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complexes of phosphanyldihydrooxazoles have angles of around 50°: H. Steinhagen, P. Sennhenn, A. Pichota, G. Helmchen, unpublished results.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-

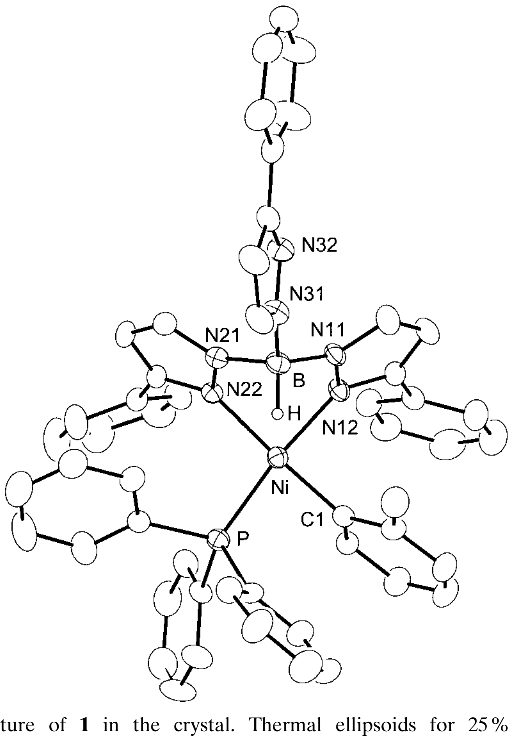

Figure 1. Structure of **1** in the crystal. Thermal ellipsoids for 25% probability, for C atoms without equators. The H atoms, with the exception of that at the B atom, are not shown for reasons of clarity. Selected bond lengths [Å], bond angles [°], and torsion angles [°]: Ni–N12 1.940(4), Ni–N22 1.961(4), 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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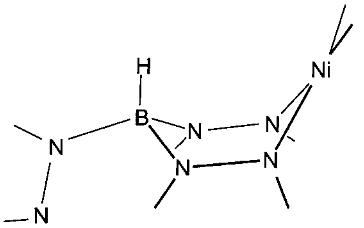
istry of the Tp^{Ph} ligand we have recently shown that the flexibility of this ligand permits a facile alteration between bidentate and tridentate coordination.[15] Apparently the potential tridenticity is not a disadvantage. However, it is evidently of significance that the nitrogen centers as relatively hard Lewis bases and the high chelate effect of the Tp^{Ph} ligand can keep the nickel center at the oxidation state +II also in the presence of carbon monoxide. This is decisive for the lifetime of the catalyst since the catalysis terminates on the occurrence of a reduction with the formation of carbonyl–phosphane–Ni^0 complexes. The orientation of the noncoordinating third pyrazole ring observed in the solid state has the effect that the borane hydrogen atom lies in the vicinity of the nickel center. This was the reason why we assumed that an intermediary nickel hydride species might be responsible for initiating the catalysis cycle. To examine this assumption we attempted to prepare analogous arylnickel Tp complexes with other substituents. The reaction of $[NiBr(o\text{-tolyl})(PPh_3)_2]$ with TlTp or $TlTp^{Me,Me}$ according to Equation (1) gave the complexes $[Ni(Tp)_2]$ and $[Ni(Tp^{Me,Me})_2]$, respectively—catalytically inactive, octahedral nickel compounds, which lack the aryl group at the nickel center. The reaction with $TlTp^{p\text{-tolyl},Me}$ only leads to decomposition products, and with the sterically even more demanding ligand Tp^{tBu} and dichloromethane as solvent the chloronickel complex $[NiCl(Tp^{tBu})]$ is formed. Only when the ligand $Tp^{p\text{-tolyl}}$ is used were we able to prepare the arylnickel complex $[Ni(o\text{-tolyl})(PPh_3)(Tp^{p\text{-Tolyl}})]$ (**2**), which is analogous to **1**. Complex **2** is catalytically significantly less active than **1**, that is the accessibility and thus the catalytic activity of aryl nickel complexes with $Tp^{R,R'}$ ligands is highly dependent on the substituents R and R′. Whether the boron–hydrogen unit plays a role for the catalytic activity cannot be determined at present.



The presented catalyst opens a route to further nickel complexes which catalyze the formation of a strictly alternating polyketone under mild conditions. Only when some of them have been synthesized will we be able to search directly for ligands with optimal steric and electronic properties. Recently undertaken density functional and ab initio MO calculations on polyketone synthesis showed that the insertion of carbon monoxide and ethene occurs with a lower selectivity in the presence of nickel complexes than with palladium catalysts.[16] This finding is in accordance with the fact that when the nickel complexes described so far are used , the polymerization of ethene must be initiated before the 1:1 copolymerization of ethene and carbon monoxide occurs.

Experimental Section

Typical procedure for the catalysis: Compound **1** (0.10 g, 0.11 mmol) was dissolved in toluene (10 mL) and allowed to react with a mixture of ethene (0.3 mol, 4000 kPa) and carbon monoxide (350 kPa) in an autoclave under stirring at 60 °C for 16 h. The colorless precipitate was filtered, washed with THF, and the polyketone was dried in vacuo. Yield 1.15 g. M.p. 260–262 °C; IR (KBr): $\tilde{\nu} = 1690\ cm^{-1}$ (C=O); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): $\delta = 36.4$ (s, CH_2), 212.7 (s, C=O); $M_w = 5770$, $M_w/M_n = 1.3$ (matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS)). Elemental analysis: calcd for $(C_3H_4O)_n$: C 64.3, H 7.2; found: C 64.2, H 7.0.

1: Under an inert atmosphere $[NiBr(o\text{-tolyl})(PPh_3)_2]$ (2.0 g, 2.7 mmol) was dissolved in dichloromethane (25 mL), treated with thallium tris(3-phenylpyrazolyl)borate ($TlTp^{Ph}$) (1.7 g, 2.7 mmol), and stirred for 1 h. The precipitated TlBr was filtered off, hexane (10 mL) was added, and the solution was concentrated to half its volume. The resulting yellow solid was washed with hexane until the filtrate remained colorless. Consequently the complex was dissolved in a little toluene, once again filtered and the solution was concentrated after the addition of hexane. Yield 1.9 g (82 %). Crystals suitable for X-ray structure analysis were obtained by recrystallization from diethyl ether. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.60$ (s, 3H; CH_3-tolyl), 5.51 (dt, 1H; tolyl), 5.78 (d, $^3J_{HH} \approx 2.3$ Hz, 1H; pyrazolyl), 6.04 (d, $^3J_{HH} \approx 2.1$ Hz, 1H; pyrazolyl), 6.20 (m, 2H; tolyl), 6.52 (d, $J \approx 8.1$ Hz, 2H), 6.69 (m, 6H), 6.87 (d, $^3J_{HH} \approx 2.1$ Hz, 1H; pyrazolyl), 7.06 (m, 6H), 7.41 (m, 19H), 8.01 (d, $J \approx 7.2$ Hz, 2H), 8.28 (d, $^3J_{HH} \approx 2.2$ Hz, 1H; pyrazolyl); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): $\delta = 23.3$, 103.1, 106.3, 107.1, 119.8, 122.7, 126.7, 127.7 (d, $J_{PC} \approx 13.9$ Hz), 128.0, 128.2 (d, $J_{PC} \approx 9.7$ Hz), 128.5, 129.1, 129.3, 130.0, 130.1, 130.4, 130.7, 134.5 (d, $J_{PC} \approx 9.8$ Hz), 135.0, 135.1, 135.4, 135.7, 139.6, 140.1 (d, $J_{PC} \approx 5.2$ Hz), 146.3; $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): $\delta = 18.4$ (s); IR (KBr): $\tilde{\nu} = 2382$ (w, BH), 1468 (w), 1438 (w), 1433 (w), 1371 (w), 1280 (w), 1207 (m), 530 cm^{-1} (m). Elemental analysis: calcd for $C_{52}H_{44}BN_6NiP \cdot C_4H_{10}O$: C 72.5, H 5.9, N 9.1; found: C 72.1, H 5.8, N 9.1

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parameters converged at $R = 0.044$ for 3122 observed reflections with $I > 2\sigma(I)$ and $wR2 = 0.096$ for all reflections. Min./max. residual electron density $-0.219/0.208\,e\,\text{Å}^{-3}$. The structure solution was carried out using SHELXS-86, the structure refinement with SHELXL-93. 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-101494". Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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How Does the Intrinsic Barrier of Intermolecular Proton Transfer Depend on Molecular Parameters?**

Martin Goez* und Rainer Heun

Especially with regard to biological systems, intermolecular proton transfer must be counted among the most important elementary chemical processes; its significance is comparable with that of electron transfer.[1] These two reaction types also have much in common conceptually, because the two lightest chemical particles are transferred and the overall structural changes are not very large. Yet, the difference in their theoretical understanding is considerable. Well established for both is that the relationship between thermodynamics and kinetics—that is, between the driving force of the reaction $-\Delta G^{\ominus}$ and the activation barrier $\Delta G^{\ddagger}$—can be expressed in terms of a single parameter, the intrinsic barrier $\Delta G^{\ddagger}_{\text{int}}$, which is the activation barrier for the (often hypothetical) reaction with $\Delta G^{\ominus}$ equal to zero.[2] However, asking for the factors that govern the magnitude of the key quantity $\Delta G^{\ddagger}_{\text{int}}$ reveals a fundamental gap in our knowledge. While $\Delta G^{\ddagger}_{\text{int}}$ of electron transfer can be predicted numerically from molecular geometries, force constants, and charge densities,[3] much less is known about the dependence of $\Delta G^{\ddagger}_{\text{int}}$ on molecular parameters in the case of proton transfer.[4–6] Here we explore the influence of electronic factors on $\Delta G^{\ddagger}_{\text{int}}$ of proton transfer experimentally, and develop a valence bond configuration mixing (VBCM) model that is capable of explaining the results.

For the substrates we chose *para*-substituted *N,N*-dimethylanilines B, because these compounds lend themselves very well to a separation of electronic and steric effects: By changing the *para* substituent the electron density at the base center can be varied with negligible influence on the geometry of this site and the steric requirements for the reaction. Intermolecular proton transfer is often complicated by participation of the solvent (relay mechanism),[7] which causes the apparent (i.e., observed) activation barrier to be a compound quantity.[6] To avoid this, we carried out the experiments in water-free acetonitrile, which does not function as a hydrogen-bond donor and is a much weaker hydrogen-bond acceptor than is water.[8] The intrinsic barriers $\Delta G^{\ddagger}_{\text{int}}$ were obtained directly from measurements of the rates of proton self-exchange [Eq. (1)] between the unprotonated and protonated forms B and BH^+ of our substrates by means of dynamic NMR spectroscopy.

$$BH^+ + B \rightleftharpoons B + BH^+ \qquad (\Delta G^{\ominus} = 0,\ \Delta G^{\ddagger} = \Delta G^{\ddagger}_{\text{int}}) \tag{1}$$

Not only is this approach more economical than the usual one—namely, using the Marcus theory[2b] to calculate $\Delta G^{\ddagger}_{\text{int}}$ from the activation barriers of a series of homologous cross reactions—it is also much more reliable because it circumvents the difficulties associated with the determination of $\Delta G^{\ominus}$, that is, the problem of acidities in a nonaqueous solvent.

All experimental details are given in a previous paper,[9] where the mechanism of these reactions was also cleared up in detail. As was shown there, thermally activated direct proton transfer between BH^+ and B is rate-determining; relayed proton transfer involving the solvent or residual water is absent, and formation of hydrogen bonds between BH^+ and B as well as tunnelling do not play a significant role. These findings mean that a unique and well-defined reaction mechanism is realized in these systems, which is an indispensible prerequisite for a study aiming to quantify the influence of molecular parameters on the intrinsic barrier of proton transfer.

As Figure 1 shows, there exists a good linear correlation between the values for $\Delta G^{\ddagger}_{\text{int}}$ obtained in this way and the Hammett parameter σ^+. While σ^+ is not a molecular property of our substrates, it is nevertheless related to such: It is well known that σ^+ is a quantitative measure of the electron density at the nitrogen atom in these compounds, and basicity as well as ionization potential I_v of B are linear functions of σ^+.[10] This correspondence will play a key role for the theoretical interpretation that follows. We stress that Figure 1 differs in its implications from a usual Hammett plot: The latter is either a linear relationship between free energies or—when it is of the type $\lg k$ versus Hammett parameter—reflects the influence of the driving force of a reaction on its rate. However, for our self-exchange reactions $\Delta G^{\ominus}$ is zero, and the plot reveals how the *intrinsic* activation barrier $\Delta G^{\ddagger}_{\text{int}}$ depends on an electronic parameter of the reactants. It is seen that the height of $\Delta G^{\ddagger}_{\text{int}}$ is a linear function of the electron density at the nitrogen atom, and the higher the latter, the lower the intrinsic barrier. As a qualitative general trend, this behavior has been reported,[4] but to the best of our knowledge a linear relationship has not been observed before.

These findings can be explained by a VBCM model (Figure 2). Such models were introduced by Pross and Shaik,

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