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Dioxygen Activation by Diiminodipyrromethane Complexes of Ni, Pd, and Pt

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Diiminodipyrromethane complexes of Ni, Pd, and Pt are able to activate O_2, resulting in a metal-dependent autoxidation of the ligand.

O_2 activation by transition-metal complexes is of prime importance in the context of bioinorganic chemistry[1] and in the area of preparative organic chemistry.[2] Several synthetic complexes have been reported that are able to activate molecular oxygen in interesting stoichiometric or catalytic reactions. This includes complexes of V,[3] Fe,[4] Ru,[5] Os,[6] Pd,[7] and Cu,[8] to name a few. Much effort has been devoted to complexes with porphyrin ligands because they resemble the naturally occurring heme complexes and because of their favorable physicochemical properties (low redox potential and high stability).[9] Multidentate ligands based on dipyrromethane fragments are structurally related to porphyrins, but the reactivity of the corresponding transition-metal complexes toward O_2 is largely unexplored.[10,12] In the following, we describe the synthesis and the reactivity of novel diiminodipyrromethane complexes of Ni, Pd, and Pt. It is shown that the complexes are able to activate O_2, resulting in a metal-dependent autoxidation of the ligand.

Recently, it has been shown by us[11] and others[12] that iminopyrroles and diiminodipyrromethanes are suited ligands for group 10 metal complexes. For the present study, we have synthesized Ni^{II}, Pd^{II}, and Pt^{II} complexes of the novel tetradentate ligand **2**. Ligand **2** was obtained by acid-catalyzed condensation of 2,2′-(5-formyl-3-methyl-4-eth-

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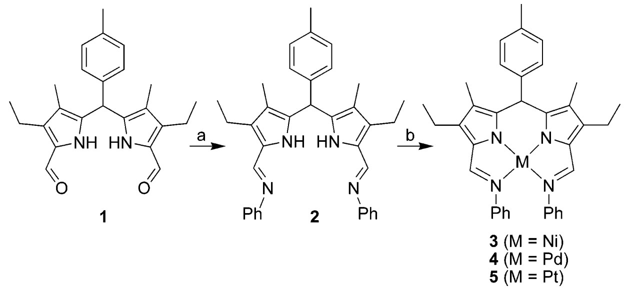
Scheme 1. Synthesis of the Complexes **3**−**5**[a]



[a] Conditions: (a) 2 equiv of $PhNH_2$, MeOH/HCl, and then neutralization with NEt_3; (b) $Ni(OAc)_2$, NEt_3, MeOH, or $PdCl_2(CH_3CN)_2$, NEt_3, (3:1) CH_3CN/MeOH, or $PtCl_2$(COD), NEt_3, CH_3CN.

ylpyrrolyl)-*p*-tolylmethane (**1**) and aniline (Scheme 1). The complexes **3**−**5** were prepared by reaction of **2** with $Ni(OAc)_2$, $PdCl_2(CH_3CN)_2$, or $PtCl_2$(COD), respectively, in the presence of NEt_3. The solvent (MeOH and/or CH_3CN) was chosen so that the product precipitated from the reaction mixture. Complex **4** can also be obtained in a metal-templated reaction from **1**, aniline, $PdCl_2(CH_3CN)_2$, and NEt_3.

Because of the close proximity of the two phenyl rings, the complexes **3**−**5** were expected to adopt a helical structure, similar to what was observed by Levy and coworkers for Zn^{II}- and Fe^{II}-salen complexes with benz[*a*]anthracene substituents.[13] For complex **4**, this chirality was evidenced in the NMR spectra, which showed diastereotopic signals for the imino groups. The complexes **3** and **5**, on the other hand, displayed no diastereotopic signals, indicating a fast epimerization on the NMR time scale.

Next we have investigated the reactivity of the complexes toward O_2. As a first test, we have reacted $CHCl_3$ solutions of the complexes with air. Whereas no reaction was observed for the Pd and Pt compounds, a slow oxidation was found to occur for the Ni complex. After 1 week, we were able to isolate a mixture of the complexes **6** and **7** (9:1) in 40% yield (Scheme 2). The same products were obtained in 28% yield when $Ni(OAc)_2$ was reacted with **1**, aniline, and NEt_3 in acetonitrile under air. Interestingly, the two complexes cocrystallize as revealed by a single-crystal X-ray analysis (Figure 1).[14] In the major product **6** (90%), the Ni^{II} ion is coordinated to a dipyrromethene ligand with one imino group and one amido group. The side product **7** (10%) was found to have a carboxylato group instead of the amido group. The presence of these two complexes was also confirmed by NMR spectroscopy. The Ni heteroatom distances of complex **6** are as follows: Ni−N2 1.829(3) Å, Ni−N3 1.845(3) Å, Ni−N1 1.943(6) Å, and Ni−N4 1.969(3) Å. In the crystal, adjacent complexes show interaction between their planes, with the distance between the Ni center of one complex and the pyrrole heterocycle of the second complex being ∼4 Å.

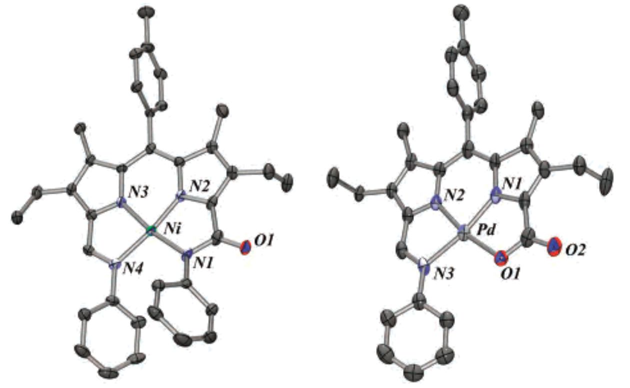
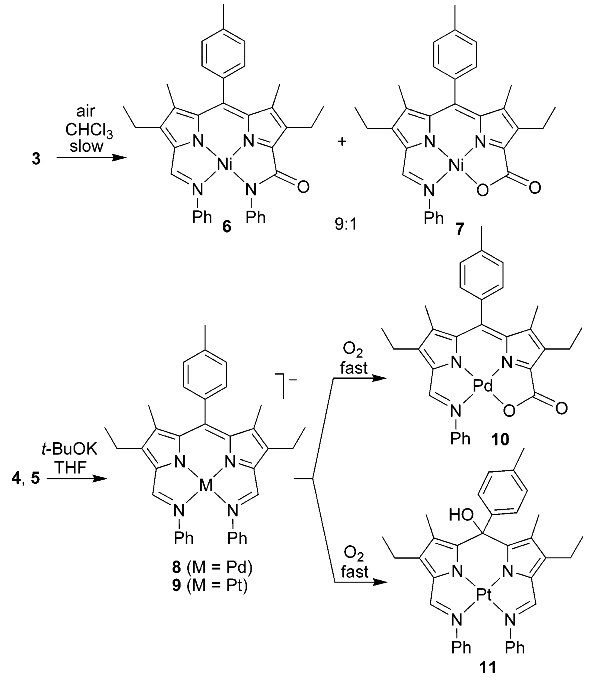


Figure 1. Graphic representation[16] of the molecular structures of the complexes **6** (left) and **10** (right) in the crystal. The H atoms and solvent molecules (**1**·THF for **10**) are omitted; the ellipsoids are shown at 50% probability level.

Scheme 2. Synthesis of the Complexes **6**−**11**



The autoxidation of the ligand by molecular oxygen has been observed for some Ni^{II} complexes with polydentate N-donor ligands, and a radical mechanism with a nickel(III) superoxide intermediate was suggested.[15] A similar mechanism might be operational for **3**, but further studies are needed to clarify this point.

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(14) Crystal data for complex **6**/**7**: CCDC 642665, $C_{35.5}H_{33.7}Cl_{0.2}N_{3.9}NiO_{1.1}$, $M = 598.36$, monoclinic, $a = 12.069(6)$ Å, $b = 24.496(16)$ Å, $c = 10.616(3)$ Å, $\beta = 112.35(3)°$, $V = 2903(3)$ Å^3, $T = 100(2)$ K, space group $P2_1/c$, $Z = 4$, μ(Mo Kα) = 0.710 73 Å, 37 951 reflections collected, 5101 independent reflections, $R_{int} = 0.0883$, R_1 [$I > 2\sigma(I)$] = 0.0536, wR_2 (all data) = 0.1061. Disorder problems arise from the presence in the same crystal structure of the two different products (with their occupancies being 0.90 for compound **6** and 0.10 for compound **7**·CH_2Cl_2). Disorder has been treated by means of the split model; the C1−O2 and C1−O3 distances have been restrained by means of DFIX, whereas the ISOR card has been used for the anisotropic refinement of O2 and C37 (the C atom belonging to the CH_2Cl_2 occupying in complex **7** almost the same site of the disordered Ph in complex **6**).

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In order to activate the Pd and Pt complexes, we thought to increase the electron density by abstraction of the acidic *meso*-CH proton. When tetrahydrofuran (THF) solutions of the complexes **4** and **5** were treated with 2 equiv of *t*-BuOK under an argon atmosphere, a dark-green solution of the anionic complexes **8** and **9** was obtained (Scheme 2). ^{1}H NMR spectroscopic analyses confirmed the formation of a conjugated dipyrromethene ligand environment. The anionic complexes with the formal oxidation state 0 were found to be highly reactive toward molecular oxygen. When the THF solutions were subjected to an atmosphere of pure O_2, dark orange-red (for **10**) or orange (for **11**) solutions were obtained within seconds. From these, the complexes **10** and **11** could be isolated in 74 or 75% yield, respectively.

The spectroscopic (**10** and **11**) and crystallographic (**10**) analyses revealed that the reaction with O_2 had resulted in very distinct products. For Pd, a dipyrromethene complex with a carboxylate group was formed (**10**), with a structure analogous to that of the side product **7** (Figure 1).[17] In the crystal, close plane contacts (~3.5 Å) are observed between the macrocyclic cores of adjacent complexes. The Pd heteroatom distances of complex **10** are as follows: Pd−N2 1.929(5) Å, Pd−N1 1.946(6) Å, Pd−O1 2.080(5) Å, and Pd−N3 2.117(6) Å. For the Pt complex **11**, on the other hand, the reaction with O_2 had resulted in the hydroxylation of the meso position. Accordingly, the complex showed only one set of NMR signals for the two iminopyrrole groups. Spectroscopic evidence for the OH group was a ^{1}H NMR signal at δ 2.44 ppm ($CDCl_3$), which disappeared upon the addition of D_2O.

In conclusion, we have synthesized novel diiminodipyrromethane complexes of Ni, Pd, and Pt that are able to activate O_2, resulting in autoxidation products. The nature of the metal ion had a pronounced influence on the reactivity. For Ni, a dipyrromethene complex with an amido group was obtained as the main product. The Pd and Pt complexes **4** and **5** required prior activation with base, leading to a formal reduction to Pd^0 and Pt^0. Subsequent reaction with O_2 gave a dipyrromethene complex with a carboxylate group in the case of Pd^{II} and a meso-hydroxylated product for Pt^{II}.[19] These results are first evidence that diiminodipyrromethane complexes of group 10 metal ions can display interesting O_2 chemistry. The design of more robust ligand environments and the investigation of catalytic processes are underway.

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Supporting Information Available: Crystallographic data for complexes **6** and **10** in CIF format and synthetic procedures and analytical data for compounds **2**−**11**. The material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Crystal data for complex **10**·THF: CCDC 642666, $C_{34}H_{37}N_3O_3Pd$, $M = 642.07$, triclinic, $a = 11.05(3)$ Å, $b = 11.334(7)$ Å, $c = 13.356(7)$ Å, $\alpha = 64.99(6)°$, $\beta = 73.74(11)°$, $\gamma = 84.03(13)°$, $V = 1455(4)$ Å^3, $T = 100(2)$ K, space group $P\bar{1}$, $Z = 2$, μ(Mo Kα) = 0.710 73 Å, 19 733 reflections collected, 5048 independent reflections, $R_{int} = 0.0777$, R_1 [$I > 2\sigma(I)$] = 0.0546, wR_2 (all data) = 0.1211.

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(19) The reactivity of Pd^0 complexes with N-donor ligands toward O_2 has been investigated experimentally and theoretically by Stahl and coworkers, and a possible mechanism for the reaction with O_2 has been suggested (see ref 18).