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Coordination Modes, Oxidation, and Protonation Levels of 2,6-Pyridinediimine and 2,2':6',2'-Terpyridine Ligands in New Complexes of Cobalt, Zirconium, and Ruthenium. An Experimental and Density Functional Theory Computational Study

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S Supporting Information

ABSTRACT: The syntheses and molecular and electronic structures of the $\Delta^{=} [(d2 + d2')/2 - (d1 + d1' + d3 + d3')/4]$ following complexes have been established by single crystal X-ray crystallography and UV-vis-NIR spectroscopy, and verified by density functional theory and UV-VIS-NIR spectroscopy, and verified by density functional theory calculations (DFT B3LYP): $[(\eta^{5}\text{-}Cp)_{2}Zr^{IV}(tpy^{2-})]^{0}$ (S = 0) 1, $[(\eta^{5}\text{-}Cp)_{2}Zr^{IV}(\tau^{OMe}pdi^{2-})]^{0}$ (S = 0) 2, $[Co^{II}(^{OMe}pdi^{0})(\eta^{2}\text{-}BH_{4})]^{0}$ (S = 0) 4, $[Ru^{II}(^{OMe}pdi^{0})Cl_{2}(PPh_{3})_{2}]^{0}$ (S = 0) 5, cis- $[Ru^{II}(^{OMe}pdi^{0})Cl_{2}(PPh_{3})]^{0}$ (S = 0) 6, and $[Ru^{II}(\eta^{2}\text{-}^{OMe}pdi^{0})(\eta^{2}\text{-}^{OMe}pdi\text{-}H)_{2}]^{0}$ (S = 0) 7, with (tpy^{0}) being neutral 2,2':6',2'-terpyridine, $(tpy^{\bullet})^{1-}$ its π radical anion, $(tpy^{2-})^{2-}$ its dianion; $(^{OMe}pdi^{0})$ neutral 2,6-bis(4-methoxyphenylmethylimine)pyridine, $(^{OMe}pdi^{\bullet})^{1-}$ its radical anion and $({}^{OMe}pdi^{2-})^{2-}$ its dianion; $({}^{OMe}pdi-H)^{1-}$ represents the deprotonated form of the $({}^{OMe}pdi^{0})$ ligand where deprotonation takes place at the *meta*-position



of the pyridine ring. Density functional theory calculations using the B3LYP functional were performed, establishing geometry optimized molecular and electronic structures. The structural parameter $\Delta = [(average distance C_{py} - C_{imine}) - (av. distance C_{py} - C_{imine})]$ $C_{py}-N_{py} + av.$ distance $C_{imine}-N_{imime}$] is introduced for the characterization of the oxidation level of pdi (and analogously of tpy) ligands of M(pdi) (or M(tpy)) motifs for first row transition metals. The $M(L^0)$ unit in second and third row low-valent transition metal ion complexes may exhibit significant π -backdonation M \rightarrow L⁰ structural effects.

■ INTRODUCTION

It is now well established that the neutral, potentially tridentate, N-heterocyclic ligands 2,2':6',2'-terpyridine (tpy⁰) and the pyridine-2,6-diimines (pdi⁰) are redox-active ligands.¹⁻⁷ Both neutral forms possess two unoccupied π^* orbitals which can successively accept up to four electrons generating (a) a π -radical monoanion ($S_{\rm L} = 1/2$), (b) a diamagnetic or triplet dianion, (c) a π -radical trianion ($S_{\rm I} = 1/$ 2), and (d) a diamagnetic tetraanion. The two π^* orbitals are antibonding with respect to the two imine (3, 3') and two pyridine C–N bonds (1, 1') but bonding with respect to the two $C_{imine}-C_{pyridine}$ bonds (2, 2') in the pdi ligand and, similarly, the tpy ligand (Scheme 1). In other words, the two

Scheme 1. Definition of the Structural Parameter Δ

$$\Delta = [(d2 + d2')/2 - (d1 + d1' + d3 + d3')/4]$$
(1)



C-C bonds shrink, whereas the four C-N bonds expand with increasing reduction. We have recently introduced the single structural parameter Δ as defined in eq 1 in Scheme 1.¹⁻³ As shown in Figure 1 Δ varies in a linear fashion with the charge *n* of the $(tpy)^n$ and $(pdi)^n$ ligands in five $Zn^{II}(tpy)^n$ and $Zn^{II}(pdi)^n$ complexes.

These Δ_{calc} values are obtained from geometry optimizations of density functional theory (DFT) (B3LYP) calculations. Both correlations hold for first row transition metal ions but not necessarily for second and third row metal ions when structurally significant π -backdonation effects M \rightarrow N must be taken into account.

In this work we describe how dramatically the electronic structures of isostructural complexes of first, second, and third row transition metal ions can vary within the series $[Cp_2M(tpy)]^0$ (M = Ti, Zr, Hf), and, similarly, $[Cp_2M(pdi)]^0$ (M = Ti, Zr, Hf). We also compare the electronic structures of the series $[M(tpy)(\eta^2-BH_4)]^0$ (M = Co, Rh, Ir) and $[M(pdi)(\eta^2-BH_4)]^0$ (M = Co, Rh, Ir).

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Figure 1. Linear dependences of calculated Δ_{calc} values of (a) $Zn^{II}(pdi^n)$ complexes (black squares) and b) $Zn^{II}(tpy^n)$ complexes (red triangles) with the charge *n* of the respective $(tpy)^n$ and $(pdi)^n$ ligands. $[Zn^{II}(pdi)^n(C_5H_4N-NMe_2)]^{2+,1+,0}$, $[Zn^{II}(tpy)^n-(NMe_3)_2]^{2+,1+,0,1-,2-4}$ and $[Zn^{II}(pdi)^n(NMe_3)]^{1-,2-}$ (this work).

Finally, this work shows the possibility of generating singly and doubly deprotonated forms at the *meta-* and *para-*positions of the pyridine rings of the (pdi) ligands.

Examples of this type of complexation are shown in Scheme 2 where the Os species⁸ is doubly deprotonated in the meta-

Scheme 2. Structures of (a) (pdi⁰) and (pdi-H)¹⁻, (b) $[{Os(H)_3(PR_3)_2}_2(pdi-2H)^{2-}]^0$, and (c) $[Fe^{II}(pdi^{2-})(pdi-H)Na(thf)_2]^0$



positions $(pdi-2H)^{2-}$ and in the Fe,Na dinuclear complex⁹ where the para-position of one pyridine ring is deprotonated. These meta- and para-deprotonations require C,H-activation.¹⁰⁻¹² Note that the pdi⁰ oxidation level of the deprotonated forms does not change.

Here we have synthesized two new complexes **5** and 7 (Chart 1) containing N,C-coordinated, bidentate (^{OMe}pdi -H)¹⁻ ligands. We compare their electronic structures with that of *cis*-[Ru^{II}(^{OMe}pdi)Cl₂(PPh₃)]⁰ **6**.

Chart 1. Complexes and Ligands

$[(\eta^{5}\text{-}Cp)_{2}Zr^{IV}(tpy^{2-})]^{0}$	S = 0	1
$[(\eta^{5}\text{-}Cp)_{2}Zr^{IV}(^{OMe}pdi^{2-})]^{0}$	S = 0	2
$[Co^{II}(tpy^{\bullet})(\eta^2\text{-}BH_4)]^0$	S = 0	313
$[Co^{II}(^{OMe}pdi^{\bullet})(\eta^2\text{-}BH_4)]^0$	S = 0	4
[Ru ^{II} (n ² - ^{OMe} pdi-H)Cl(PPh ₃) ₂]	S = 0	5
cis-[Ru ^{II} (^{OMe} pdi ⁰)Cl ₂ (PPh ₃)] ⁰	S = 0	6
$[Ru^{II}(\eta^2\text{-}{}^{OMe}pdi^0)(\eta^2\text{-}{}^{OMe}pdi\text{-}H)_2]^0$	S = 0	7
Ligands: $\bigcirc \bigcirc \bigcirc$		
$(tpy^0) \qquad \qquad$	1–	

RESULTS

Synthesis and Characterization of Complexes. Complexes 1–7 of this work are shown in Chart 1. Two neutral complexes $[(\eta^5-\text{Cp})_2\text{Zr}(L^0)]^0$ 1 and 2 have been synthesized by combining $[(\eta^5-\text{Cp})_2\text{Zr}\text{Cl}_2]^0$ in tetrahydrofuran (thf) solution with sodium amalgam beads under strictly anaerobic conditions (Ar) and the tridentate (L⁰) ligands 2,2':6',2'-terpyridine (tpy⁰) and 2,6-bis-[1-(4-methoxyphenyl-iminoethyl)]pyridine (^{OMe}pdi⁰), eq 2.

$$[(\eta^{5}-Cp)_{2}Zr^{IV}Cl_{2}]^{0} + L^{0} + 2Na \xrightarrow{\text{THF}} [(\eta^{5}-Cp)_{2}Zr(L^{0})]^{0} + \text{NaCl}$$

$$(2)$$

where $L^0 = (tpy0) 1$; $(^{OMe}pdi^0) 2$.

Complexes $[Co^{II}(tpy^{\bullet})(\eta^2-BH_4)]^{013}$ 3 and $[Co^{II}(^{OMe}pdi^{\bullet})-(\eta^2-BH_4)]^0$ 4 have been prepared from methanol solutions of CoCl₂ and 1 equiv of (tpy^0) or $(^{OMe}pdi^0)$ affording green solids of $[Co^{II}(tpy^0)Cl_2]^0$ and $[Co^{II}(^{OMe}pdi^0)Cl_2]^{0.14,15}$ The reaction of these complexes with 1 equiv of Na[BH₄] in THF under strictly anaerobic conditions affords black-purple crystals of 3 and 4, respectively.

$$[\operatorname{Co}^{\mathrm{II}}\operatorname{Cl}_{2}]^{0} + \mathrm{L}^{0} + 2\operatorname{Na} \xrightarrow{\operatorname{CH}_{3}\operatorname{OH}} [\operatorname{Co}^{\mathrm{II}}(\mathrm{L}^{0})\operatorname{Cl}_{2}]^{0}$$
(3)
$$[\operatorname{Co}^{\mathrm{II}}(\mathrm{L}^{0})\operatorname{Cl}_{2}]^{0} + 2\operatorname{Na}[\operatorname{BH}_{4}] \rightarrow [\operatorname{Co}^{\mathrm{II}}(\mathrm{L})(\eta^{2}\operatorname{-BH}_{4})]^{0}$$
(4)

$$+ 0.5B_2H_6 + 0.5H_2$$
 (4)

where $L^0 = (tpy^0)$ 3; $({}^{OMe}pdi^0)$ 4.

The reaction of $[Ru^{II}(PPh_3)_3Cl_2]^0$ with 1 equiv of Na[BH₄] in THF solution (Ar atmosphere) is known to yield the hydrido complex $[Ru^{II}(H)Cl(PR_3)_3]^{0,10-12}$ which in turn reacts with 1 equiv of the ligand $(^{OMe}pdi^0)$ affording the neutral complex $[Ru^{II}(^{OMe}pdi-H)Cl(PPh_3)_2]^0$ 5 in 70% isolated yield, eqs 5 and 6.

$$[\operatorname{Ru}^{II}\operatorname{Cl}_{2}(\operatorname{PPh}_{3})_{3}]^{0} + \operatorname{BH}_{4}^{-} \xrightarrow{\operatorname{THF}} [\operatorname{Ru}^{II}(\operatorname{H})\operatorname{Cl}(\operatorname{PPh}_{3})_{3}]^{0} + \operatorname{Cl}^{-} + 0.5\operatorname{B}_{2}\operatorname{H}_{6}$$
(5)

$$[\operatorname{Ru}^{II}(H)\operatorname{Cl}(\operatorname{PPh}_{3})_{3}]^{0} + (^{\operatorname{OMe}}\operatorname{pdi}^{0})$$

$$\rightarrow [\operatorname{Ru}^{II}\operatorname{Cl}(^{\operatorname{OMe}}\operatorname{pdi} H)(\operatorname{PPh}_{3})_{2}]^{0} + \operatorname{PPh}_{3} + \operatorname{H}_{2} \qquad (6)$$

Interestingly, from the reaction of $[Ru^{II}(PPh_3)_3Cl_2]^0$ with 1 equiv of the ligand $(^{OMe}pdi^0)$ in a THF/methanol mixture (1:1 vol) but *without* the activator BH_4^- the neutral, octrahedral complex *cis*- $[Ru^{II}(^{OMe}pdi^0)Cl_2(PPh_3)]^0$ **6** has been obtained in ~60% yield, eq 7.

$$[\operatorname{Ru}^{II}\operatorname{Cl}_{2}(\operatorname{PPh}_{3})_{3}]^{0} + (^{\operatorname{OMe}}\operatorname{pdi}^{0}) \rightarrow cis$$
$$-[\operatorname{Ru}^{II}(^{\operatorname{OMe}}\operatorname{pdi}^{0})\operatorname{Cl}_{2}(\operatorname{PPh}_{3})]^{0}$$
(7)

Finally, the addition of an excess of KC₈ and KOH (~3 equiv each) to the above THF/methanol solution and heating to reflux for 48 h under anaerobic conditions affords purple crystals of $[\text{Ru}^{II}(\eta^2-^{\text{OMe}}\text{pdi-H})_2(\eta^2-^{\text{OMe}}\text{pdi}^0)]^0$ 7.

Complexes 1-7 possess a singlet ground state as has been established by temperature-dependent (3-300 K) magnetic susceptibility measurements on solid samples (SQUID).

Electronic spectra of new complexes have been recorded in the range 350-1600 nm in methanol, tetrahydrofuran, or toluene solution at ambient temperature. The spectra are shown in Figure 2 (for 1 and 2) in Figure 3 (for



Figure 2. Electronic spectra of $[(\eta^5-Cp)Zr^{IV}(tpy^{2-})]^0$ 1 (black) and $[(\eta^5-Cp)_2Zr^{IV}(^{OMe}pdi^{2-})]^0$ 2 (red) in toluene solution at 20 °C.



Figure 3. Electronic spectra of $[Co^{II}(^{OMe}pdi^{0})Cl_{2}]^{0}$ (black), $[Co^{II}(^{OMe}pdi^{\bullet})(\eta^{2}\text{-}BH_{4})]^{0}$ 4 (red), $[Co^{II}(tpy^{\bullet})(\eta^{2}\text{-}BH_{4})]^{0}$ 3 (green) in MeOH, THF, and THF solution at 20 °C, respectively.

 $[Co^{II}(pdi^{0})Cl_{2}]^{0}$, $[Co^{II}(^{OMe}pdi^{\bullet})\eta^{2}$ -BH₄)]⁰, and $[Co^{II}(tpy^{\bullet})-(\eta^{2}$ -BH₄)]⁰), and in Figure 4 (for $[Ru^{II}(^{OMe}pdi-H)Cl(PPh_{3})]^{0}$ 5, *cis*- $[Ru^{II}(^{OMe}pdi^{0})Cl_{2}(PPh_{3})]^{0}$ 6, and $[Ru^{II}(\eta^{2}-^{OMe}pdi-H)_{2}-(\eta^{2}-^{OMe}pdi^{0})]^{0}$ 7). The spectrum of $[Co(tpy^{0})Cl_{2}]^{0}$ has been reported.¹⁶

Table 1 summarizes the observed transitions. The spectra of 1, 2, 3, and 4 display characteristic intense ($\varepsilon > 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) transitions in the near-infrared region (~800–1600 nm) which are assigned to π,π^* transitions of coordinated (pdi[•])^{1–},



Figure 4. Electronic spectra of $[Ru^{II}(^{OMe}pdi-H)Cl(PPh_3)]^0$ 5 (black), $[Ru^{II}(^{OMe}pdi^0)Cl_2(PPh_3)]^0$ 6 (red), and $[Ru^{II}(\eta^2-^{OMe}pdi-H)_2-(\eta^2-^{OMe}pdi^0)]^0$ 7 (green) in THF solution at 20 °C.

Table 1. Electronic Spectra of Complexes (300–1600 nm, 20 °C)

	complex	solvent	λ_{\max} , nm (ε , M ⁻¹ cm ⁻¹)
1	l	toluene	402 (1.75×10^4) , 700 (0.3×10^4) , 1290 (1.25×10^4) , 1480 (1.75×10^4)
2	2	toluene	320 (3.0 × 10 ⁴), 490 (1.8 × 10 ⁴), 700 (sh), 1250 (0.75 × 10 ⁴)
3	3	THF	320 (sh), 425 (1.3×10^4) , 558 (1.1×10^4) , 1000 (sh), 1300 (1.9×10^4)
4	ł	THF/ CH ₃ OH	397 (3.7×10^4) , 490 (3.7×10^4) , 700 (sh), 780 (2.3×10^4) , 1200 (sh)
[Co ^{II} (^{OMe} pdi ⁰) Cl ₂] ⁰	CH ₃ OH	323 (2.4 × 10 ⁴), 426 (1.8 × 10 ⁴), 544 (0.3 × 10 ⁴), 618 (0.1 × 10 ⁴)
5	5	THF	320 (3.3 \times 10 ⁴), 520 (1.5 \times 10 ⁴), 650 (sh ,0.75 \times 10 ⁴), 800 (sh,0.3 \times 10 ⁴)
e	5	THF	360 (sh, 2.7 \times 10 ⁴), 450 (1.1 \times 10 ⁴), 495 (1.2 \times 10 ⁴)
7	7	THF	400 (sh), 540 (0.9 \times 10 {), 820 (0.1 \times 10 {)

 $(tpy^{\bullet})^{1-} \pi$ radical anions, and their corresponding singlet dianions pdi²⁻ and tpy²⁻. These bands are absent in the spectrum of $[Co^{II}(pdi^0)Cl_2]^0$ (S = 3/2) containing a neutral $^{OMe}pdi^0$ ligand. The spectra of **5** and **7** each containing an η^2 -coordinated (η^2 - ^{OMe}pdi -H)¹⁻ ligand and **6** with a neutral ($^{OMe}pdi^0$) ligand also lack transitions >900 nm.

Crystal Structure Determinations. Table S1 summarizes crystallographic details of the structure determinations. Crystals of **1** consist of neutral molecules of $[(\eta^{5}-Cp)_{2}Zr^{IV}(tpy^{2-})]^{0}$ and uncoordinated, disordered thf solvent molecules which have been removed from the final refinement cycles by using the program Platon/Squeeze.¹⁷

Figure 5 (top) shows the structure of the neutral complex 1: there are two η^5 -coordinated cyclopentadienyl anions and a tridentate terpyridine dianion bound to a central Zr^{IV} ion. The structure of the tpy²⁻ exhibits a small static disorder of one terminal pyridine ring which has not been possible to resolve by a split atom model. The anisotropic thermal parameters of the carbon atoms (C(13) to C(17)) of one-half of the tpy²⁻ ligand are significantly larger than those of the corresponding C-atoms of the other half (C(2) to C(7)). This indicates that the N,N',N'-coordinated tpy²⁻ ligand is in fact not quite planar and that the Zr(tpy) moiety is not $C_{2\nu}$ symmetric.

The C–C bonds in the two terminal pyridine rings display distinct short–long–short–long bond alternation (see Scheme 3) due to the dearomatization (reduction) of these rings. The two C_{py} – C_{py} bonds between the terminal and central pyridine are among the shortest reported for M(tpy) units at 1.411(8)



Figure 5. Structures of 1 (top) and 2 (bottom) at 30% and 50% probability ellipsoids, respectively.

and 1.417(8) Å. This is also typical for a highly reduced character of the (tpy) ligand ($\Delta_{exp} \approx 0.02$). In contrast, the two C–N bonds of the central pyridine ring are long (av. 1.414(7) Å), approaching C–N single bond distances. In summary, we interpret these structural parameters as indication of an *asymmetrically* bound tpy^{2–} dianion. The two Zr–N_t bonds of the terminal pyridines are also not identical at 2.307(4) and 2.383(4) Å (the Zr–N_c bond distance to the central pyridine is the shortest at 2.159(4) Å).

The structure of the neutral complex 2 is shown in Figure 5 (bottom). It consists also of an $(\eta^5\text{-}Cp)_2Zr^{IV}$ -moiety and an N,N',N''-coordinated (^{OMe}pdi) ligand which has the characteristic C–C and C–N bond distances of a closed-shell dianion (^{OMe}pdi²⁻)²⁻. This pdi²⁻ ligand is also asymmetrically coordinated (Scheme 3). Here, no static disorder problems are detected: The C(9)–N(10) bond at 1.333(1) Å is shorter than its (C2)–N(1) counterpart at 1.360(1) Å, and the former exhibits more C==N double bond character than the latter. The central pyridine ring is again dearomatized (short–long alternating C–C bond lengths). Thus, the crystallographic data support a description of the structure as $[(\eta^5-Cp)_2Zr^{IV}-(^{OMe}pdi^{2-})]^0$ with $\Delta_{exp} = 0.026$ Å and an asymmetrically coordinated ($^{OMe}pdi^{2-}$) dianion (Zr–N_t 2.385(1) and 2.303(1) Å, Zr–N_c 2.154(1) Å).

The structure of $[Co^{II}(tpy^{\bullet})(\eta^2-BH_4)]^0$ (3) has been determined previously by X-ray and neutron scattering crystallography.¹³ The experimental Δ_{exp} values of 0.063 and 0.066 Å, respectively, are in excellent agreement with the notion of a $(tpy^{\bullet})^{1-}$ radical anion.¹⁻³ We note that the average Δ_{exp} parameter for $[Co^{II}(tpy^0)Cl_2]^0$ is 0.145 Å,¹⁴ and for

Scheme 3. Structures and Selected Bond Distances (Å) of (a) Uncoordinated (tpy⁰) and (pdi⁰) Ligands, (b) the $Zr^{IV}(tpy^{2-})$ Unit in 1, and (c) the $Zr^{IV}({}^{OMe}pdi^{2-})$ Unit in 2



 $[Co^{II}(pdi^0)Cl_2]^{18}$ it is in the range 0.165–0.190 Å, indicating in both cases the presence of a neutral (tpy^0) and a (pdi^0) ligand, respectively.

Figure $\hat{6}$ shows the structure of neutral $[Co^{II}(^{OMe}pdi^{\bullet})(\eta^2-BH_4)]^0$ (4). Scheme 4 compares selected bond lengths in the $Co(tpy^{\bullet})$ and $Co(^{OMe}pdi^{\bullet})$ units (see also Table S2). In 4 the $(^{OMe}pdi^{\bullet})^{1-}$ ligand is symmetrically coordinated (C_{2v}) ; no disorder problems have been identified. The arithmetic mean value of the two $C_{py}-C_{imine}$ bonds at 1.436(2) Å, the average $C_{imine}-N_{imine}$ bond length at 1.325(2) Å and the av. $C_{py}-N_{py}$ bond distance at 1.372(2) Å indicate an oxidation level of a $(pdi^{\bullet})^{1-} \pi$ -radical anion; the Δ_{exp} value of 0.088 Å is in reasonable agreement with this notion (Figure 1).

reasonable agreement with this notion (Figure 1). The structures $[Ru^{II}(^{OMe}pdi-H)Cl(PPh_3)_2]^0$ (5), *cis*- $[Ru^{II}(^{OMe}pdi^0)Cl_2(PPh_3)]^0$ (6), and $[Ru^{II}(\eta^{2}-^{OMe}pdi-H)_2-(\eta^{2}-^{OMe}pdi^0)]^0$ (7) are shown in Figure 7, panels a-*c*, respectively.

The five-coordinate, neutral complex **5** possesses a slightly distorted trigonal bipyramidal structure where two (PPh₃) groups occupy axial positions; the bidentate N,C-bound anion η^2 -(^{OMe}pdi-H)¹⁻ together with a chloride ion is in the equatorial plane. Scheme 5 summarizes selected bond distances (experimental and DFT calculated) of the Ru^{II}(^{OMe}pdi-H) unit. Its Δ_{exp} value of 0.156 Å suggests that the oxidation level remains the same as in a protonated, neutral ligand (^{OMe}pdi⁰).



Figure 6. Structure of 4 at 50% probability ellipsoids.

Scheme 4. Structures and Selected Bond Distances (Å) of the $Co^{II}(tpy^{\bullet})$ Unit in 3 (top) and $Co^{II}(^{OMe}pdi^{\bullet})$ Unit in 4 (bottom)



The structure of the neutral, octahedral complex **6** (Figure 7) consists of a Ru^{II}(^{OMe}pdi⁰)-unit, two Cl⁻ ions in *cis*-position relative to each other and a (PPh₃) ligand. Three previously reported structures of this type exhibit an average Δ_{exp} value of 0.122 Å.^{19,20} The corresponding *trans*-isomers are also known; seven structures have been reported (av. $\Delta_{exp} = 0.129$ Å).^{19,21–23} Scheme 6 summarizes selected bond distances of the tridentate, neutral (^{OMe}pdi⁰) ligand in **6** with a Δ_{exp} value of 0.128 Å. As shown below, the rather low Δ_{exp} values are a consequence of some Ru^{II} \rightarrow (pdi⁰) π -backdonation.

The complex 7 (Figure 7) contains neutral, octahedral molecules with two bidentate, N,C-coordinated $(^{OMe}pdi-H)^{1-}$ anions and one, also bidentate but N,N'-coordinated, neutral $(\eta^2-^{OMe}pdi^0)$ ligand: $[Ru^{II}(\eta^2-^{OMe}pdi-H)_2(\eta^2-^{OMe}pdi^0)]^0$ 7. The central Ru ion possesses a low spin + II oxidation state.

Scheme 7 summarizes metrical data of bond distances in both ligands. Interestingly, the Δ_{exp} values for both types of η^2 -



Figure 7. Structures of 5 (top), 6 (middle), and 7 (bottom) at 50% probability ellipsoids.

Scheme 5. Structure and Selected Experimental (red) and Calculated (blue) Bond Distances (Å) of N-C-Coordinated (OMe pdi-H) Ligand in 5



coordinated (pdi) ligands are within experimental error identical at 0.15 \pm 0.01 Å, which indicates that both ligands have the same oxidation level.

Scheme 6. Structure and Selected Experimental Bond Distances (Å) of the $Ru^{II}(^{OMe}pdi^{0})$ Unit in 6



Scheme 7. Structures and Selected Experimental Bond Distances (Å) of the Ru^{II}(η^2 -pdi-H) (top) and Ru^{II}(η^2 -pdi⁰) unit in 7







DFT (B3LYP) Calculations. In order to obtain a better understanding of the electronic structures of complexes 1–7, we have performed a series of DFT calculations with the B3LYP functional for geometry optimizations, employing experimental X-ray data as a starting point.²⁴ Table 2 summarizes the Δ_{exp} and Δ_{calc} values of these complexes and, in addition, of two reference compounds from the literature.

In 2001 Nitschke and Tilley^{26⁺} reported the synthesis and crystal structure of diamagnetic $[(\eta^5 - \text{Cp})_2 \text{Zr}(\text{bpy})]^0$ (S = 0) (bpy = 2,2'-bipyridine) and discuss the nature of the N,N'-coordinated (bpy) ligand from the observation of regular bond alternations and "partial" dearomatization of both pyridine rings as originating from the donation of electron density from a Zr^{II} center (4d²) into antibonding π^* levels of the neutral (bpy⁰) unit: $[(\eta^5 - \text{Cp})_2 \text{Zr}^{II}(\text{bpy}^0)]^0$. As we have shown subsequently from DFT (B3LYP) calculations²⁷ an electronic structure description as $[(\eta^5 - \text{Cp})_2 \text{Zr}^{IV}(\text{bpy}^{2-})]^0$ (S = 0) is the correct formulation ($\Delta_{exp} = 0.003$ Å; $\Delta_{calc} = 0.005$ Å). Its HOMO possesses only 23% Zr d but 72% bpy character. The Zr–N bonds are quite covalent with, possibly, some π -donation of electron density Zr^{IV} \leftarrow N. Thus, the $(\eta^5 - \text{Cp})_2 \text{Zr}^{IV}$ unit (4d⁰) is a π -acid and the closed-shell dianion (bpy²⁻)²⁻ is a good π -donor ligand.

Table 2. Summary	of Δ_{exp}	and	Δ_{calc}	Values	of Selected
Complexes	1				

complex	Δ_{exp} , Å	Δ_{calc} Å	ref
$[(\eta^{5}-Cp)_{2}Zr^{IV}(tpy^{2-})]^{0} 1$ (S = 0)	0.021	0.023	this work
$[(\eta^{5}-Cp)(\eta^{1}-Cp)Ti^{III}(tpy^{\bullet})]^{0}$ (S = 1)		0.083	this work
$[(\eta^{5}-Cp)(\eta^{1}-Cp)Hf^{V}(tpy^{2-})]^{0}$ (S = 0)		0.019 ^c	this work
$[(\eta^{5}\text{-}Cp)_{2}Zr^{IV}({}^{OMe}pdi^{2-})]^{0} 2 (S = 0)$	0.026	0.030	this work
$[(\eta^{5}\text{-}Cp)_{2}\text{Ti}^{\text{III}}(\eta^{2}\text{-}^{\text{OMe}}p\text{di}^{\bullet})]^{0}$ $(S = 1)$		0.122	this work
$[(\eta^{5}-Cp)(\eta^{4}-Cp) Hf^{V}(^{OMe}pdi^{2-})]^{0} (S = 0)$		0.024 ^c	this work
$[\mathrm{Co}^{\mathrm{II}}(\mathrm{tpy}^{\bullet})(\eta^2\text{-}\mathrm{BH}_4)]^0 \ 3$	0.063 (X-ray) 0.066 (neutron)	0.077	13
$[\mathrm{Co}^{\mathrm{II}}(^{\mathrm{OMe}}\mathrm{pdi}^{\bullet})(\eta^2\text{-}\mathrm{BH}_4)]^0$ 4	0.088	0.101	this work
$[Rh^{I}(tpy^{0})(\eta^{2}-BH_{4})]^{0}$		0.085	this work
$[{ m Ir}^{ m I}({ m tpy}^0)(\eta^2{ m -BH}_4)]^0$		0.062 ^c	this work
$[\mathrm{Rh}^{\mathrm{I}(\mathrm{xyl}\mathrm{pdi}^{0})}(\eta^{2}-\mathrm{BH}_{4})]^{0}$	0.100	0.099	25
$[\mathrm{Ir}^{\mathrm{I}(\mathrm{xyl}\mathrm{p}\mathrm{di}^{0})}(\eta^{2}\text{-}\mathrm{BH}_{4})]^{0}$		0.070 ^c	this work
$[Pd^{II}(tpy^0)(\eta^1-BH_4)]^{1+}$		0.125	this work
$[Pd^{II}(pdi^0)(\eta^1-BH_4)]^{1+}$		0.168	this work
$ \begin{bmatrix} \operatorname{Ru}^{II}(\eta^{2}-\operatorname{OMe}pdi-H)Cl \\ (PPh_{3})_{2} \end{bmatrix}^{0} 5 $	0.152	0.158	this work
$\begin{array}{c} cis-[\mathrm{Ru}^{\mathrm{II}}(^{\mathrm{OMe}}\mathrm{pdi}^{0})\mathrm{Cl}_{2}\\ (\mathrm{PPh}_{3})]^{0} 6 \end{array}$	0.128	0.133	this work
$\frac{trans - [Ru^{II}(xy^lpdi^0))}{Cl_2(PMe_3)]^0}$	0.132	0.138	19, 21–23
$\begin{array}{c} \textit{trans-}[\text{Ru}^{\text{II}}({}^{\text{iPr}}\text{pdi}^{0})\\ \text{Cl}_{2}(\text{PPh}_{3})]^{0} \end{array}$	0.140	0.136	19, 21–23
$\textit{cis-}[Os^{II}({}^{tol}pdi^0)Cl_2(P^iPr_3)]^0$	0.087	0.093 ^c	8
$ \begin{array}{c} [\operatorname{Ru}^{\text{II}}(\eta^2 \operatorname{-}^{\text{OMe}} p \text{di}^0)(\eta^2 \operatorname{-}^{\text{OMe}} \\ p \text{di} \operatorname{-} H)_2]^0 7 \end{array} $	0.157 ^a	0.164	8
	0.154 ^b	0.158	8

^{*a*}Average Δv alues for N,N'-coordinated (^{OMe}pdi⁰) ligands; ^{*b*} Δv alue for the N,C-coordinated (^{OMe}pdi⁰-H)¹⁻ ligand. ^{*c*}For 3rd row transition metal complexes, the geometry optimization convergence criteria were slightly loosened (TolE 5e-5, TolRMSG 1e-3, TolMaxG 3e-2, TolRMSD 2e-2, TolMaxD 4e-2).

Interestingly, the first row transition metal analogue $[(\eta^{5}-Cp)_{2}Ti(bpy)]^{0}$ (S = 0) has also been synthesized and structurally characterized.²⁸ Its electronic structure has been elucidated by DFT (B3LYP) calculation²⁷ and shows an open-shell diradical $[(\eta^{5}-Cp)_{2}Ti^{III}(bpy^{\bullet})]^{0}$ (S = 0). A broken symmetry (BS(1,1)) calculation [BS(a,b): a and b stand for the number of unpaired electrons at the metal and the ligand, respectively] for an open-shell (S = 0) species is 9 kcal/mol lower in energy than the corresponding closed shell singlet. The Δ_{exp} and Δ_{calc} values of 0.042 and 0.037 Å, respectively, are in excellent agreement with the presence of a π -radical anion (bpy[•])^{1–}. The HOMO (spin up) possesses ~2% Ti-d, and the HOMO (spin down) has 89% Ti-d-character.

In contrast to experiments the closed-shell optimized geometries of the Zr complexes 1 and 2 show the presence of symmetrically coordinated $Zr(\eta^3$ -tpy) and $Zr(\eta^3$ -pdi) moieties, respectively. It is remarkable that in spite of these small structural differences the Δ_{exp} and Δ_{calc} values are nearly identical (see Table 2); they indicate the presence of $(tpy^{2-})^{2-}$

and $(^{OMe}pdi^{2-})^{2-}$ dianions. The very small structural differences between calculated and experimental structures may be because the experimental data are derived from solid-state single crystals, whereas the calculated structures represent gasphase structures. There are five unoccupied 4d orbitals, characteristic for a central Zr^{IV} ion in 1 and 2. The two HOMOs are predominantly ligand-based orbitals (~9% Zr-d-character). Therefore, we describe their electronic structures as closed-shell singlet species—no BS(1,1) solutions have been found. A significant structural contribution of $Zr^{IV} \leftarrow$ (heterocycle²⁻) π -donation has also not been identified.

In the following we present our DFT calculations of the corresponding hypothetical titanium and hafnium analogues of 1 and 2, namely, $[(Cp)_2Ti(tpy)]^0$, $[(Cp)_2Ti(^{OMe}pdi)]^0$, $[(Cp)_2Hf(tpy)]^0$, and $[(Cp)_2Hf(^{OMe}pdi)]^0$, all of which have not been synthesized to date. In all cases we have geometry optimized the structures of the (S = 1) and (S = 0) states (open shell, closed shell, and BS(1,1)). The geometry optimizations of $[(Cp)_2Ti(tpy)]^0$ in its closed shell (S = 0) state, and the open shell (BS 1,1 S = 0) and (S = 1) states reveal an unexpected structural change: the (S = 1) state is the ground state which is 5.6 kcal/mol more stable than the BS(1,1), S = 0 solution, and 8.2 kcal/mol more stable than the closed shell S = 0 solution. Figure 8 shows the structure of the



Figure 8. Geometry optimized structure of the (S = 1) ground state of hypothetical $[(\eta^5-Cp)(\eta^1-Cp)Ti^{III}(\eta^3-tpy^{\bullet})]^0$.

ground state which contains one η^5 -coordinated Cp⁻ and one η^1 -bound Cp⁻ as well as a tridentate (tpy[•])¹⁻ π -radical anion. Thus, the structure is best described as $[(\eta^5-\text{Cp})(\eta^1-\text{Cp})-\text{Ti}^{\text{III}}(\eta^3-\text{tpy}^{•})]^0$ (S = 1). Δ_{calc} of 0.083 Å is in excellent agreement with this assignment. The excited state singlet structure with a Δ_{calc} of 0.045 Å is in accord with a structure $[(\eta^5-\text{Cp})(\eta^2-\text{Cp})\text{Ti}^{\text{IV}}(\eta^3-\text{tpy}^{2-})]^0$ (S = 0).

The corresponding hypothetical hafnium complex $[(Cp)_2Hf(tpy)]^0$ also exhibits η^5,η^1 -coordination of the Cp ligands. However, the electronic ground state is found to be S = 0 (closed shell, $[(\eta^5-Cp)(\eta^1-Cp)Hf^{IV}(\eta^3-tpy^{2-})]^0$) with $\Delta_{calc} 0.019$ Å, in close resemblance to the Zr complex. The S = 1 excited state lies 6 kcal/mol higher in energy than the ground state.

For the hypothetical molecule $[(Cp)_2Ti(^{OMe}pdi)]^0$, the geometry optimization also yields a triplet ground state, which is 13 kcal/mol more stable than the closed shell singlet (*S* = 0) and 6.9 kcal/mol more stable than the open shell (BS 1,1 *S* = 0) solution.

Figure 9 shows the structure of the (S = 1) ground state which possesses two η^{5} -coordinated Cp⁻ ligands, but the $(^{OMe}pdi^{\bullet})^{1-}$ is only η^{2} -coordinated and has an *uncoordinated* imine arm: $[(\eta^{5}-Cp)_{2}Ti^{III}(\eta^{2}-^{OMe}pdi^{\bullet})]^{0}$ (S = 1). The excited S= 0 state possesses a different structure with one $(\eta^{2}-Cp)^{1-}$, one $(\eta^{3}-Cp)^{1-}$ monoanion, and a tridentate $(^{OMe}pdi^{2-})^{2-}$ dianion: $[(\eta^{2}-Cp)_{2}Ti^{IV}(\eta^{3}-^{OMe}pdi^{2-})]^{0}$. The Hf analogue exhibits a closed shell (S = 0) ground state $(\Delta_{calc} = 0.024$ Å), yielding $[(\eta^{5}-Cp)(\eta^{4}-Cp)Hf^{IV}(^{OMe}pdi^{2-})]^{0}$.

Using BS(1,1) DFT calculations, we have previously shown that the electronic structure of $[Co(tpy)(\eta^2-BH_4)]^0$ (S = 0) (3), which has been synthesized and crystallographically characterized by X-ray and neutron diffraction, ¹³ is best described as $[Co^{II}(tpy^{\bullet})(\eta^2-BH_4)]^0$ with a central low spin Co^{II} ion $(d^7, S_{Co}=1/2)$ coupled antiferromagnetically to a $(tpy^{\bullet})^{1-} \pi$ -radical anion.¹⁻³ Here the BS(1,1) solution is 5 kcal/mol lower in energy than the closed shell solution. The Δ_{exp} value of 0.066 Å (neutron data) is close to the Δ_{calc} value of 0.077 Å from the geometry optimized structure. Similar calculations for complex 4 reveal the same electronic properties, also with a 5 kcal/mol more stable BS(1,1) solution. The calculated Mulliken spin population displays 0.81 electrons at the low spin Co^{II} ion and 0.88 electrons at the (^{OMe}pdi[•])¹⁻ radical.

In contrast, for hypothetical $[Rh^{I}(tpy^{0})(\eta^{2}-BH_{4})]^{0}$ (S = 0) and its (also hypothetical) iridium analogue $[Ir^{I}(tpy^{0})(\eta^{2}-BH_{4})]^{0}$ (S = 0), we found only closed shell singlet solutions. The same is true for $[Rh^{I}(xy^{I}pdi^{0})(\eta^{2}-BH_{4})]^{0}$ which has been synthesized and structurally characterized (X-ray)²⁵ as well as its hypothetical Ir analogue $[Ir^{I}(^{OMe}pdi^{0})(\eta^{2}-BH_{4})]^{0}$ (S = 0). Interestingly, the structural parameters Δ_{exp} (and Δ_{calc}) are all in the narrow range 0.062–0.100 Å, which could be typical for an open shell singlet with π -radical anions and low spin Rh^{II} and Ir^{II}. However, this cannot be the case because attempts to find energetically low lying BS(1,1) solutions converge to closed shell solutions. Here we encounter a case where the



Figure 9. Geometry optimized structure of the (*S* = 1) ground state of hypothetical $[(\eta^5-Cp)_2 Ti^{III}(\eta^2-OMepdi^{\bullet})]^0$ (left) and of the closed-shell (*S* = 0) excited state $[(\eta^2-Cp)(\eta^3-Cp)Ti^{IV}(\eta^3-OMepdi^{2-})]^0$ (right).

observed structural ligand parameters alone do not allow an unambiguous assignment of the oxidation level of the ligand or metal ion. The closed shell calculations show that the neutral forms (tpy⁰) and (pdi⁰) experience a structurally significant π backdonation $M \rightarrow$ (heterocycle⁰). Nückel and Burger have proposed this for their [Rh^I(xylpdi⁰)(η^2 -BH₄)]⁰ complex.²⁵

We have also computationally studied the two hypothetical diamagnetic monocations $[Pd(tpy)(BH_4)]^{1+}$ (S = 0) and $[Pd(^{OMe}pdi)(BH_4)]^{1+}$ (S = 0) which are isoelectronic with the above neutral Rh^I and Ir^I complexes. The closed shell geometry optimizations yield a square planar geometry with an η^{1-} coordinated BH₄⁻ anion (Scheme 8) with an agostic Pd…H interaction at ~2.3 Å (2.422 Å for the tpy complex and 2.296 Å for the pdi species).

Scheme 8. Selected Bond Distances (Å) of Geometry Optimized Structure of Hypothetical $[Pd^{II}(^{OMe}pdi^{0})(\eta^{1}-BH_{4})]^{1+}$ (top) and Selected Bond Distances of $[Rh^{I}(pdi^{0})(\eta^{2}-BH_{4})]^{0}$ (bottom)



The Δ_{calc} values at 0.125 Å for the $[Pd^{II}(tpy^0)(BH_4)]^{1+}$ and 0.168 Å for the corresponding $[Pd^{II}(pdi^0)(BH_4)]^{1+}$ complex are in relatively good agreement with the presence of neutral (pdi⁰) ligands with little structurally significant π -back-donation. Another structural aspect needs consideration. A weak direct M–B bonding interaction has been proposed in $[Rh^{I}(xy^{I}pdi^{0})(\eta^{2}-BH_{4})]^{0.25}$ Our DFT calculations for the Rh, Ir, and Pd species confirm this notion (see Discussion section).

The closed shell geometry optimized structure of octahedral, diamagnetic 6 yields a Δ_{calc} value of 0.133 Å in fair agreement with a neutral (pdi⁰) oxidation level. There are five trans- $[Ru^{II}(pdi^{0})Cl_{2}(PPh_{3})]^{0}$ structures in the literature^{19,21–23} exhibiting such a low average Δ_{exp} value of 0.13 ± 0.01 Å. Furthermore, three *cis*-structures as in **6** exhibit an average $\Delta_{exp} = 0.122$ Å.^{19,20} These structures (including **6**) may display structurally significant $Ru^{II} \rightarrow (pdi^0) \pi$ -backdonation. The DFT calculations identify three doubly occupied 4d orbitals (Ru^{II} 4d⁶), and the HOMO is one of these with 59% Ru d character, whereas the LUMO is a $(pdi^0) \pi^*$ -orbital (13% Ru d). Note that PR₃ ligands are strong σ -donors but weak π acceptors, and, therefore, one must consider 6 (and the other complexes of this type) as "electron rich" species. Replacement of PR₃ by a CO ligand (which is a strong π -acceptor) generates an electron poorer Ru^{II} center in $[Ru^{II}(pdi^{0})Cl_{2}(CO)]^{0}$ (S = 0) which has an average Δ_{exp} of 0.150 Å ($\Delta_{calc} = 0.159$ Å).²⁹

The corresponding experimental structure of the complex cis- $[Os(^{tol}pdi^0)Cl_2(P^iPr_3)]^0$ (S = 0) exhibits an extremely low

The DFT geometry optimized structure of diamagnetic, fivecoordinate complex **5** with a bidentate N,C-coordinated η^2 - $(^{OMe}pdi-H)^{1-}$ monoanion is in very good agreement with experiment (Scheme 5). The η^2 -N,C coordinated anion displays average C–N and C_{imine}–C_{py} distances from which Δ_{exp} and Δ_{calc} values of 0.152 and 0.158 Å, respectively, are derived. This is characteristic for neutral (pdi⁰) ligands. There are three occupied 4d metal orbitals of which the HOMO possesses 77% Ru d character, and the LUMO is a (pdi⁰) centered ligand orbital (3.7% Ru d character): [Ru^{II}(η^{2} -OMe</sup>pdi-H)Cl(PPh₃)]⁰.

Closed shell geometry optimization of the structure of diamagnetic, octahedral $[\text{Ru}^{II}(\eta^{2}\text{-}^{\text{OMe}}\text{pdi-H})_{2}(\eta^{2}\text{-}^{\text{OMe}}\text{pdi}^{0})]^{0}$ (S = 0) (7) is again in very good agreement with experiment: average $\Delta_{\text{exp}} = 0.157$ Å and $\Delta_{\text{calc}} = 0.164$ Å for the neutral N,N-coordinated $(\eta^{2}\text{-}\text{pdi}^{0})$ ligand, and 0.158 and 0.157 Å, respectively, for the $(\eta^{2}\text{-}\text{pdi}\text{-}\text{H})$ monoanion. The HOMO is one of the three filled 4d orbitals (75%, 67%, 65% Ru d character) confirming the Ru^{II} assignment, whereas the LUMO (7.4% Ru d) is ligand centered.

DISCUSSION AND CONCLUSION

Three aspects of the present work are discussed: (a) the characteristic features of the structural parameter Δ of tridentate π -radical anions and their corresponding dianions coordinated to first, second, and third row transition metal ions; (b) the nature of the M…B interaction in complexes $[M(tpy)(BH_4)]^0$ and $[M(pdi)(BH_4)]^0$ (M = Co, Rh, Ir); and (c) the observed variations of Δ in bidentate N,N'-coordinated (pdi)ⁿ ligands (n = 0, 1-, 2-) in transition metal ion complexes.

Inspection of good to excellent quality structures^{1-3,30,31} of transition metal ions coordinated to a tridentate dianion (tpy^{2-}) revealed that the Δ_{exp} value is found in the narrow range 0.041 ± 0.02 Å, which agrees with the Δ_{exp} value of 1. Notably, the M(pdi²⁻) unit does not show structurally significant π -bonding effects (M \rightarrow N or M \leftarrow N), neither in "electron rich" nor "electron poor" complexes (Ti^{IV}, V^{IV}, Mo^{IV}, U^{IV}).

The available database for $M(pdi^{2-})$ complexes is dramatically larger. We have identified 54 first row transition metal ion complexes with a κ^3 -coordinated (pdi^{2-}) dianion, all of which display Δ_{exp} values in the narrow range of 0.05 \pm 0.02 Å irrespective of their d^n electron configuration.³² Complex 2 with $\Delta_{exp} = 0.026$ Å is therefore a further example for the notion that (pdi^{2-}) -to-metal π -bonding is structurally not effective.

Nückel and Burger²⁵ have proposed that in $[Rh^{I}(pdi^{0})(\eta^{2}-BH_{4})]^{0}$ a weak Rh…B bonding interaction exists by employing DFT (B3LYP) calculations. The experimental Rh…B interaction at 2.271(3) Å is relatively short, and the Mulliken overlap population analysis confirms a direct bonding Rh…B interaction (0.21 e). Table 3 summarizes the M…B distances

Table 3. Distances (Å) and Mayer Bond Order of M…B interactions

complex	exp. d(M…B), Å	calcd. d(M…B), Å	Mayer bond order
$\begin{bmatrix} Co^{II}(tpy^{\bullet})(\eta^2 - BH_4) \end{bmatrix}^0$	2.16(3)	2.173	0.40
$[\operatorname{Co}^{II}(\operatorname{pdi}^{\bullet})(\eta^{2}-\operatorname{BH}_{4})]^{0}$	2.123(2)	2.148	0.42
$[Rh^{I}(tpy^{0})(\eta^{2}-BH_{4})]^{0}$		2.310	0.23
$[Rh^{I}(pdi^{0})(\eta^{2}\text{-}BH_{4})]^{0}$	2.271(3)	2.284	0.18
$[Ir^{I}(tpy^{0})(\eta^{2}-BH_{4})]^{0}$		2.280	0.50
$[Ir^{I}(pdi^{0})(\eta^{2}-BH_{4})]^{0}$		2.252	0.45
$[ext{Pd}^{ ext{II}}(ext{tpy}^0)(\eta^1- ext{BH}_4)]^{1+}$		2.434	0.26
$[{ m Pd}^{ m II}({ m pdi}^0)(\eta^1-{ m BH}_4)]^{1+}$		2.398	0.27

(experimental and calculated) for the corresponding Co, Rh, Ir, and Pd complexes with tpy and (pdi) ligands, respectively. In our DFT calculations we have analyzed the Mayer bond order for the $M^{-}B$ interactions. We confirm the presence of a weak $M^{-}B$ interaction (Table 3).

Finally, we discuss the metrical details of bidentate, η^2 coordinated (pdi)ⁿ ligands (n = 0, 1-, 2-) (Table 4). It is

Table 4. Summary of Structurally Characterized η^2 -Coordinated (pdi) Complexes (Δ^a)

complex	Δ, Å	ref
$[\mathrm{Ru}^{\mathrm{II}}(\eta^2\text{-pdi}^0)(\eta^2\text{-pdi}\text{-H})_2]^0$	0.130	this work
$[Mo^0(\eta^2-pdi^0)(CO)_4]^0$	0.150	34
$[\mathrm{Mn}^{\mathrm{II}}(\eta^2 - \mathrm{pdi}^{\bullet})_2]^0$	av. 0.075	35
$[\operatorname{Ru}^{\mathrm{II}}(\eta^2\operatorname{-pdi}^{2-})(\eta^6\operatorname{-toluene})]^0$	0.019	21
$^{a}\Delta$ is defined in eq 1.		

notable that the uncoordinated (dangling) imine part of the $(pdi)^n$ ligand possesses a nearly invariant C = N imine double bond at 1.29 ± 0.01 Å and a $C_{imine}-C_{py}$ single bond at 1.48 ± 0.02 Å irrespective of the transition metal ion to which the (pdi) ligand is bound. This is a consequence of the fact that the planar η^2 -coordinated part and the plane of the dangling part are not coplanar as in η^3 -coordinated (pdi) ligands. The observed dihedral angle between the planes is not 0° but in the range of 50–90° which inhibits electronic π -communication between the dangling imine and the η^2 -coordinated part. Thus, the redox activity of η^2 -ligands can only be observed in the coordinated pyridine-imine part. The structural coordination chemistry of redox-noninnocent iminopyridine ligands in first row transition metal ions has been reported.³³

Table 4 summarizes a few structurally characterized η^2 coordinated (pdi)^{*n*} complexes where Δ represents the structural parameter as defined in eq 1 (Scheme 1) of the η^2 -bound iminopyridine part. Δ is ~0.14 Å for a neutral iminopyridine ligand, ~0.075 Å for an iminopyridine π -radical anion, and ~0.02 Å for a dianion. It is notable that the η^2 - coordinated at the pyridine ring deprotonated (pdi) ligands display Δ values indicating their pdi⁰ parentage.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under an argon atmosphere using standard Schleck techniques or a glovebox in the strict absence of water and dioxygen using rigorously dried solvents. The reagents $[(Cp)_2 ZrCl_2]^0$ (Cp = cyclopentadienyl¹⁻), sodium amalgam beads (10%), 2,2':6'2"-terpyridine (tpy), [Ru-(PPh_3)_3Cl_2]^0, CoCl₂, and NaBH₄ are commercially available. The ligand 2,6-bis[1-(4-methoxyphenyliminoethyl)]pyridine ($^{OMe}pdi^0$) was prepared according to the literature.³⁶ The complexes [Co(tpy)-(BH₄)]⁰ (3),¹³ [Co(tpy)Cl_2]^{0,37} and [Co($^{OMe}pdi^0$)Cl_2]⁰³⁸ have been synthesized as described in the literature.

 $[(\eta^5-\text{Cp})_2\text{Zr}(\text{tpy})]^0$ (S = 0) (1). The complex was prepared in 27% yield (0.12 g) via an analogous procedure as described below for (2) by using the ligand tpy instead of ($^{OMe}pdi^0$). X-ray quality blackbrown crystals were grown at -20 °C by vapor diffusion of diethyl ether into a saturated tetrahydrofuran (THF) solution of 1. Anal. Calcd for $C_{25}H_{21}N_3\text{Zr}$: C, 66.04; H, 4.66; N, 9.24. Found: C, 65.79; H, 4.68; N, 9.13.

 $[(\eta^5-Cp)_2Zr(^{OMe}pdi^0)]^0$ (S = 0) (2). The ligand ($^{OMe}pdi^0$) (0.37 g, 1.0 mmol) was added to a suspension of $[(Cp)_2ZrCl_2]^0$ (0.29 g, 1.0 mmol), and sodium amalgam (10 wt %, 0.5 g, ~2 mmol Na) in 25 mL of THF and stirred at 20 °C for 24 h. The resulting dark-brown solution was filtered, and the volume was reduced to 10 mL under a vacuum. Diethyl ether was added (10 mL) which initiated the precipitation of a brown-black solid which was collected by filtration and dried in vacuo. Yield: 0.13 g (22%). X-ray quality crystals were grown by vapor diffusion of diethyl ether into a saturated THF solution of 2. Anal. Calcd for $C_{33}H_{33}N_3O_2Zr$: C, 66.63; H, 5.59; N, 7.06. Found: C, 66.35; H, 6.18; N, 6.71.

[Co(^{OMe}pdi⁰)(η²-BH₄)]⁰ (**5** = 0) (4). A mixture of CoCl₂ (0.13 g, 1.0 mmol) and the ligand (^{OMe}pdi⁰) (0.37 g, 1.0 mmol) in methanol (10 mL) was stirred at 20 °C for 12 h after which time the solvent was removed in vacuo. The residual green solid of $[Co^{II}(^{OMe}pdi^0)Cl_2]^0$ and 2 equiv of NaBH₄ (0.076 g, 2.0 mmol) were suspended in 20 mL of THF and stirred at 20 °C for 12 h. After filtering, the solvent was removed under reduced pressure affording dark, almost black microcrystals in ~80% yield (0.38 g) of 4. X-ray quality crystals were grown by vapor diffusion of diethyl ether into a saturated THF solution of 4 at 20 °C. Anal. Calcd for C₂₃H₂₇BCoN₃O₂: C, 61.77; H, 6.09; N, 9.40. Found: C, 61.92; H, 5.81; N, 9.20.

[Ru(^{OMe}pdi-H)Cl(PPh₃)₂]^o (S = 0) (5). A mixture of (^{OMe}pdi⁰) (0.37 g, 1.0 mmol), [Ru(PPh₃)₃Cl₂]^o (0.96 g, 1 mmol) and NaBH₄ (0.019 g, 0.5 mmol) in 30 mL of THF was heated to reflux at 66 °C for 24 h. The resulting dark-red solution was filtered, and all volatiles were removed under reduced pressure yielding a black-red microcrystalline solid which was washed with diethyl ether and dried. Yield: 0.37 g (37%). X-ray quality crystals were grown by vapor diffusion of diethyl ether into a saturated toluene solution of 5 at -20 °C. Anal. Calcd for C₅₉H₅₂ClN₃O₂P₂Ru: C, 68.56; H, 5.07; N, 4.07. Found: C, 68.13; H, 5.37; N, 4.98.

cis-[Ru($^{OMe}pdi^{0}$)Cl₂(PPh₃)]⁰ (*S* = 0) (6). A mixture of ($^{OMe}pdi^{0}$) (0.37 g, 1.0 mmol) and [Ru(PPh₃)₃Cl₂]⁰ (0.96 g, 1 mmol) in 30 mL of THF/methanol (1:1) was heated to reflux for 18 h. The red-black solution was filtered, and all volatiles were removed in vacuo. The black residue was washed with diethyl ether and dried. Yield: 0.47 g (51%). X-ray quality black-purple crystals of 6·Et₂O·0.5 THF were grown by vapor diffusion of diethyl ether into a saturated THF solution of 6 at -20 °C. Anal. Calcd for C₄₇H₅₂ClN₃O_{3.5}PRu: C, 61.50; H, 5.71; N, 4.58. Found: C, 62.31; H, 5.72; N, 5.54.

 $[\mathbf{Ru}^{II}(\eta^{2}-\mathbf{OMe}\mathbf{pdi}^{0})(\eta^{2}-\mathbf{OMe}\mathbf{pdi}^{-1}\mathbf{H})_{2}]^{0}$ (5 = 0) (7). A mixture of $(^{OMe}\mathbf{pdi}^{0})$ (1.12 g, 3.0 mmol), $[\mathrm{Ru}(\mathrm{PPh}_{3})_{3}\mathrm{Cl}_{2}]^{0}$ (0.96 g, 1 mmol), KC_{8} (0.41 g, 3 mmol), and KOH (0.17 g, 3 mmol) in 30 mL of THF was heated to reflux for 48 h. The resulting red-black solution was filtered, and all volatiles were removed in vacuo. The residue was washed with diethyl ether and dried. Yield: 0.33 g (27%). X-ray quality crystals were grown by vapor diffusion of diethyl ether into a

saturated THF solution of 7 at -20 °C. Anal. Calcd for $C_{69}H_{67}N_9O_6Ru;$ C, 67.96; H, 5.54; N, 10.34. Found: C, 67.65; H, 4.92; N, 9.75.

X-RAY CRYSTALLOGRAPHIC DATA COLLECTION AND REFINEMENT OF THE STRUCTURES

Single crystals of complexes were coated with perfluoropolyether, picked up with nylon loops, and were mounted in the nitrogen cold stream of the diffractometers at 100 K. Graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) from a Mo-target rotating-anode X-ray source was used throughout. Final cell constants were obtained from least-squares fits of several thousand strong reflections. Intensity data were corrected for absorption using intensities of redundant reflections with the program SADABS.¹⁷ The structures were readily solved by Patterson methods and subsequent difference Fourier techniques. The Siemens ShelXTL³⁹ software package was used for solution, refinement, and artwork of the structures. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters.

A methoxyphenyl group (fragment C19 to C26) in the pdi ligand of $[Co(pdi)(BH_4)]^0$ was found to be disordered next to a crystallographic center of inversion. A split atom refinement with occupation factors of 0.67:0.33 was used to satisfactorily model the disorder. SADI and EADP restraints in ShelXL were used (18 restraints).

Methoxo groups in crystals of 7 were found to be disordered and two groups containing carbon atoms C24 and C84 were split on two positions with occupation factors of about 0.55 and 0.52 respectively. O–C distances were restrained to be equal (SADI), and thermal displacement parameters were restrained to be equal using the EADP instruction of ShelXL (6 restraints).

Crystals of ^{MePh}tpy contained a large solvent accessible void of about 1260 Å³ in which THF and Et₂O molecules could be identified. These solvent molecules were severely disordered and could not be satisfactorily refined. Platon/SQUEEZE^{17,40} was used to remove solvent contributions from the refinement (about 196 electrons in the void). Crystallographic data of complexes are summarized in Table S1.

COMPUTATIONAL DETAILS

All calculations have been performed with the ORCA program in its version 4.0.x.⁴¹ Geometry optimizations were carried out on structures derived from experimental X-ray data if available (references thereof are given in the manuscript). We employed the B3LYP functional^{42–44} together with the def2-TZVP basis set^{45,46} in combination with Weigends auxiliary basis set (def2/J)⁴⁷ (for Ti, Co, Zn), the scalar-relativistic recontraction of the TZVP basis set (old-Zora-TZVP) in combination with the SARC/J auxiliary basis set (for Zr, Ru, Rh, Pd) or the SARC-ZORA-TZVP basis set (for Os, Ir, Hf). During integral generation, the resolution of identity and chain of spheres approximations (RIJCOSX)⁵³ have been applied to Coulomb and exchange integrals, respectively. Counterions were not included in any calculation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b01949.

Computational details, model input file, Cartesian coordinates of the geometry optimized structures as well as crystallographic data of the complexes (PDF)

Accession Codes

CCDC 1565814, 1811210, 1819350, and 1854899–1854902 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc. cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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