# Zero-Valent Palladium Complexes with Monodentate Nitrogen σ-Donor Ligands**

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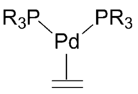
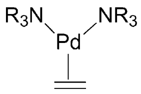
Compared to the large number of known, well-characterized zero-valent [bis(phosphanyl)palladium(alkene)] complexes **A**,[1] the number of [$Pd^0(\eta^2$-alkene)] complexes that contain nitrogen ligands is very limited.[2] Moreover, only complexes containing bidentate ligands that display both σ-donor and π-acceptor properties are known. Thus far, zero-valent palladium–alkene complexes **B** that contain simple monodentate nitrogen ligands have not been isolated and characterized. The elusiveness of zero-valent palladium complexes containing ligands that only behave as σ donors has been attributed to the alleged instability of such compounds, which arises from the combination of a soft, low-valent metal center and a hard nitrogen donor atom.[3] In contrast, $Ni^0$ complexes with one simple N-donor ligand are formed already with ethene as the coligand (e.g. [$(L)Ni(C_2H_4)_2$] ($L = NH_3$, pyridine, etc.)[4] and related bisamine complexes [$(L)_2Ni(C_2H_4)$], when the strength of coordination of the N ligands is increased by steric effects.[5] Zero-valent palladium compounds are generally either formed in situ by reduction of a suitable palladium(II) compound, or by starting from a zero-valent palladium complex with labile ligands.



**A**

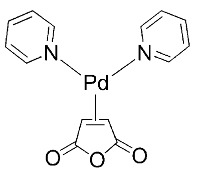


**B**

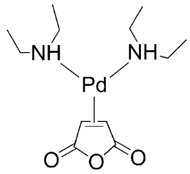
Pörschke and co-workers described the synthesis and use of "naked palladium" complexes, which contain coordination-labile 1,6-diene and other {$L–Pd^0$} fragments as highly reactive building units.[6] It was shown that the homoleptic dinuclear [$Pd_2$(1,6-diene)$_3$] and [$Pt_2$(1,6-diene)$_3$] complexes are very useful starting materials for preparing mononuclear complexes of the general formula [L–M(1,6-diene)] (L = phosphane, phosphite, or nitrile). However, by using this route, the authors did not succeed in preparing similar complexes based on ligands with strong σ-donor character, such as pyridine or an amine.

We now report the synthesis and characterization of several unprecedented $Pd^0$ compounds with monodentate N ligands as well as an X-ray structure of one such compound, [$Pd(py)_2$(ma)] (py = pyridine, ma = maleic anhydride). For the synthesis of the new $Pd^0$ compounds [$Pd(L)_2$(ma)], and [Pd(L′)(ma)] in which L′ is a bidentate N ligand, we used [Pd(nbd)(ma)] (nbd = norbornadiene)[7] as a versatile precursor. Dibenzylideneacetone (dba) complexes are not very suitable in this case, as dba is nonvolatile and difficult to separate from many $Pd^0$ compounds, especially those that are labile. [Pd(nbd)(ma)] is one of the few zero-valent palladium precursors containing volatile, readily dissociating ligands, that can be stored and used at room temperature (similar to some of the dinuclear 1,6-diene complexes[6]) and can even be handled in air for a short time without decomposition. By this new route one can readily prepare a number of zero-valent palladium complexes of the generic formula [$Pd(L)_2$(ma)] (L = pyridine, amine, aniline, or ammonia).

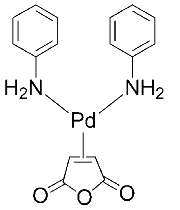
We prepared [Pd(nbd)(ma)][7] by a modified literature procedure (THF was used as the solvent instead of acetone) and found that decomposition to palladium black was appreciably reduced. Next, the zero-valent [$Pd(L)_2$(ma)] complexes **1**–**4** were prepared in typical yields of 65–70% by substitution of the norbornadiene ligand in [Pd(nbd)(ma)] by an excess of the monodentate nitrogen ligand in THF. Importantly, isolation of the product was carried out quickly to prevent undesired side reactions such as decomposition to palladium black. The products **1**–**4** were isolated as yellow



**1**



**2**



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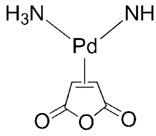

**4**

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crystalline solids, which are stable at room temperature for days in a closed vessel.

The isolated products were characterized by $^1$H, $^{13}$C NMR, and IR spectroscopy and by exact mass determination. From the NMR spectra, the coordination-induced shifts (CIS) of the signals for the protons of maleic anhydride, $\Delta\delta(\mathrm{H}) = -3.44$ ppm for **1** to $-3.87$ ppm for **4** and for the coordinated carbon atoms $\Delta\delta(\mathrm{C}) = -92.32$ ppm for **1** and $-74.35$ ppm for **4**, are indicative of a highly electron-rich Pd$^0$ center.

We also carried out several calculations at the BP86/ECP1 level[8] to assess the stabilities of a number of selected [Pd$^0$(L)$_2$(alkene)] compounds in terms of the driving force for their formation from the corresponding tris(alkene) model complexes [Eq. (1)].

$$[\mathrm{Pd(C_2H_4)_2(alkene)}] + 2\,\mathrm{L} \rightarrow [\mathrm{Pd(L)_2(alkene)}] + 2\,\mathrm{C_2H_4} \qquad (1)$$

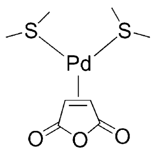
These calculations revealed that when one electron-deficient alkene is coordinated to Pd, the Gibbs free energy $\Delta G^{298}$ of this process is only slightly positive or even negative (Table 1). Such thermo-neutral Pd$^0$–alkene complexes ($\Delta G^{298} \approx 0$) can, in principle, be synthesized if an appropriate kinetic route is chosen. In such a case, the starting compound should contain highly labile ligands, which can be readily displaced in solution to form the desired complex. Calculated thermodynamic data (BP86/ECP1 level) of several relevant compounds are collected in Table 1. The $\Delta G^{298}$ values calculated for the [Pd(L)$_2$(ethene)] complexes are all positive, suggesting that compounds of this type are likely to be unstable under standard conditions and should not be formed from precursors with simple, unactivated olefins. Substitution of ethene by maleic anhydride as the alkene ligand leads to a decrease in the $\Delta G^{298}$ values by approximately 40 kJ mol$^{-1}$. The [Pd(py)$_2$(ma)] complex (**1**) still has a positive $\Delta G^{298}$ value, consistent with the limited stability of this compound at ambient temperature and pressure. Comparing, for instance, entries 1 and 4 (or 10 and 13), the chelate effect (bipyridine vs. pyridine) is clearly reflected in the calculated values of enthalpies ($\Delta H^{298}$) relative to Gibbs free energies ($\Delta G^{298}$), and gives rise to a further stabilization by up to 40 kJ mol$^{-1}$.

***Table 1:*** Calculated (BP86/ECP1 level) energies, enthalpies, and free energies for the formation of [Pd$^0$(L)$_2$($\eta^2$-alkene)] complexes according to Equation (1).[a]

| Entry | Alkene | (L)$_2$ | $\delta E$ [kJ mol$^{-1}$] | $\Delta H^{298}$ [kJ mol$^{-1}$] | $\Delta G^{298}$ [kJ mol$^{-1}$] |
|---|---|---|---|---|---|
| 1 | C$_2$H$_4$ | (py)$_2$ | 57.9 | 56.0 | 52.7 |
| 2 | | (NH$_3$)$_2$ | 50.0 | 47.8 | 32.1 |
| 3 | | (NHMe$_2$)$_2$ | 69.1 | 69.9 | 61.3 |
| 4 | | bipy | 75.7 | 67.9 | 19.8 |
| 5 | | tmeda | 79.5 | 74.9 | 35.6 |
| 6 | | dab | 61.4 | 54.3 | 8.4 |
| 7 | | (SMe$_2$)$_2$ | 59.7 | 57.7 | 49.5 |
| 8 | | C$_7$H$_{12}$ | 14.3 | 7.9 | −23.1 |
| 9 | | PMe$_3$ | −31.6 | −33.3 | −41.0 |
| 10 | ma | (py)$_2$ | 11.9 | 10.5 | 11.9 |
| 11 | | (NH$_3$)$_2$ | 1.7 | 4.9 | −11.4 |
| 12 | | (NHMe$_2$)$_2$ | 16.6 | 18.8 | 19.3 |
| 13 | | bipy | 36.1 | 28.8 | −14.3 |
| 14 | | tmeda | 30.1 | 26.2 | −10.5 |
| 15 | | dab | 37.9 | 31.0 | −11.6 |
| 16 | | (SMe$_2$)$_2$ | 17.5 | 15.9 | 17.4 |
| 17 | | C$_7$H$_{12}$ | 9.2 | 2.3 | −26.6 |
| 18 | | PMe$_3$ | −78.9 | −79.6 | −77.5 |

[a] ma = maleic anhydride, bipy = 2,2′-bipyridine, tmeda = tetramethylethylenediamine, dab = 1,4-diazabutadiene.

Furthermore, the bis(dimethylsulfide) complex [Pd(Me$_2$S)$_2$(ma)] (**5**) as well as the chelate compounds [Pd(1,6-heptadiene)(ma)] (**6**) and [Pd(tmeda)(ma)] (**7**) were prepared following the same synthetic route. The monodentate dialkyl sulfide complex can be isolated, even though the somewhat lower stability of the resulting complexes could have been expected based on the calculations (see Table 1, entry 16). Of course, the calculated $\Delta G^{298}$ values for compounds with mono- and bidentate phosphane as well as with bidentate N ligands are negative (see Table 1, entries 14, 15, and 18); in particular, the stabilization for PMe$_3$ is large. However, the latter complexes can also be obtained by using more conventional starting materials.



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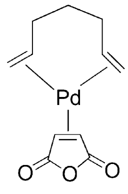
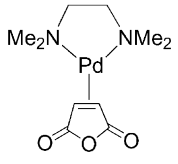


**6**



**7**

Crystals of **1** were obtained by crystallization from pyridine/THF/diethyl ether.[9] The molecular structure of compound **1** with the adopted atom numbering is presented in Figure 1. The structure of **1** shows that the palladium centre

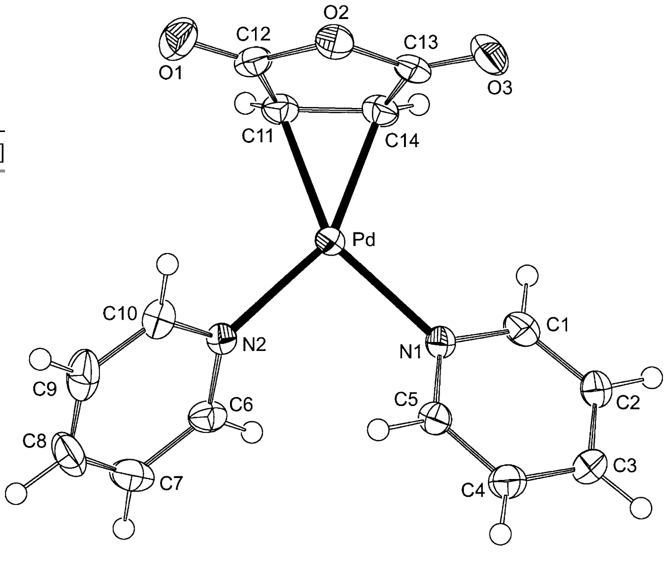


***Figure 1.*** Displacement ellipsoid plot (50% probability level) of compound **1**. Selected distances [Å] and angles [°]: Pd-N1 2.1472(19), Pd-N2 2.1462(18), Pd-C11 2.068(2), Pd-C14 2.062(2), C11-C14 1.430(3), C11-Pd-C14 40.51(10), N1-Pd-N2 94.44(7), C11-Pd-N1 151.96(9), C14-Pd-N2 153.81(8), C11-Pd-N2 113.32(9), C14-Pd-N1 111.73(8), Pd-C11-C12 108.29(17), Pd-C14-C13 105.07(17).

is trigonal planar, as expected for zero-valent complexes of the type $[M(L)_2(\text{alkene})]$ ($M = Pd, Pt$). The dihedral angle between the least-squared planes N1/N2/Pd and C11/C14/Pd is 4.74(16)° and thus the complex is slightly distorted from planarity. The Pd–N interatomic distances observed for compound **1** are equal within standard deviation and amount to 2.1472(19) and 2.1462(19) Å, slightly smaller than the BP86/ECP1-optimized values (2.162 and 2.160 Å). The alkene bond length C11=C14 is 1.430(3) Å and is 0.098(3) Å longer than in the free alkene, which is slightly longer than the C=C bond lengthening in the previously reported $[Pd(o,o'\text{-}i\text{Pr}_2C_6H_3\text{-bian})(\text{ma})]$ (bian = bisiminoacenaphthene) of 1.408(11) Å and [Pd(R′N-SR)(ma)] (R′N-SR = 2-methyl(sulfanylmethyl)pyridine) of 1.413(5) Å.[2d,13,14] The maleic anhydride moiety forms a typical angle of 78.16(16)° with the C11/C14/Pd plane. The other distances in the coordinated maleic anhydride part are similar to the reported complexes and the free molecule.

In summary, the first zero-valent complexes $[Pd(L)_2(\text{ma})]$ with σ-donor N ligands (L = ammonia, aniline, diethylamine, pyridine) have been synthesized and isolated. These $[Pd(L)_2(\text{ma})]$ complexes are stable at room temperature for days and are useful as catalyst precursors.[15]

## Experimental Section

General procedure: To a mixture of dry THF (10 mL) and the appropriate N ligand (5 mL) was added solid $[(\eta^2,\eta^2\text{-nbd})(\eta^2\text{-ma})Pd^0]$ (0.15 g, 0.5 mmol). In the case of ammonia, 3–4 mL was condensed at −70 °C, to which cold THF (10 mL) was slowly added, followed by the $Pd^0$ complex as above. After complete dissolution of the latter, the solution was filtered through Celite and washed with THF (2 × 5 mL). Diethyl ether (15 mL) was then added to the solution, after which the products were obtained as yellow microcrystalline solids in a typical yield of 65%. Selected data: **1**: $^1H$ NMR (500 MHz, $[D_6]$acetone, 25 °C, TMS): $\delta = 8.58$ (m, 4H; py-2-H), 7.97 (m, 2H; py-4-H), 7.54 (m, 4H; py-3-H), 3.9 ppm (br, 2H; C=CH); $^{13}C$ NMR (125 MHz, $[D_6]$acetone, 25 °C, TMS): $\delta = 151.68$ (py-C2), 137.70 (py-C4), 125.40 (py-C3), 39.80 ppm (CH), (C=O not observed); IR (THF): $\tilde{\nu} = 1780$, 1726 $cm^{-1}$ (C=O). **2**: $^1H$ NMR (500 MHz, $CD_2Cl_2$, 25 °C, TMS): $\delta = 3.5$ (br, 2H; C=CH), 2.7 (br, 8H; $CH_2$), 1.3 ppm (br, 12H; $CH_3$); $^{13}C$ NMR (125 MHz, $[D_6]$acetone, 25 °C, TMS): $\delta = 171.9$ (C=O), 48.0 (C=C), 38.3 ($CH_2$), 15.1 ppm ($CH_3$); IR (THF): $\tilde{\nu} = 1793$, 1726 $cm^{-1}$ (C=O). **3**: $^1H$ NMR (500 MHz, $[D_6]$acetone, 25 °C, TMS): $\delta = 7.06$ (t, $J = 8.0$ Hz, 4H; ArH), 6.68 (d, $J = 7.5$ Hz, 4H; ArH), 6.59 (t, $J = 7.5$ Hz, 2H; ArH), 4.59 (br, 2H; C=CH), 2.81 ppm (s, 4H; $NH_2$); HRMS: calcd for $C_{16}H_{17}N_2O_3Pd$: 391.0281; found 391.0233. **4**: $^1H$ NMR (500 MHz, $[D_6]$acetone, 25 °C, TMS): $\delta = 3.47$ (s, 2H; C=CH), 3.57 ppm (s, 6H; $NH_3$); $^{13}C$ NMR (125 MHz, $[D_6]$acetone, 25 °C, TMS): $\delta = 177.70$ (C=O), 62.77 ppm (C=C). **5**: $^1H$ NMR (500 MHz, $[D_6]$acetone, 25 °C, TMS): $\delta = 4.1$ (br, 2H; C=CH), 2.4 ppm (s, 12H). **6**: $^1H$ NMR (500 MHz, $[D_8]$THF, 25 °C, TMS): $\delta = 4.98$ (s, 2H), 4.76 (m, 4H), 3.98 (br, 2H), 3.86 (br, 2H; C=CH), 2.02 (br, 2H), 1.75 (s, 2H), 0.92 ppm (br, 2H); $^{13}C$ NMR (125 MHz, $[D_8]$THF, 25 °C, TMS): $\delta = 168.31$ (C=O), 99.96, 73.91, 60.73, 31.29, 30.89 ppm. **7**: $^1H$ NMR (500 MHz, $CD_2Cl_2$, 25 °C, TMS): $\delta = 3.55$ (s, 2H; C=CH), 2.73 (s, 6H; NMe), 2.72 (s, 6H; NMe), 2.5 ppm (m, 4H; $CH_2CH_2$); $^{13}C$ NMR (125 MHz, $CD_2Cl_2$, 25 °C, TMS): $\delta = 172.22$ (C=O), 59.94 (C=C), 50.64 ($CH_3$), 50.14($CH_3$), 39.54 ppm ($CH_2$).

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**Keywords:** coordination compounds · density functional calculations · donor–acceptor systems · N ligands · palladium

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[9] $C_{14}H_{12}N_2O_3Pd$, $F_w = 362.66$, yellow needle, $0.48 \times 0.12 \times 0.09$ $mm^3$, orthorhombic, *Pbca* (no. 61), $a = 8.1477(1)$, $b = 16.0499(3)$, $c = 20.5190(4)$ Å, $V = 2683.27(8)$ Å$^3$, $Z = 8$, $\rho_x = 1.795$ $g\,cm^{-3}$, $\mu = 1.391$ $mm^{-1}$; 19822 reflections were measured on a Nonius KappaCCD diffractometer with rotating anode ($\lambda = 0.71073$ Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å$^{-1}$; 3073 reflections were unique ($R_{int} = 0.051$); an absorption correction based on multiple measured reflections was applied (0.77–0.91 transmission); the structure was solved with direct methods (SIR-97[10]) and refined with SHELXL-97[11] against $F^2$ of all reflections; non-hydrogen atoms were refined freely with anisotropic displacement parameters; H atoms of the maleic anhydride ligand were refined freely with isotropic displacement parameters; H atoms of the pyridine ligands were refined as rigid groups; 189 refined parameters, no restraints; *R* values ($I > 2\sigma(I)$): $R1 = 0.0262$, $wR2 = 0.0579$; *R* values (all reflections): $R1 = 0.0429$, $wR2 = 0.0634$; GoF = 1.025; residual electron density between −0.48 and 0.63 e Å$^{-3}$; molecular illustration, structure checking, and calculations were performed with the PLATON package.[12] CCDC-201446 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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