Dinuclear palladium complexes with two ligand-centered radicals and a single bridging ligand

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Dinuclear Complexes

Dinuclear Palladium Complexes with Two Ligand-Centered Radicals and a Single Bridging Ligand: Subtle Tuning of Magnetic Properties

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Abstract: The facile and tunable preparation of unique dinuclear $[(L)Pd-X-Pd(L)]$ complexes ($X=Cl$ or N_3), bearing a ligand radical on each Pd, is disclosed, as well as their magnetochemistry in solution and solid state is reported. Chloride abstraction from $[PdCl(NNO^{ISQ})]$ (NNO^{ISQ} = iminosemiquinonato) with $TIPF_6$ results in an unusual monochlorido-bridged dinuclear open-shell diradical species, $[(Pd(NNO^{ISQ}))_2(\mu-Cl)]^+$, with an unusually small Pd-Cl-Pd angle (ca. 93° , determined by X-ray). This suggests an intramolecular d^8-d^8 interaction, which is supported by DFT calculations. SQUID measurements indicate moderate antiferromagnetic spin exchange between the two ligand radicals and an overall singlet ground state in the solid state. VT EPR spectroscopy shows a transient signal corresponding to

a triplet state between 20 and 60 K. Complex **2** reacts with PPh_3 to generate $[Pd(NNO^{ISQ})(PPh_3)]^+$ and one equivalent of $[PdCl(NNO^{ISQ})]$. Reacting an 1:1 mixture of $[PdCl(NNO^{ISQ})]$ and $[Pd(N_3)(NNO^{ISQ})]$ furnishes the 1,1-azido-bridged dinuclear diradical $[(Pd(NNO^{ISQ}))_2(\kappa^1-N;\mu-N_3)]^+$, with a Pd-N-Pd angle close to 127° (X-ray). Magnetic and EPR measurements indicate two independent $S=1/2$ spin carriers and no magnetic interaction in the solid state. The two diradical species both show no spin exchange in solution, likely because of unhindered rotation around the Pd-X-Pd core. This work demonstrates that a single bridging atom can induce subtle and tunable changes in structural and magnetic properties of novel dinuclear Pd complexes featuring two ligand-based radicals.

Introduction

Dinuclear transition metal complexes are receiving widespread attention as both structural mimics for naturally occurring metalloenzyme active sites—where metal-metal interactions play

an important role in the cooperative activation of small molecules^[1]—and for their potential use in bimetallic catalysis.^[2] Systems with metal-metal bonds are particularly interesting due to their potential use as electron-reservoirs.^[3] A special class are dimers of square-planar Rh^I , Ir^I , Pt^{II} and Pd^{II} complexes that display (weak) metal-metal bonds due to d^8-d^8 interactions. These interactions arise from overlap in the axial direction between the valence d_{z^2} orbitals of the two square planar metal centers, resulting in both filled bonding ($d\sigma$) and antibonding ($d\sigma^*$) orbitals. There is a net overall bonding interaction due to symmetry-allowed mixing with the $(n+1)$ metal p_z orbitals.^[4]

Few dinuclear Pd^{II} complexes with intramolecular d^8-d^8 interactions have been identified to date. In most cases, a bridging acetate^[5] or neutral ligand^[4d] is required to pre-organize both metals for this bonding interaction to occur, but an unsupported Pd-Pd interaction has also been reported.^[4b] However, dinuclear palladium complexes bridged by a single donor ligand are scarce and none featuring an intramolecular d^8-d^8 interaction have been reported to the best of our knowledge (Figure 1).

Redox-active ligands have recently emerged as an attractive strategy to provide necessary redox equivalents for bond-activation and bond-formation processes.^[6] As a logical extension, dinuclear transition metal complexes containing redox-active ligand radicals are receiving significant attention lately.^[7] Dirad-

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Figure 1. Schematic representation of the potentially tunable spin-exchange interaction in dinuclear palladium complexes with redox-active ligand diradicals.

icals are intriguing species which show interesting properties^[8] and can potentially trigger or facilitate special (e.g., spin-forbidden) reactions. However, our current understanding of the properties of diradicals is limited, and a deeper understanding is important to allow the targeted synthesis of diradicals with predefined properties and/or reactivity patterns. Furthermore, exchange interactions between the unpaired electrons can lead to interesting magnetic properties. Dinuclear metal complexes with purely ligand-based diradical character might allow for facile tuning of the exchange interactions through changes in the linker between the metal centers. This strategy would permit the use of redox-active metals and metalloids, which greatly widens the synthetic scope compared to systems where the diradical character is purely metal-based. Strikingly, the synthesis of dinuclear complexes with one redox-active ligand on each metal is ill-explored and hence little is known about magnetic exchange phenomena for such species.^[9]

Especially in case of only a single bridging ligand, subtle variations potentially influence the overall magnetic properties of the system. Depending on the relative orientation and/or distance between the two spin carriers, diradicals can exist in a triplet (ferromagnetic coupling) or singlet (antiferromagnetic coupling) ground state due to spin-exchange coupling (J).^[10,11] These species are of interest for applications in tunable electronic switching and molecular magnetic materials.^[12] Modular synthesis routes that allow facile installment of different types of bridging ligands would be of interest in order to quickly assess their impact on the magnetic properties of these complexes.

We recently reported novel paramagnetic Pd^{II} complexes bearing a redox-active **NNO** ligand (Scheme 1) or a phosphine derivative thereof (**PNO**), which were shown to undergo selective intramolecular ligand-to-substrate single-electron transfer upon one-electron reduction.^[13] Inspired by these results, we herein detail our efforts to manipulate the neutral Pd^{II} -radi-

Scheme 1. Redox states of Pd^{II} -coordinated **NNO** ligand.

cal $[\text{PdCl}(\text{NNO}^{\text{SQ}})]$ (**1**) and to investigate its behavior upon substitution of the chloride ligand. This has resulted in the unique dinuclear $\text{Pd}(\mu\text{-Cl})$ complex $[\{\text{Pd}(\text{NNO}^{\text{SQ}})\}_2(\mu\text{-Cl})]^+$ (**2**), featuring a ligand-centered radical on each $\{\text{Pd}(\text{NNO})\}$ moiety and a very small bond angle for the Pd-Cl-Pd fragment. A combined experimental and computational study suggests a favorable d^8-d^8 interaction for the chloride bridged dinuclear complex in the solid state. Besides this monohalide bridgehead structure, we also developed a selective route to a dinuclear Pd complex bearing a single pseudo-halide bridging ligand. Given the frequent use of complexes with a bridging azide ligand in molecular magnetism studies,^[14] the $\text{Pd}(\text{N}_3)\text{-Pd}$ core was deemed a relevant target. Using the first example of a palladium azide bearing a ligand radical, the 1,1-bridged azide-analogue of **2** is reported. Magnetic measurements show that there is a significant influence of the bridging atom on the electron exchange in the ligand-centered diradicals. The underlying facile hetero-coupling chemistry of two different Pd precursors illustrates the convenient synthesis of these species, which might aid the development of versatile routes to other dinuclear ligand diradical complexes.

Results and Discussion

Synthesis and characterization of dinuclear Pd complex **2** in solution

Abstraction of the chlorido ligand in complex **1** with Ag salts resulted in one-electron oxidation of the ligand backbone to give diamagnetic cationic $[\text{PdCl}(\text{NNO}^{\text{BQ}})]^+$ species (Scheme 1). Treatment of **1** with the softer, non-oxidizing thallium(I) hexafluorophosphate (TlPF_6) in a non-coordinating solvent (CH_2Cl_2) led to a color change from brown to brownish-green (Scheme 2). CSI-MS studies indicate the presence of an intact dinuclear species in solution with m/z 923.2468 $[M]^+$, indicat-

Scheme 2. Synthesis of complex **2**.

ing the formation of diradical **2**. Notably, addition of up to five equivalents of TlPF_6 resulted in the same product, with no indication for additional chloride abstraction. Dark-brown single crystals of **2** suitable for X-ray structure determination were obtained by diffusion of pentane into a CHCl_3 solution.

The molecular structure (Figure 2) exhibits slightly distorted square-planar geometries around both metal centers and a single bridging chlorido ligand. Well-defined dinuclear palladium complexes with just a single chlorido bridging ligand are

Figure 2. Left: Displacement ellipsoid plot (50% probability level) of complex **2**. Hydrogen atoms, PF₆ anion and lattice solvent molecules are omitted for clarity. Right: Table showing relevant bond lengths.

rare^[15] and no examples bearing ligand radicals have been reported. The intra-ligand bond lengths are characteristic for the iminosemiquinonato (NNO^{1.5Q}) oxidation state^[16] for both ligands. The two Pd–Cl bond lengths are similar and slightly longer than for complex **1**. Most noteworthy is the very small Pd–Cl–Pd angle of 93.11(2)°, which hints at an interaction between the two {Pd(NNO)} fragments.^[17] Other crystallographically characterized dinuclear {Pd₂(μ-Cl)} species have much larger Pd–Cl–Pd angles of 120–130°.^[15] The short Pd–Pd distance of 3.4083(3) Å is longer than the sum of the van der Waals radii (3.26 Å), ruling out a formal bond. The torsion angle of 66° between the two {Pd(NNO^{1.5Q})} segments seems to rule out any involvement of π–π stacking between the ligands, but rather suggests the existence of a d⁸–d⁸ interaction.

To find an explanation for the unusually skewed [LPd–Cl–PdL] geometry, complex **2** was studied computationally by using DFT calculations (Figure 3, top). It was found that dispersion corrections^[18] were essential to obtain structures that

Figure 3. Top: DFT optimized geometry and relevant experimental and computational metric parameters. Bottom: CPK model of DFT optimized geometry of complex **2** (b3-lyp-D3/def2-TZVP).

were in good agreement with the experimental data (Figure 3, middle). This is in agreement with earlier reports which also state that d⁸–d^{8/10}-type interactions are best described as dispersion interactions.^[19] Employing either i) the b3-lyp-D3 functional with the def2-TZVP basis-set or ii) the PBE0-D3 functional with the 6-31+G(d,p) basis-set for light atoms and the LanL2DZ-mod basis-set for Pd afforded a geometry in agreement with the experimental parameters. Notably, where the b3-lyp-D3/def2-TZVP combination slightly overestimated the Pd–Pd distance (α) and the Pd–Cl–Pd angle (θ), the PBE0-D3/6-31+G(d,p)/LanL2DZ-mod combination slightly underestimated both. AIM analysis showed no formal bond between the Pd atoms, but it provided support for a possible interaction involving d orbitals.^[20] The CPK model of the optimized structure (Figure 3, bottom) suggests a close contact between one *t*Bu group of fragment and one of the *gem*-Me groups of the second fragment. To exclude that the respective van der Waals interaction is the sole contributor to the short intramolecular Pd–Pd distance, the structure was optimized with the *t*Bu groups removed.^[20] Analysis of the resulting structure showed a shortening of the Pd–Pd distance suggesting that the steric bulk of the *tert*-butyl groups actually weakens any interaction between the two d⁸ metal centers.

The open-shell singlet (OSS) and the (optimized) triplet state lie very close in energy ($E_{\text{OSS}} - E_{\text{T}} = -0.3 \text{ kcal mol}^{-1}$), indicative of a moderate spin-exchange interaction ($2 J_{\text{calc}} = -106.1 \text{ cm}^{-1}$; b3-lyp-D3/def2-TZVP). In both the OSS and triplet state, both unpaired electrons reside on separate iminosemiquinonato fragments (Figure 4, left). Analysis of the molecular orbitals clearly indicates a weak bonding overlap between the d_{z²} orbitals of the two metal centers (Figure 4, right). Indeed, as is common for d⁸–d⁸ interactions, a weakly antibonding orbital (ca. 0.25 eV higher in energy) is also filled.^[20] Natural bond order (NBO) analysis showed a bonding interaction of approximately 6 kcal mol^{–1}.

Figure 4. Left: Spin density plots of the OSS (top) and triplet (bottom) spin states. Right: Bonding orbital between the two Pd atoms (Triplet α HOMO-5, b3-lyp-D3/def2-TZVP).

Magnetic behavior of complex **2** in the solid state

For a definitive insight into the magnetic behavior of complex **2**, magnetic measurements were performed on a polycrystalline sample using a SQUID magnetometer. The $\chi_m T$ value at room temperature is approximately $0.6 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, corresponding to an effective magnetic momentum of $2.19 \mu_B$. Upon lowering the temperature, $\chi_m T$ approaches to zero, revealing a singlet ground state. The χ_m vs. T plot (Figure 5, inset) exhibits a broad

Figure 5. Temperature dependence of $\chi_m T$ and χ_m (inset) of complex **2**. The solid lines show the simulated data and the empty squares the experimental data.

maximum at 110 K, again indicating an antiferromagnetic (AF) interaction. Modeling the experimental data using a fitting procedure to the Heisenberg–Dirac–van Vleck (HDvV) spin Hamiltonian for isotropic exchange coupling and Zeeman splitting [Eq. (1)] leads to an exchange coupling constant J of -63 cm^{-1} .

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 + g\mu_B\vec{B}(\vec{S}_1 + \vec{S}_2) \quad (1)$$

Therefore the singlet–triplet energy gap ΔE_{S-T} (which is equal to $2J$) is -126 cm^{-1} or $-0.36 \text{ kcal mol}^{-1}$, confirming a singlet ground state for **2** with a moderate spin-exchange interaction. These observations are fully supported by the DFT calculations, predicting a similarly moderate AF exchange coupling constant (ORCA, b3-lyp, def2-TZVP, D3ZERO: -45.3 cm^{-1} ; Turbomole, b3-lyp, def2-TZVP, disp3: -53.1 cm^{-1}).

VT EPR spectroscopy on a polycrystalline sample of **2** is in agreement with the SQUID measurement revealing a triplet signal in the temperature range between 20–60 K (Figure 6). At temperatures $> 60 \text{ K}$ the signal broadens and rapidly becomes very weak due to fast relaxation (likely induced by Pd).^[20] Below 60 K the intensity of the triplet signal shows the typical temperature dependence expected for an AF coupled system, and the signal vanishes completely at temperatures below 20 K (Figure 6).^[20] Fitting the temperature dependence of the triplet signal intensity versus T yielded an exchange coupling

Figure 6. Detection of the triplet signal of **2** and its temperature dependence (20–60 K range).

parameter $J = -47 \text{ cm}^{-1}$, similar to the DFT-calculated value ($J = -45 \text{ cm}^{-1}$) and the value obtained from the SQUID measurements ($J = -63 \text{ cm}^{-1}$).^[20]

Magnetic behavior complex **2** in solution

Interestingly, in solution there is no evidence for exchange coupling between the two unpaired electrons of complex **2**. Contrary to the solid state data, the EPR spectrum of **2** in rapidly frozen toluene at 20 K shows only a $S = 1/2$ signal, reflecting a more random orientation of the two Pd subunits than in the crystalline solid state. In benzene solution at room temperature, a well-resolved $S = 1/2$ signal is observed, with similar hyperfine couplings as previously observed for **1** (Figure 7 and the Supporting Information). Magnetic susceptibility measurement of **2** at 298 K in CDCl_3 using Evans' method^[21] gave an effective magnetic moment (μ_{eff}) of $2.18 \mu_B$, which is close to the value predicted for a system with two noninteracting $S = 1/2$

Figure 7. Experimental and simulated EPR spectrum of complex **2** in benzene solution. Experimental parameters: Freq = 9.368164 GHz, $T = 298 \text{ K}$, Mod Ampl. = 1, power = 2 mW. Parameters used in the simulation: $A^{\text{Pd}} = 12.5 \text{ MHz}$, $A^{\text{N}} = 23.3 \text{ MHz}$, $A^{\text{H}1} = 11.0 \text{ MHz}$, $A^{\text{H}2} = 2.2 \text{ MHz}$.

spins ($2.45 \mu_B$). The UV/Vis spectrum of **2** in solution is similar to that of **1**, with an additional absorption at 441 nm.

Paramagnetic **2** shows relatively sharp resonances in the ^1H NMR spectrum at $\delta = -2$ – -20 ppm at room temperature.^[20] VT NMR spectroscopy of **2** in CDCl_3 showed a temperature dependence for the ^1H NMR chemical shifts. Increasing the temperature from -60 to $+60^\circ\text{C}$ led to a narrowing of the spectral range by ± 8 ppm. Plots of the ^1H NMR shifts versus T^{-1} are shown in Figure 8. The linear dependence of the paramagnetic shift with T^{-1} over this temperature range for all seven

Figure 8. Curie plots of the ^1H NMR shifts versus T^{-1} of complex **2** in CDCl_3 in the range -60 to $+60^\circ\text{C}$.

observable proton types (one signal is obscured by the *t*Bu group) allowed for tentative assignment of the observed resonances.^[20] The linear Curie plots reveal an uncomplicated spin state with no sign of exchange coupling in solution in this temperature range. The linearity of these plots, combined with the fact that no additional NMR signals are generated over the temperature range -60 to $+60^\circ\text{C}$ (dissociation of the dinuclear complex should result in additional) further indicates that the dinuclear complex stays intact in solution over this broad temperature range. These observations confirm that in solution the two unpaired electrons of **2** behave as essentially non-interacting spin carriers over a broad temperature range. Hence, the magnetic behavior of this complex in solid state and solution phase is very different, which is likely related to rotational flexibility in the Pd-Cl-Pd core (Figure 9). HR-MS data also support the proposal that **2** remains intact as a dinuclear species in solution.

Figure 9. Solution vs. solid-state magnetic properties of **2**.

Reactivity of dinuclear Pd complex **2**

To confirm whether this novel dinuclear diradical species only forms in the absence of suitable donor ligands, complex **2** was treated with one equivalent of PPh_3 .^[22] This led selectively to paramagnetic complex **3**, together with one equivalent of complex **1** (Scheme 3). This result confirms that the chlorido-

Scheme 3. Reactivity of complex **2** with PPh_3 to form complex **3** and independent synthesis of **3** directly from **1**.

bridged dinuclear complex, although stable, does not persist in the presence of a better ligand. It also suggests that it might be possible to exchange bridgehead groups in case a non-neutral co-ligand is employed. When a solution of complex **1** in CH_2Cl_2 is treated with an equimolar amount of TIPF_6 in the presence of PPh_3 , complex **3** is formed as the only product with full conversion of **1**. Notably, ^{31}P NMR spectroscopy on paramagnetic **3** reveals the coordinated phosphine as a sharp singlet at $\delta = 28.63$ ppm (the chemical shift is indicative of coordination to Pd)^[23] and the PF_6 anion as a fully resolved septet, while the ^1H NMR spectrum displays four broad resonances between $\delta = 8.36$ and 1.19 ppm.

Although it appears that dinuclear **2** is susceptible to reaction with additional ligand and potentially also metalloligand species, we reasoned that access to other monoatom-bridged dinuclear palladium diradical species could be more easily achieved by using a mixture of chloride species **1** and a neutral, non-chloride-containing analogue, $[\text{Pd}(\text{X})(\text{NNO}^{\text{ISQ}})]$. The in situ-generated cationic $[\text{Pd}(\text{NNO}^{\text{ISQ}})]$ species should then be trapped selectively by this non-chlorido derivative to form a new monoatom-bridged dinuclear diradical. Therefore, the azido derivative was prepared by substitution of the chlorido ligand in **1** through salt metathesis with sodium azide. The reaction proceeded smoothly in MeOH, yielding the corresponding $[\text{Pd}(\text{N}_3)(\text{NNO}^{\text{ISQ}})]$ complex **4** as a purple crystalline material (Figure 10, top), which showed similar EPR spectral features as **1**. The IR spectrum contains a strong absorption at $\tilde{\nu} = 2035 \text{ cm}^{-1}$, which is in the characteristic range for metal azides. Cyclic voltammetry of **4** in CH_2Cl_2 solution revealed fully reversible one-electron oxidation and reduction events at $+0.07 \text{ V}$ and -0.97 V vs. Fc/Fc^+ , respectively. The observed redox potentials reflect the higher electron-withdrawing character of the azido, relative to the chlorido ligand in complex **1** (-0.04 and -1.1 V),^[13] showing that the redox behavior of the **NNO** ligand is also strongly dependent on the additional ligand. Similar to **1**, in situ reduction using $[\text{CoCp}_2]^{\text{[13a]}}$ allowed for the formation of a diamagnetic species which could be characterized by NMR spectroscopy.^[20] Crystals for neutral azido-species

Figure 10. Top: Synthesis of complex **4**. Bottom: Displacement ellipsoid plot (50% probability level) of complex **4**. Hydrogen atoms are omitted for clarity.

4 suitable for X-ray structure determination were obtained by layering a concentrated CHCl_3 solution of **4** with pentane.

The molecular structure of this species shows very similar metric parameters (Figure 10, bottom) to parent species **1**. The main difference is the short Pd1–N2 ($\text{N}\alpha$) bond length (2.0504(14) Å) relative to the Pd–Cl bond length in **1** (ca. 2.31 Å),^[13] which is in the usual range for Pd–N₃ complexes.^[24] In contrast to **1**, which is brown in the solid state and in solution, **4** is a purple solid showing negative solvatochromism (blue in aromatic solvents, purple in CH_2Cl_2), indicative of metal-to-ligand charge transfer.

Formation of dinuclear azido-bridged Pd complex **5**

Treatment of a equimolar solution of **1** and **4** with one equivalent of TIPF_6 resulted in a color change from purple-brown to yellow-brown. Cold-spray ionization mass spectrometry (CSI-MS) contained a signal at m/z 932.2841 that is proposed to represent the parent cation, which indicates the formation of a new dinuclear azido complex **5** (Scheme 4). The IR spectrum

Scheme 4. Selective synthetic route to azide-bridged complex **5**.

showed a strong absorption at 2073 cm^{-1} that can be attributed to a palladium azide fragment, although this signal is clearly shifted to a higher wavenumber than found for **4** ($\Delta\tilde{\nu} = 38\text{ cm}^{-1}$).

Dark yellowish-green needles suitable for X-ray diffraction were obtained by slow diffusion of pentane into a chloroform solution (Figure 11), which unambiguously confirmed the composition of complex **5** as $[\{\text{Pd}(\text{NNO}^{\text{ISO}})\}_2(\kappa^1\text{-N};\mu\text{-N}_3)]\text{PF}_6$. The

Bond	NNOPd1	NNOPd2
C1–C2	1.413(8)	1.432(9)
C2–C3	1.361(9)	1.385(9)
C3–C4	1.426(10)	1.428(9)
C4–C5	1.366(9)	1.362(9)
C5–C6	1.420(8)	1.427(8)
C6–C1	1.454(8)	1.454(9)
C1–O1	1.308(7)	1.312(7)
C6–N1	1.337(8)	1.337(8)
Pd–N1	1.927(5)	1.933(5)
Pd–O1	1.998(4)	2.002(4)
Pd–N1'	2.058(6)	2.053(6)

Figure 11. Left: Displacement ellipsoid plot (50% probability level) of cationic part of complex **5**. Hydrogen atoms, the PF_6^- anion and lattice solvent molecules are omitted for clarity. Right: Relevant metric parameters. Relevant distances [Å] and angles [$^\circ$]: N1'–N2' 1.225(12), N2'–N3' 1.148(13); Pd1–N1'–Pd2: 127.3(3).

metric parameters for the intramolecular bond lengths are characteristic for the iminosemiquinonato oxidation state for both **NNO** ligands, just as in complex **2**. Due to the 1,1-bridging mode of the azide, the Pd–N α bonds are slightly elongated with respect to **4**. The elongated Pd–Pd distance of 3.6843(3) Å and the large Pd–N–Pd angle of approximately 127° contradict the presence of a d^8 – d^8 interaction between the two metal centers, which is in stark contrast with what is observed for complex **2**. Another interesting observation is the elongation of the N α –N β bond compared to the value in $[\text{Pd}(\text{N}_3)(\text{NNO}^{\text{ISO}})]$ (1.225(12) Å vs. 1.168(2) Å in **4**) and a slight contraction of the N β –N γ bond (1.148(13) Å vs. 1.168(3) Å for **4**), which is suggestive of azide activation.

The EPR spectrum of **5** at room temperature is similar to those of **1** and **2**. EPR spectroscopy on a polycrystalline sample showed no triplet signal at both ambient and low temperatures. Notably, magnetic susceptibility measurements on the same solid (Figure 12, squares) showed a nearly temperature-independent $\chi_{\text{M}}T$ value of $0.757\text{ cm}^3\text{ mol}^{-1}\text{ K}^{-1}$ (corresponding to $2.46\text{ }\mu_{\text{B}}$), as expected for two independent $S = 1/2$ spin carriers ($2.45\text{ }\mu_{\text{B}}$) with no significant magnetic interaction. Hence, the magnetic behavior is similar to that of **1** (Figure 12, rounds), where no intramolecular spin-exchange is possible by default.

Conclusions

In conclusion, chloride abstraction from **1** in the absence of a suitable additional ligand results in the formation of the unique mono-chloride bridged dinuclear diradical **2**, wherein the separated unpaired electrons are located on the redox-active **NNO** ligands. Single crystal X-ray crystallography indi-

Figure 12. Temperature dependence of $\chi_M T$ of complex **1** (circles) and complex **5** (squares).

cates the existence of a very small $\angle\text{Pd-Cl-Pd}$ of $\sim 93^\circ$ and an intramolecular d^8-d^8 interaction, which is also supported by DFT calculations. Magnetic measurements showed a moderate spin-exchange coupling ($J = -62.9 \text{ cm}^{-1}$) and a singlet ground state in the solid state. Chloride abstraction from **1** in the presence of PPh_3 yields mononuclear species **3**, with no **2** detected. Complex **2** also reacts very rapidly with phosphine to give complex **3**, illustrating the lability of the dinuclear complex toward exogenous donor ligands. Reacting an equimolar mixture of **1** and **4** in the presence of TiPF_6 results in the formation of mono-azide bridged dinuclear diradical **5**. In contrast to complex **2**, magnetic and EPR measurements shows the presence of two independent $S = 1/2$ spin carriers with no magnetic interaction in the solid state. In solution, species **2** and **5** both behave as systems with two independent $S = 1/2$ spin carriers, due to unhindered rotation around the M-X-M core. The combined data obtained for these dinuclear diradical species demonstrate how subtle variation of the bridging ligand can have a significant effect on the electronic spin state of these mono-bridgehead dinuclear diradicals,^[25] which might be different in solution vs. the solid state. The versatile and convenient synthesis of the reported dinuclear Pd complexes call for more thorough investigations into these phenomena.

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