **10a** (entries 1–3). The touchstones for our concept are the diastereomeric ligands **11a** and **11b**. In analogy to **9** and **10**, **11a** induced only low (entry 4), but **11b** very high selectivity (entry 5), as expected for a complex of type **D**. By optimization of the reaction conditions, enantioselectivities of up to more than 99:1 were achieved with **11b** (entries 5–13). Comparatively low selectivities were obtained with the phosphanes **12b** and **13b**, containing substituents with differing electronic properties, and the particularly bulky phosphane **14a** (entries 14–16). Overall, **11b** induced higher reactivity and selectivity in this reaction than the previously known phosphanyldihydrooxazoles and other asymmetric ligands.

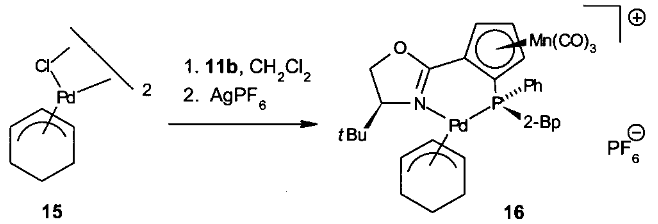
To test our hypothesis about the structure of complexes of type **D**, the allyl complex **16** was prepared by treatment of the known complex **15**[11] with the phosphane **11b** in dichloro-

Table 1. Palladium complex catalyzed substitution of cyclic allyl acetates **1**[a] (Scheme 1).

Entry	Ligand	Substrate	*t* [min]	*T* [°C]	Solvent	Yield [%]	*ee*[b] [%]
1	**9a**	**1b**	10	20	THF	98	30
2	**9c**	**1b**	10	20	THF	98	20
3	**10a**	**1b**	10	20	THF	97	31
4	**11a**	**1b**	10	20	THF	91	31
5	**11b**	**1b**	10	20	THF	95	85
6	**11b**	**1a**	10	20	THF	86	80
7	**11b**	**1a**	120	−50	DMF	73	96
8	**11b**	**1b**	40	20	DMF	97	87
9	**11b**	**1b**	90	0	DMF	86	90
10	**11b**	**1b**	180	−20	DMF	62	93
11	**11b**	**1c**	5	20	THF	96	78
12	**11b**	**1c**	75	0	DMF	86	98
13	**11b**	**1c**	180	−20	DMF	32	> 99.9
14	**12b**	**1c**	75	0	DMF	71	87
15	**13b**	**1c**	120	0	DMF	79	92
16	**14a**	**1c**	120	0	DMF	82	44

[a] A solution of dimethyl malonate (198.0 mg, 1.5 mmol) in 2 mL of solvent was treated with NaH (33.6 mg, 1.4 mmol). The mixture was added to a solution of $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$ (1.83 mg, 5.0 µmol), 11.0 µmol of the dihydrooxazole ligand (**9a**—**14a**) and 1.0 mmol of the cyclic allyl substrate (**1a**–**1c**) in the solvent given. The mixture was stirred for the stated period, treated with saturated NH_4Cl solution, and extracted three times with 20-mL portions of diethyl ether. The organic phase was dried with Na_2SO_4 and concentrated in vacuo. Products were purified by flash chromatography (silica, *n*-hexane/ethyl acetate 97/3). [b] In each case the product with *R* configuration was favored. Enantiomeric purities of **2b** and **2c** were determined by gas chromatography on a Chrompack CP Chirasil DEX CB column (25 m × 0.25 mm, 0.25 mm film thickness); **2b** (110 °C): t_R((−)-(*S*)-**2b**) = 37.7 min, t_R((+)-(*R*)-**2b**) = 38.2 min; **2c** (120 °C), t_R((−)-(*S*)-**2c**) = 36.9 min, t_R((+)-(*R*)-**2c**) = 37.8 min. The optical purity of **2a** was determined on the basis of the reference value (100% *ee*) $[\alpha]_D^{20} = +98.7$ ($c = 2.3$ in $CHCl_3$). For control, a sample of **2** was saponified and decarboxylated to give 2-cyclopentenylacetic acid; this was transformed into the iodolactone, the enantiomers of which can be separated by gas chromatography (column as given above, 145 °C, $t_R = 34.5$ and 38.3 min).[6]

methane and subsequent replacment of the chloride counterion with hexafluorophosphate (Scheme 4). The X-ray crystal structure[12] (Figure 1) revealed a structure of type **D**. Only one species was observed by ^{31}P NMR spectroscopy for a solution of the complex in $[D_8]$THF at −78 °C. Isomerization was not observed on warming. Accordingly, it can be concluded that the products are formed from allyl complexes of type **D** by attack at the allyl terminus *trans* to the phosphorus atom. The bond lengths and angles are typical for (η^3-cyclohexenyl)palladium complexes with phosphanyl-dihydrooxazole ligands. An unusual feature of the structure are the positions of the *P*-aryl groups, the P–C bonds of which have an almost symmetrical arrangement with respect to the coordination plane (N-Pd-P). The reason for this is an interaction between the 2-biphenylyl group and the $Mn(CO)_3$ moiety, which precludes the usual pseudoaxial position of one *P*-aryl group.[13]



15 **16**

Scheme 4. Preparation of the η^3-cyclohexenylpalladium complex **16**.

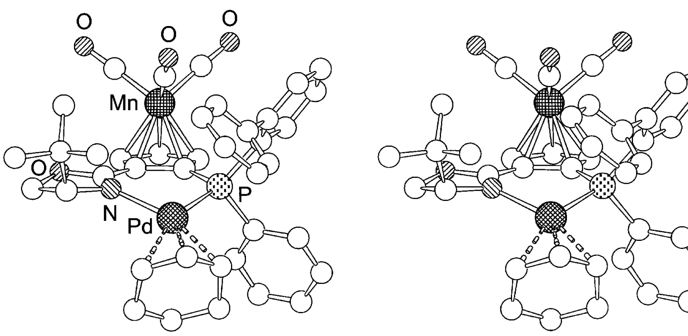


Figure 1. Stereoview of the crystal structure of the cation of complex **16**. Hydrogen atoms are omitted.

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Keywords: allyl complexes · asymmetric catalysis · ligand effects · N ligands · P ligands · palladium

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[12] Crystal data for **16**: $C_{39}H_{38}ClF_6MnO_4P_2Pd$, $M_r = 957.43$. Crystal dimensions 0.23 × 0.20 × 0.20 mm, triclinic, space group *P*1, $a = 11.2672(2)$, $b = 11.3084(2)$, $c = 18.6163(4)$ Å, $\alpha = 93.367(1)$, $\beta = 94.108(1)$, $\gamma = 104.114(1)°$, $V = 2287.33(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.390$ g cm^{-3}; $\mu = 0.858$ mm^{-1}, $\theta_{max} = 25.56°$; 16586 reflections measured, 13304 unique reflections; $R_1 = 0.0678$, $wR_2 = 0.1495$. Siemens SMART CCD diffractometer (200 K, radiation $\lambda(Mo_{K\alpha}) = 0.71073$ Å). The structure was solved by direct methods and refined against F^2 for all observed reflexes; program used: SHELXTL (G. M. Sheldrick, Universität Göttingen). Crystallographic data (excluding structure factors) for the structure reported in this paper have been

deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101206. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[13] The angle between the coordination plane and the ligand plane is only 28°. Other η^3-cyclohexenylpalladium complexes of phosphanyldihydrooxazoles have angles of around 50°: H. Steinhagen, P. Sennhenn, A. Pichota, G. Helmchen, unpublished results.

Catalytic Copolymerization of Ethene and Carbon Monoxide on Nickel Complexes**

Bernd Domhöver, Wolfgang Kläui,* Andreas Kremer-Aach, Ralf Bell, and Dietrich Mootz

Dedicated to Professor Peter Böttcher
on the occasion of his 60th birthday

Polyketones from olefins and carbon monoxide, which were first industrially produced under the name "carilon" in 1996, are new plastics with interesting material properties. Among these are a strong rigidity and impact strength, good chemical resistance to acids, bases, and solvents as well as a high tracking resistance and stability against electrolytic corrosion—properties, which make polyketones superior to polyolefins, polyamides, and polyacetals.[1–3] Although copolymerization of ethene and carbon monoxide on tetracyanonickelate(II) at 100–200°C was already described by Reppe in 1951 and by Shryne and Holler in 1976,[4, 5] the resulting polymers have never been prepared on an industrial scale. The breakthrough was achieved with a palladium–phosphane complex, which catalyzes the formation of a perfectly alternating 1:1 copolymer from ethene or propene and carbon monoxide under mild reaction conditions.[6, 7]

Can nickel replace the relatively expensive palladium, which is not recovered in the industrial production of plastics? So far only a few nickel(II) complexes are known that catalyze the alternating copolymerization of ethene and carbon monoxide under mild conditions: Klabunde et al. showed that polyketone formation is catalyzed by arylnickel(II) compounds with P,O chelate ligands of the same type that is used in SHOP procedures (SHOP = *S*hell *H*igher *O*lefins *P*rocess).[8, 9] Cavell et al. described similarly active arylnickel(II) compounds with N,O chelate ligands.[10] However, in both cases the polymerization must be initially started with ethene alone since carbon monoxide acts as a catalyst poison prior to the beginning of the reaction. This problem is circumvented by applying a catalyst for polyketone synthesis described by Keim et al. Apparently, this catalyst is formed in situ from thiolcarboxylic acids and nickel compounds.[11] We have now for the first time synthesized and structurally characterized an arylnickel(II) complex, which like the palladium–phosphane complexes catalyzes the polymerization of ethene and carbon monoxide already at above 20°C and below 50 bar total pressure; a strictly alternating polyketone is formed exclusively. The reaction can be started without loss of activity by pressurizing with the carbon monoxide . Thus the aroyl complex is formed, which on addition of ethene initiates the formation of polyketone. The arylnickel(II) complex **1** was synthesized according to Equation (1).

$$[\mathrm{NiBr}(o\text{-tolyl})(\mathrm{PPh_3})_2] + \mathrm{TlTp^{Ph}} \longrightarrow [\mathrm{Ni}(o\text{-tolyl})(\mathrm{PPh_3})(\mathrm{Tp^{Ph}})]\ \mathbf{1} + \mathrm{TlBr} + \mathrm{PPh_3} \qquad (1)$$

As shown in Figure 1 the tripodal tris(pyrazolyl)borate ligand $\mathrm{Tp^{Ph}}$[12] of **1** is coordinated as a bidentate chelate ligand to the nickel atom.[13] So far it could not be explained why this particular nickel complex catalyzes the polyketone formation. A priori one might expect that the presence of a third coordinating donor center rather impedes the formation of reversibly liberated coordination sites and thus suppresses the catalysis.[14] From investigations on the coordination chem-

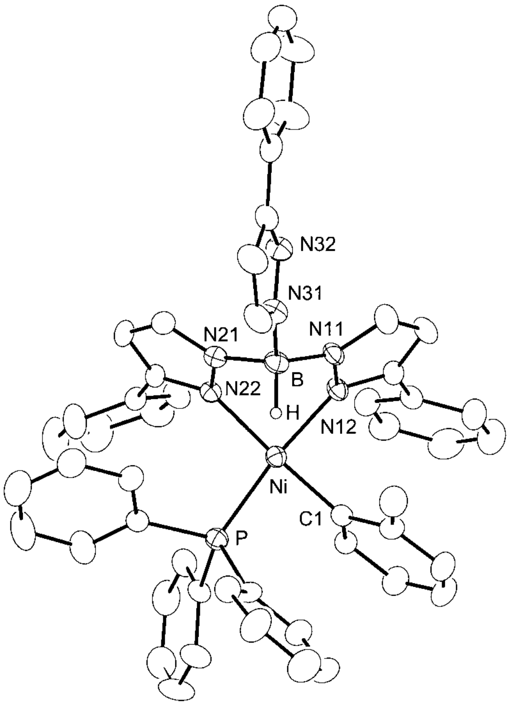

Figure 1. Structure of **1** in the crystal. Thermal ellipsoids for 25% probability, for C atoms without equators. The H atoms, with the exception of that at the B atom, are not shown for reasons of clarity. Selected bond lengths [Å], bond angles [°], and torsion angles [°]: Ni–N12 1.940(4), Ni–N22 1.961(4), Ni–C1 1.906(5), Ni–P 2.182(1), Ni⋯H 2.92(3), B–N11 1.544(6), B–N21 1.560(6), B–N31 1.517(5), B–H 1.20(3), N11–N12 1.384(4), N21–N22 1.369(4), N31–N32 1.371(5); N12-Ni-N22 87.0(2), N12-Ni-C1 90.4(2), N22-Ni-C1 174.9(2), P-Ni-C1 85.9(1), P-Ni-N12 164.3(1), P-Ni-N22 97.8(1), N11-B-N21 107.3(4), N11-B-N31 111.7(4), N21-B-N31 107.8(4), N11-B-H 112(2), N21-B-H 108(2), N31-B-H 110(2); N22-Ni-N12-N11 56.1(3), N12-Ni-N22-N21 −56.6(3).

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