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Para-Quinone-Containing Bis(pyrazol-1-yl)methane Ligands: Coordination Behavior Toward Co^{II} and a C−H Activation Reaction with Ce^{IV}

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Two series of sterically demanding *para*-dimethoxyphenyl-substituted bis(pyrazol-1-yl)methane ligands have been synthesized, i.e., $\mathbf{L2^{R,R'}}$ = $((MeO)_2C_6H_3)C(H)(pz^{R,R'})_2$ and $\mathbf{L3^{R,R'}}$ = $((MeO)_2C_6H_3)C(Me)(pz^{R,R'})_2$ (R,R′ = 3-Me,5-Me; 3-Ph,5-H; 3-*t*Bu,5-H). In the solid state, already the sterically least encumbered derivative $\mathbf{L2^{Me2}}$ is able to stabilize Co^{II} complexes of the form $[X_2Co(\mathbf{L2^{Me2}})]$ (X = Cl, NO_3); in solution, these complexes are at an equilibrium with the 1:2 species $[Co(\mathbf{L2^{Me2}})_2]^{2+}$. Oxidative demethylation of $\mathbf{L3^{Ph}}$ and $\mathbf{L3^{tBu}}$ with $[Ce(NH_4)_2(NO_3)_6]$ leads to the corresponding *para*-benzoquinonyl-substituted bis(pyrazol-1-yl)methane ligands $\mathbf{L4^{Ph}}$ and $\mathbf{L4^{tBu}}$. Contrary to that, the methyl derivative $\mathbf{L3^{Me2}}$ is transformed into the *ortho*-benzoquinone species $\mathbf{L5^{Me2}}$, which still contains one methoxy substituent while one oxygen atom has been newly introduced. The formation of $\mathbf{L5^{Me2}}$ requires (i) the admission of air, (ii) the presence of both methoxy substituents of $\mathbf{L3^{Me2}}$, and (iii) the presence of (methyl) substituents both at the exocyclic carbon atom and at the 5- positions of the pyrazolyl rings. The parent *ortho*-hydroquinonyl-substituted bis(pyrazol-1-yl)methane ligand $((HO)_2C_6H_3)C(H)(pz^{H,H})_2$ is readily available from 3,4-dihydroxybenzaldehyde and $(pz^{H,H})_2SO$/pyridine.

Introduction

The importance of transition metal ions in homogeneous catalysis rests to a large extent on their ability to adopt different oxidation states. However, in several cases, like in some catalytic oxidation reactions of organic compounds with dioxygen,[1,2] the presence of an additional redox cocatalyst is required for efficient substrate conversion. One prominent example is the Pd^{II}-mediated oxidation of ethylene to acetaldehyde (Wacker oxidation), which employs $CuCl_2$ in order to promote the aerobic reoxidation of intermediately formed Pd^0 and to close the catalytic cycle.[3]

Later developments led to *para*-benzoquinone (BQ) derivatives as oxidizing agents in Wacker-related syntheses[2] as well as in Ru-catalyzed dehydrogenation reactions of alcohols[4] and amines.[5] A drawback, however, results from the fact that stoichiometric quantities of BQ are consumed,[6] because the reoxidation of *para*-hydroquinone (HQ) to BQ by O_2 is usually slow under the reaction conditions applied.[2] In order to regenerate BQ with O_2 as the final oxidizing agent, a second redox catalyst is therefore necessary. Among other compounds, transition metal complexes with macrocyclic ligands ($[ML^m]$) have proven to be efficient electron transfer reagents for this purpose (e.g., $[ML^m]$ = iron phthalocyanine, cobalt tetraphenylporphyrin, cobalt salenes).[7−9]

Further developments with the aim to increase the overall rate of electron transfer from Pd^0 to O_2 focused on hybrid redox catalysts, $\{Q\text{-}[ML^m]\}$, in which *para*-quinone moieties are covalently tethered to cobalt salene or cobalt porphyrine complexes (*note*: in this paper, the general term "quinone (Q)" will be used whenever the oxidation state of any derivative of hydroquinone/benzoquinone needs not to be specified).[10−12]

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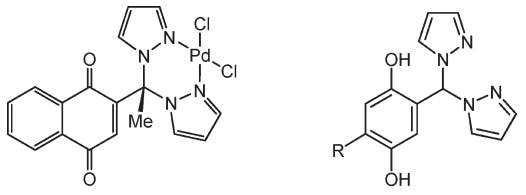


Figure 1. The *para*-naphthoquinone-substituted bis(pyrazol-1-yl)methane complex **A** and the *para*-hydroquinone-based bis(pyrazol-1-yl)methane ligands **B** and **C**; pz = pyrazol-1-yl.

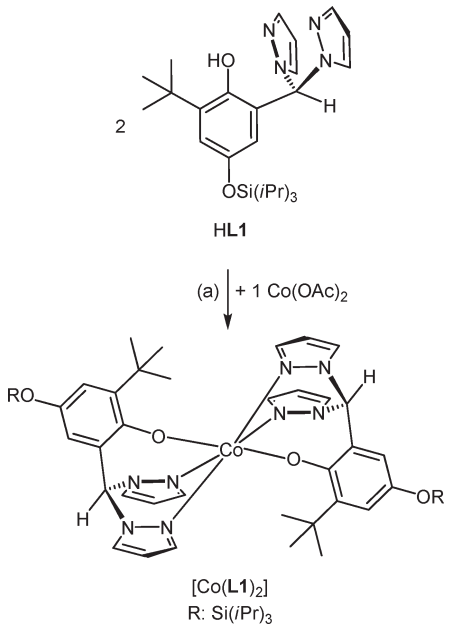
In a complementary approach, our group has recently reported on the *para*-naphthoquinone-substituted bis(pyrazol-1-yl)methane[13] complex **A** (Figure 1).[14] Here, the *substrate-selective* catalyst is connected to the redox mediator ({[PdL_n]-Q}). Using **A** as model system, we have monitored the formation of a *para*-naphthosemiquinonate radical after selective $Pd^{II} \rightarrow Pd^0$ reduction.[14] This result clearly indicates that **A** is properly designed to allow for a single-electron transfer from the metal atom to the *para*-naphthoquinone moiety, which is an important proof-of-concept on the way to functional monomolecular oxidation catalysts {[PdL_n]-Q-[ML^m]}.

The question thus arises whether bis(pyrazol-1-yl)methane ligands with *para*-quinone substituents are also suitable for the preparation of alternative hybrid redox systems {Q-[ML^m]}. If this is the case, ditopic ligands like **B**[15] (Figure 1) would have promising potential as linkers between the two metal complex parts [PdL_n] and [ML^m] (after synthesis protocols leading to *hetero*bimetallic compounds have been worked out).

Given this background, we decided to explore the coordination properties of derivatives of the monotopic bis(pyrazol-1-yl)methane **C**[15] (Figure 1) toward Co^{II}. The Co^{II} ion was chosen, because it has already been found to be an efficient redox mediator in other combined redox systems {Q-[ML^m]}.[7−9] Moreover, tris(pyrazol-1-yl)borate complexes of the form [$CoTp^{tBu,Me}(\eta^2\text{-}O_2)$][16] are known, and dioxygen binding to cobalt complexes in general has been extensively reviewed.[17−19]

The purpose of this paper is to report on Co^{II} complexes with selected **C**-type ligands. Special emphasis is put on the influence of the secondary coordination sphere (i.e., the substitution pattern of the pyrazolyl rings) on the molecular structures of the compounds. Since we are interested in the redox behavior of the new compounds, it was necessary to prepare each ligand both in its reduced and in its oxidized state. In one case, oxidation with [$Ce(NH_4)_2(NO_3)_6$] led to an unexpected C−H activation reaction with the formation of an *ortho*- rather than a *para*-benzoquinone moiety; key factors governing this unusual transformation will be unveiled.

Scheme 1. Synthesis of the Co^{II} Complex [$Co(\mathbf{L1})_2$][a]



[a] Reagents and conditions: (a) + NaOMe, MeOH, rt.

Results and Discussion

Synthesis and Characterization of the Hexacoordinate Complex [$Co(\mathbf{L1})_2$]. For a start, we chose the known ligand $[\mathbf{L1}]^-$ (Scheme 1),[15] because it contains a solubilizing $Si(^iPr)_3$ group. Moreover, the molecule carries a *tert*-butyl substituent and thus possesses similar steric bulk as 2,6-di-*tert*-butylbenzoquinone, which has been shown to be superior to parent *para*-benzoquinone in triple catalytic systems (Ru-catalyst/2,6-^{t}Bu-BQ/Co-macrocycle) for the aerobic oxidation of secondary alcohols.[20]

[$Co(\mathbf{L1})_2$] was prepared from $Co(OAc)_2$ and **HL1** in MeOH and in the presence of NaOMe as a base (Scheme 1).

Single crystals of [$Co(\mathbf{L1})_2$] suitable for X-ray diffraction were grown from a CH_2Cl_2 solution at −20 °C (Table 1). The compound crystallizes with two crystallographically independent molecules, $[Co(\mathbf{L1})_2]_A$ (C_1 symmetry) and $[Co(\mathbf{L1})_2]_B$ (C_i symmetry), in the asymmetric unit. Since all key structural parameters of the two molecules are very similar, only the centrosymmetric $[Co(\mathbf{L1})_2]_B$ will be discussed further (Figure 2).

The Co^{II} ion of $[Co(\mathbf{L1})_2]_B$ is located in an octahedral coordination environment made up by two tripodal, tridentate $[\mathbf{L1}]^-$ ligands. The Co2−O5 bond length amounts to 2.020(2) Å; the average Co−pyrazolyl bond length is 2.130(2) Å. These values are close to the corresponding bond lengths in a related complex, which also adopts a *trans* configuration but features methyl groups instead of $OSi(^iPr)_3$ substituents (Co−O = 1.998(2) Å; av. Co−N = 2.145(2) Å).[21]

An important piece of information gained from the solid-state structure of [$Co(\mathbf{L1})_2$] is that the *tert*-butyl group on the HQ fragment does not provide sufficient steric hindrance to prevent the formation of homoleptic [$M(\mathbf{L})_2$]

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Table 1. Selected Crystallographic Data and Structure Refinement Details for $[Co(\mathbf{L1})_2]$, $\mathbf{L2^{tBu}}$, and $\mathbf{L3^{Me2}}$

compound	$[Co(\mathbf{L1})_2]$	$\mathbf{L2^{tBu}}$	$\mathbf{L3^{Me2}}$
formula	$C_{52}H_{78}CoN_8O_4Si_2 \times {}^4/_3\ CH_2Cl_2$	$C_{23}H_{32}N_4O_2$	$C_{20}H_{26}N_4O_2$
fw	1107.57	396.53	354.45
color, shape	brown, block	colorless, block	colorless, plate
temp (K)	160(2)	165(2)	173(2)
radiation	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	9.4947(10)	9.5910(18)	8.0829(4)
b (Å)	18.288(3)	11.048(2)	30.7570(17)
c (Å)	26.640(5)	12.917(4)	8.7926(4)
α (deg)	94.370(9)	71.396(11)	90
β (deg)	93.364(9)	71.334(16)	116.165(3)
γ (deg)	104.378(11)	65.837(13)	90
V (Å^3)	4453.4(11)	1154.8(4)	1961.90(17)
Z	3	2	4
D_{calcd} (g cm^{-3})	1.239	1.140	1.200
$F(000)$	1767	428	760
μ (mm^{-1})	0.498	0.074	0.079
cryst size (mm)	0.72 × 0.60 × 0.30	0.60 × 0.44 × 0.26	0.41 × 0.37 × 0.15
no of reflns coll	72853	16982	19156
no of ind reflns (R_{int})	24618 (0.0559)	5069 (0.0590)	3676 (0.0474)
data/restr/params	24618/5/959	5069/0/264	3676/0/243
GOF on F^2	1.392	1.069	1.045
R1, wR2 ($I > 2\,\sigma(I)$)	0.0841, 0.2320	0.0514, 0.1001	0.0386, 0.1035
R1, wR2 (all data)	0.1389, 0.2528	0.0865, 0.1143	0.0493, 0.1090
largest diff peak and hole (e Å^{-3})	2.457, −1.875	0.245, −0.197	0.227, −0.207

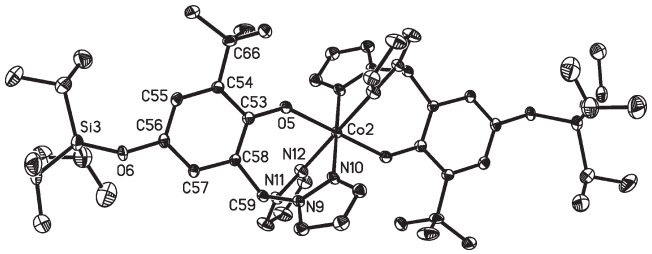

Figure 2. Molecular structure and numbering scheme of compound $[Co(\mathbf{L1})_2]_B$ (50% displacement ellipsoids; H atoms omitted for clarity). Selected bond lengths [Å] and bond angles [deg]: Co2−O5 = 2.020(2), Co2−N10 = 2.137(3), Co2−N12 = 2.121(3), O5−C53 = 1.301(4), O6−C56 = 1.394(4); O5−Co2−N10 = 87.7(1), O5−Co2−N12 = 90.0(1), N10−Co2−N12 = 86.2(1).

complexes. In conclusion, we need to increase the steric bulk on the pyrazolyl rings in order to be able to prepare more reactive heteroleptic species of the form $[X_nM(\mathbf{L})]$.

Synthesis and Characterization of Sterically Demanding Quinone-Substituted Bis(pyrazol-1-yl)methane Ligands. The ligand syntheses were performed as outlined in Scheme 2.

First, commercially available *para*-dimethoxybenzaldehyde was treated with the appropriate $(pz^{R,R'})_2SO$ derivative (prepared in situ from $Hpz^{R,R'}$, NaH, and $SOCl_2$) in a pyridine-catalyzed reaction.[22,23] Thereby, we obtained the bis(pyrazol-1-yl)methane ligands $\mathbf{L2^{Me}}$−$\mathbf{L2^{tBu}}$ in yields between 52% and 80% (*note*: in our hands, the alternative approach[24−26] using $(pz^{R,R'})_2CO$ and catalytic amounts of $CoCl_2$ gave either prohibitively low yields ($\mathbf{L2^{Me}}$, $\mathbf{L2^{Me2}}$) or met with failure). It has to be mentioned that in the case of $\mathbf{L2^{Me}}$ an isomeric mixture of products was obtained: the 3,3′-isomer and the 3,5′-isomer. In the crude product, the stoichiometric ratio between both isomers is 4:1, respectively. Repeated recrystallizations from hexane led to samples containing 90% of the 3,3′-isomer. However, due to these difficulties in obtaining isomerically pure $\mathbf{L2^{Me}}$, the compound was not considered further (cf. the Supporting Information for details of the X-ray crystal structure analysis of $\mathbf{L2^{Me}}$).

In the next step, the acidic methine protons of $\mathbf{L2^{Me2}}$−$\mathbf{L2^{tBu}}$ were replaced by inert methyl groups in order to avoid future unwanted side reactions—especially when the ligands will be in their BQ states (cf. previous negative experiences with the base-lability of BQ-substituted bis(pyrazol-1-yl)methanes[14,15]). To this end, the methine protons were first abstracted with 1 equiv of *n*BuLi, which is why the synthesis sequence had to start with *para*-dimethoxybenzaldehyde instead of *para*-dihydroxybenzaldehyde. Subsequent addition of MeI (1 equiv) to the anionic intermediate gave the corresponding ligands $\mathbf{L3^{Me2}}$−$\mathbf{L3^{tBu}}$. In the case of the sterically encumbered derivative, $\mathbf{L3^{tBu}}$, increasing the bulk by methylation results in partial isomerization of the bis(pyrazol-1-yl)methane fragment (3,3′-isomer/3,5′-isomer ≈ 8:1; *note*: upon prolonged storage, the 3,5′-isomer of $\mathbf{L3^{tBu}}$ slowly converts back to the 3,3′-isomer).

Oxidative *O*-demethylation of $\mathbf{L3^{Ph}}$ and $\mathbf{L3^{tBu}}$ to their BQ state ($\mathbf{L4^{Ph}}$, $\mathbf{L4^{tBu}}$) was achieved by treatment with 2−3 equiv of $[Ce(NH_4)_2(NO_3)_6]$ in H_2O/MeCN. Much to our surprise, however, $\mathbf{L3^{Me2}}$ was not transformed into a *para*-benzoquinone under identical reaction conditions. Instead, we observed C−H activation with the formation of the *ortho*-benzoquinone derivative $\mathbf{L5^{Me2}}$ (Scheme 2; results of an investigation into mechanistic details of this reaction are presented in a subsequent paragraph).

$CDCl_3$ solutions of all ligands of the **L2** series are stable toward hydrolysis over a period of several days, even when

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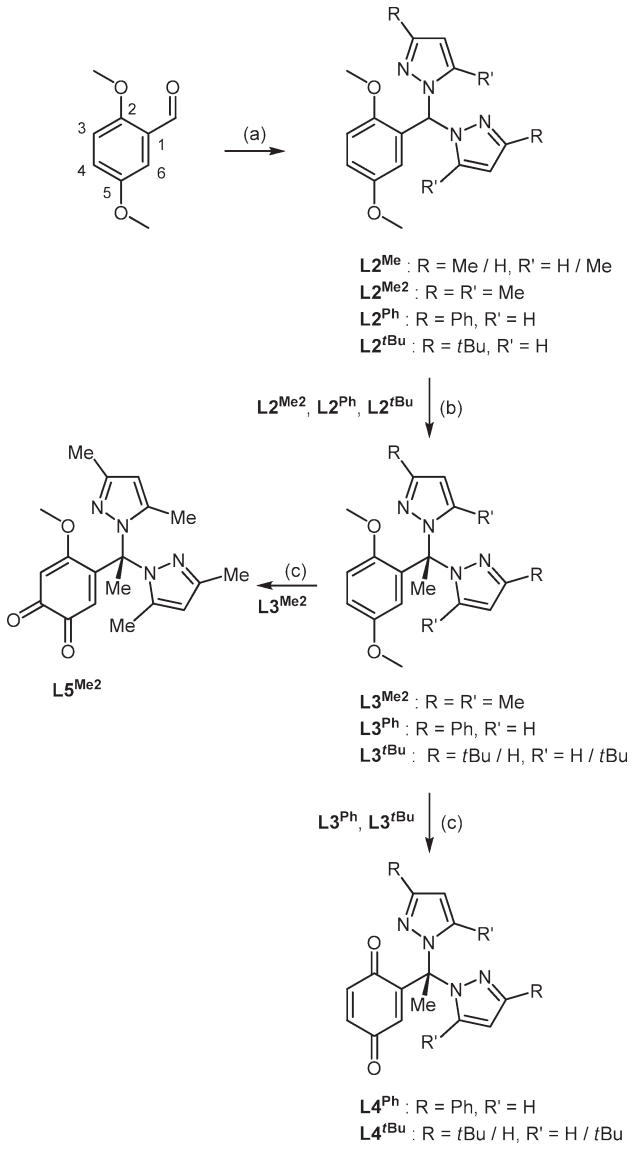
Scheme 2. Synthesis of the Sterically Demanding Ligand Systems $L2^{Me}/L2^{Me2}/L2^{Ph}/L2^{tBu}$, $L3^{Me2}/L3^{Ph}/L3^{tBu}$, $L4^{Ph}/L4^{tBu}$, and $L5^{Me2}$[a]



[a] (a) + 1 $(pz^{R,R'})_2SO$, + 1 pyridine, THF, reflux, 12 h. (b) 1: + 1 *n*BuLi, THF/hexane, 0 °C, 30 min; 2: + 1 MeI, THF/hexane, rt, 30 min. (c) + exc. $[Ce(NH_4)_2(NO_3)_6]$, H_2O/MeCN, 0 °C to rt, 3 h.

small amounts of aqueous HCl are added (NMR spectroscopic control). $L3^{Ph}$ and $L3^{tBu}$ are still fairly inert toward water, but decompose slowly in the presence of (aqueous) HCl. $L3^{Me2}$ is the most sensitive compound within the **L3** series. The addition of 1 equiv of oxalyl chloride to $L3^{Me2}$ in aqueous d^6-DMSO led to the immediate formation of a 1:1 mixture of $((MeO)_2C_6H_3)C(pz^{Me2})=CH_2$ and Hpz^{Me2} (NMR spectroscopic control); in the presence of excess HCl, decomposition to the ketone $((MeO)_2C_6H_3)C(O)CH_3$ takes place.

The ^{1}H NMR spectrum ($CDCl_3$) of $L2^{Me2}$ is characterized by one set of pyrazolyl resonances and one set of *para*-dimethoxyphenyl signals in an overall integral ratio of 2:1 (the numbering scheme is given in Scheme 2). We observe two singlets at 2.12/2.20 ppm for the methyl groups on the pyrazolyl rings and further singlets at 3.65/3.67 ppm for the two methoxy substituents. The pz-H4 resonance appears at 5.83 ppm (s, 2 H), and the aromatic protons on the *para*-dimethoxyphenyl fragment give rise to signals at 6.35 ppm (d, 1 H; H6) and 6.83 ppm (m, 2 H; H3,4). The resonance of the methine proton appears at 7.72 ppm. In the ^{1}H NMR spectrum ($CDCl_3$) of $L3^{Me2}$, this signal has vanished, and a new resonance is visible at 2.70 ppm (s, 3 H; CH_3).

The 3-phenylpyrazolyl derivative $L2^{Ph}$ (d^6-DMSO) shows the typical proton resonance pattern of monosubstituted pyrazolyl rings, i.e., $\delta(^1H) = 6.83$ (d, 2 H; pz-H4) and 7.85 (d, 2 H; pz-H5). Upon going to $L3^{Ph}$, successful H/Me exchange is evidenced by the absence of a methine proton resonance at 8.02 ppm and the presence of a new methyl signal at 2.75 ppm in the ^{1}H NMR spectrum of this compound (d^6-DMSO).

The *tert*-butyl group of $L2^{tBu}$ resonates at $\delta(^1H) = 1.32$ (C_6D_6) and the methine proton at 8.18 ppm. The corresponding *tert*-butyl signal of $L3^{tBu}$ (C_6D_6) appears at 1.37 ppm (18 H); the signal for the newly introduced methyl group is observed at 3.05 ppm. Apart from the signals for the 3,3′-isomer, another set of resonances with smaller intensities is detectable in the ^{1}H NMR spectrum of freshly prepared $L3^{tBu}$. The number of these signals indicates a less symmetrical molecular structure. Especially, two *tert*-butyl resonances at 1.35 ppm (9 H) and 1.39 ppm (9 H) lead to the conclusion that the deprotonation/methylation sequence has led to partial 3,3′ → 3,5′ isomerization.

Oxidation of $L3^{Ph}$ with $[Ce(NH_4)_2(NO_3)_6]$ results in a compound which shows no methoxy ^{1}H/^{13}C NMR signals but two ^{13}C NMR resonances in the typical range of benzoquinone carbonyl moieties (184.7 ppm, 187.2 ppm; d^6-DMSO). These features, together with all other NMR data, are in accord with the proposed product $L4^{Ph}$. Compound $L4^{tBu}$ reveals corresponding *C*O resonances for the 3,3′-isomer at $\delta(^{13}C) = 184.7$ and 186.9 (C_6D_6). The ratio of the 3,3′- vs the 3,5′-isomer was the same for $L4^{tBu}$ and $L3^{tBu}$ (*note*: upon prolonged storage, the 3,5′-isomer of $L4^{tBu}$ also slowly converts back to the 3,3′-isomer).

In contrast to $L3^{Ph}$ and $L3^{tBu}$, oxidation of $L3^{Me2}$ reproducibly led to a product that still contained one methoxy group ($\delta(^1H) = 2.74$; $\delta(^{13}C) = 57.1$). Moreover, one of the three proton resonances of the quinone core went missing, and the two remaining resonances then appeared as singlets (5.06 ppm, 5.45 ppm). The ^{13}C NMR spectrum of the oxidation product revealed two low-field signals at 178.0 ppm and 180.8 ppm, which suggested the presence of a benzoquinone moiety. All of these NMR data are consistent with the molecular structure of the *ortho*-benzoquinone derivative $L5^{Me2}$; this structure proposal was further corroborated by X-ray crystallography (see below).

In order to get an estimate of the degree of steric crowding in our bis(pyrazol-1-yl)methane ligands, X-ray crystal structure analyses of $L2^{tBu}$ and $L3^{Me2}$ were performed (Figures 3 and 4, Table 1; cf. the Supporting Information for details of the X-ray crystal structure analysis of $L2^{Me2}$, $L2^{Ph}$, and $L3^{Ph}$).

$L2^{tBu}$ has both *tert*-butyl substituents in the 3- positions of its pyrazolyl rings. The C11−N11 = 1.459(2) Å, C11−N21 = 1.459(2) Å, and C1−C11 = 1.525(2) Å bond lengths are almost the same as in the parent system[15] without *tert*-butyl groups. Since this also applies for the bond angles about C11 and for the dihedral angles between the ring planes, the *tert*-butyl substituents apparently have no significant influence on the ligand skeleton.

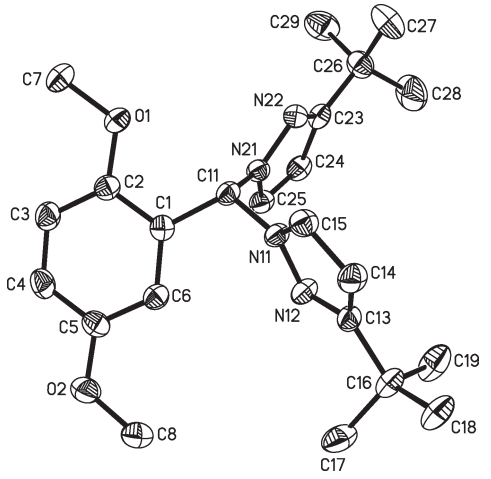


Figure 3. Molecular structure and numbering scheme of compound $\mathbf{L2^{tBu}}$ (50% displacement ellipsoids; H atoms omitted for clarity). Selected bond lengths [Å], bond angles [deg], torsion angles [deg], and dihedral angles [deg]: C11−N11 = 1.459(2), C11−N21 = 1.459(2), C1−C11 = 1.525(2), C2−O1 = 1.373(2), C5−O2 = 1.381(2); C1−C11−N11 = 114.4(1), C1−C11−N21 = 110.5(1), N11−C11−N21 = 110.1(1); C1−C11−N21−N22 = 149.0(1), C2−C1−C11−H11A = 35; HQ//pz(N11) = 56.9, HQ//pz(N21) = 78.6, pz(N11)//pz(N21) = 80.8.

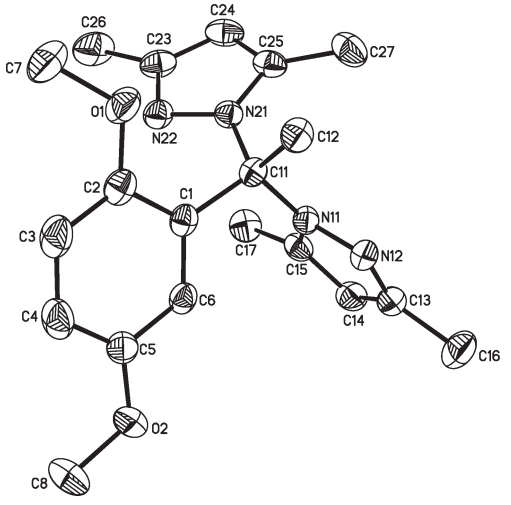


Figure 4. Molecular structure and numbering scheme of compound $\mathbf{L3^{Me2}}$ (50% displacement ellipsoids; H atoms omitted for clarity). Selected bond lengths [Å], bond angles [deg], torsion angles [deg], and dihedral angles [deg]: C11−N11 = 1.476(2), C11−N21 = 1.472(2), C1−C11 = 1.536(2), C2−O1 = 1.371(2), C5−O2 = 1.370(2); C1−C11−N11 = 110.1(1), C1−C11−N21 = 110.6(1), N11−C11−N21 = 107.3(1); C1−C11−N21−N22 = −7.9(2), C2−C1−C11−C12 = 58.3(2); HQ//pz(N11) = 87.8, HQ//pz(N21) = 67.5, pz(N11)//pz(N21) = 85.9.

The X-ray crystal structure analysis of $\mathbf{L3^{Me2}}$ (Figure 4) provides evidence for a higher degree of steric crowding about the carbon atoms C2 and C11 than is the case in $\mathbf{L2^{tBu}}$: (i) The C−N bonds (1.472(2) Å, 1.476(2) Å) and the C1−C11 bond (1.536(2) Å) are slightly elongated compared to the corresponding bonds in the *tert*-butyl derivative. (ii) In $\mathbf{L3^{Me2}}$, there are two short contacts between the *ipso* carbon atom C2 and atoms belonging to substituents on C11 (C2···N22 = 2.985(2) Å and C2···C12 = 3.077(2) Å), while there is only one such contact in $\mathbf{L2^{tBu}}$ (C2···N21 = 3.173(2) Å).

None of the C/N−C11−C/N angles in $\mathbf{L3^{Me2}}$ deviates by more than 3.4(1)° from the ideal tetrahedral angle of 109.5°.

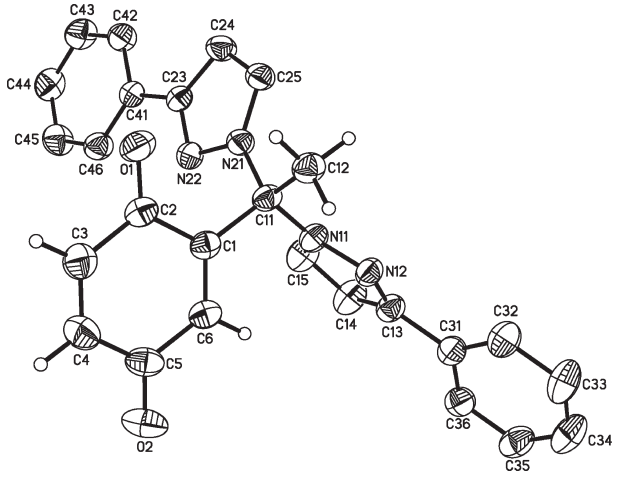


Figure 5. Molecular structure and numbering scheme of compound $\mathbf{L4^{Ph}}$ (50% displacement ellipsoids; H atoms on the pyrazolyl moieties omitted for clarity). Selected bond lengths [Å], bond angles [deg], torsion angles [deg], and dihedral angles [deg]: C11−N11 = 1.476(2), C11−N21 = 1.459(2), C1−C11 = 1.529(3), C2−O1 = 1.218(2), C5−O2 = 1.226(2), C1−C2 = 1.497(2), C1−C6 = 1.336(2), C2−C3 = 1.474(3), C3−C4 = 1.326(3), C4−C5 = 1.459(3), C5−C6 = 1.470(3); C1−C11−N11 = 109.1(1), C1−C11−N21 = 109.2(1), N11−C11−N21 = 107.4(1); C1−C11−N21−N22 = 37.7(2), C2−C1−C11−C12 = −66.4(2); BQ//pz(N11) = 86.7, BQ//pz(N21) = 74.7, pz(N11)//pz(N21) = 63.4.

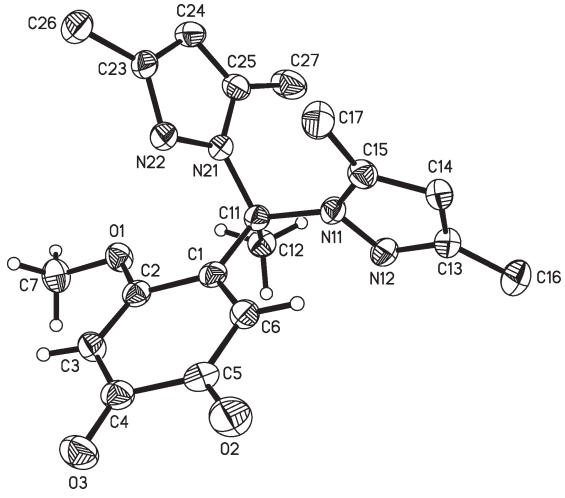


Figure 6. Molecular structure and numbering scheme of compound $\mathbf{L5^{Me2}}$ (50% displacement ellipsoids; H atoms on the pyrazolyl moieties omitted for clarity). Selected bond lengths [Å], bond angles [deg], torsion angles [deg], and dihedral angles [deg]: C11−N11 = 1.485(2), C11−N21 = 1.463(2), C1−C11 = 1.541(3), C2−O1 = 1.336(2), C4−O3 = 1.228(2), C5−O2 = 1.213(3), C1−C2 = 1.497(3), C1−C6 = 1.340(3), C2−C3 = 1.356(3), C3−C4 = 1.442(3), C4−C5 = 1.539(3), C5−C6 = 1.463(3); C1−C11−N11 = 110.0(2), C1−C11−N21 = 108.2(1), N11−C11−N21 = 108.7(2); C1−C11−N21−N22 = 10.9(2), C2−C1−C11−C12 = −58.1(2); BQ//pz(N11) = 83.0, BQ//pz(N21) = 69.2, pz(N11)//pz(N21) = 88.4.

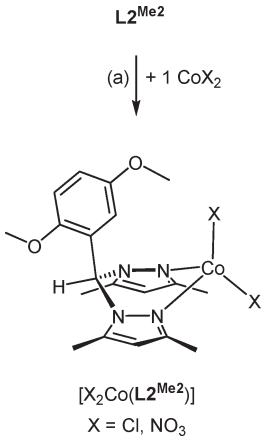
In order to corroborate the molecular structures of $\mathbf{L4^{Ph}}$ on the one hand and $\mathbf{L5^{Me2}}$ on the other, single crystals of these compounds have been investigated by X-ray crystallography (Figures 5 and 6; Table 2).

In line with the NMR spectroscopic results, $\mathbf{L4^{Ph}}$ still features both phenyl groups in the 3- positions of its pyrazolyl substituents; no 3,3′ → 3,5′ isomerization has occurred during the oxidation process. The successful generation of a *para*-benzoquinone fragment is evidenced by (i) the missing O*Me* groups and (ii) a characteristic bond length alternation

Table 2. Selected Crystallographic Data and Structure Refinement Details for $\mathbf{L4^{Ph}}$, $\mathbf{L5^{Me2}}$, and $[Cl_2Co(\mathbf{L2^{Me2}})]$

compound	$\mathbf{L4^{Ph}}$	$\mathbf{L5^{Me2}}$	$[Cl_2Co(\mathbf{L2^{Me2}})]$
formula	$C_{26}H_{20}N_4O_2$	$C_{19}H_{22}N_4O_3 \times Et_2O$	$C_{19}H_{24}Cl_2CoN_4O_2 \times 1/2$ MeCN
fw	420.46	428.53	490.78
color, shape	orange-red, block	red, rod	blue, needle
temp (K)	173(2)	165(2)	173(2)
radiation	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$P2_12_12_1$	$C2/c$
a (Å)	13.5748(10)	8.4840(12)	32.053(2)
b (Å)	8.6772(4)	14.384(3)	8.6594(8)
c (Å)	18.9711(15)	19.216(2)	16.5253(11)
α (deg)	90	90	90
β (deg)	100.306(6)	90	104.463(5)
γ (deg)	90	90	90
V (Å^3)	2198.6(3)	2345.0(6)	4441.4(6)
Z	4	4	8
D_{calcd} (g cm^{-3})	1.270	1.214	1.468
$F(000)$	880	920	2032
μ (mm^{-1})	0.083	0.084	1.038
cryst size (mm)	$0.35 \times 0.23 \times 0.22$	$0.60 \times 0.28 \times 0.25$	$0.31 \times 0.11 \times 0.11$
no of reflns coll	20929	34676	11201
no of ind reflns (R_{int})	4024 (0.0898)	3129 (0.0561)	4140 (0.0691)
data/restr/params	4024/0/290	3129/0/287	4140/0/283
GOF on F^2	0.914	1.049	0.906
R1, wR2 ($I > 2\sigma(I)$)	0.0418, 0.0887	0.0386, 0.0783	0.0396, 0.0905
R1, wR2 (all data)	0.0714, 0.0977	0.0627, 0.0862	0.0613, 0.0957
largest diff peak and hole (e Å^{-3})	0.177, −0.235	0.176, −0.137	0.483, −0.770

Scheme 3. Synthesis of the Co^{II} Complexes $[X_2Co(\mathbf{L2^{Me2}})]$[a]



[a] (a) X = Cl: MeOH, rt; X = NO_3: EtOH, rt.

within the benzoquinone ring (C1−C6 and C3−C4 are significantly shorter than the other four C−C bonds).

The solid-state structure of $\mathbf{L5^{Me2}}$ reveals a methoxy-substituted *ortho*-benzoquinone molecule (C2−O1 = 1.336(2) Å vs C4−O3 = 1.228(2) Å/C5−O2 = 1.213(3) Å). The newly introduced O3 atom occupies the sterically least shielded position, while the methoxy substituent that resisted oxidative demethylation is the one next to the bis(pyrazol-1-yl)methyl group. As is expected for an *ortho*-benzoquinone derivative, the six-membered ring contains two short (C1−C6 = 1.340(3) Å, C2−C3 = 1.356(3) Å) and four long C−C bonds (C1−C2 = 1.497(3) Å, C3−C4 = 1.442(3) Å, C4−C5 = 1.539(3) Å, C5−C6 = 1.463(3) Å). The bond lengths, bond angles, and dihedral angles within the bis(pyrazol-1-yl)methyl fragment are similar to those in $\mathbf{L3^{Me2}}$ and therefore do not merit further discussion.

Synthesis and Characterization of the Heteroleptic Complexes $[X_2Co(\mathbf{L2^{Me2}})]$ (X = Cl, NO_3). To find out whether methyl groups in the 3- positions of the pyrazolyl rings do already provide sufficient steric bulk to prevent the formation of homoleptic complexes like $[Co(\mathbf{L1})_2]$, $CoCl_2$ and $Co(NO_3)_2$ were treated with 1 equiv of $\mathbf{L2^{Me2}}$ in MeOH and EtOH, respectively (Scheme 3).

Single crystals suitable for X-ray crystallography were grown from MeCN ($[Cl_2Co(\mathbf{L2^{Me2}})]$; Figure 7, Table 2) and EtOH ($[(NO_3)_2Co(\mathbf{L2^{Me2}})]$; cf. the Supporting Information for details of the X-ray crystal structure analysis).

Complex $[Cl_2Co(\mathbf{L2^{Me2}})]$ features four-coordinate Co^{II} ions in a distorted tetrahedral environment that is composed of one chelating $\mathbf{L2^{Me2}}$ ligand and two chloride ions. The oxygen atom O1 does not bind to the metal center. As can be anticipated, the average Co−N bond length (2.019(2) Å) is considerably shorter than the corresponding bond length in the hexa-coordinate compound $[Co(\mathbf{L1})_2]_B$ (2.130(3) Å), but it fits well to the value in $[Cl_2Co(dmpzm)]$ (dmpzm = bis(3,5-dimethylpyrazol-1-yl)methane; Co−N = 2.034(7) Å[27]). A similar good agreement is found between the average Co−Cl bond lengths of $[Cl_2Co(\mathbf{L2^{Me2}})]$ (2.229(1) Å) and $[Cl_2Co(dmpzm)]$ (2.229(2) Å[27]). The bond angles about the Co^{II} center deviate considerably from the ideal value of 109.5°, the smallest angle being N12−Co1−N22 = 93.0(1)° and the largest being Cl1−Co1−N22 = 120.0(1)°.

The solid-state structure of $[(NO_3)_2Co(\mathbf{L2^{Me2}})]$ is similar to that of $[Cl_2Co(\mathbf{L2^{Me2}})]$, apart from the fact that the former complex contains a five-coordinate central metal atom because one of the two nitrate ions acts as a bidentate ligand. According to the τ_5 parameter[28] of 0.27, the geometry of $[(NO_3)_2Co(\mathbf{L2^{Me2}})]$ is best described as distorted square-pyramidal with the η^1-coordinating

(27) Li, Q.-Y.; Zhang, W.-H.; Li, H.-X.; Tang, X.-Y.; Lang, J.-P.; Zhang, Y.; Wang, X.-Y.; Gao, S. *Chin. J. Chem.* **2006**, *24*, 1716–1720.

(28) For five-coordinate complexes, the geometry index $\tau_5 = (\theta - \varphi)/60°$ provides a quantitative measure of whether the ligand sphere more closely approaches a square-pyramidal ($\tau_5 = 0$) or a trigonal-bipyramidal geometry ($\tau_5 = 1$; θ, φ are the two largest bond angles and $\theta \geq \varphi$): Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.

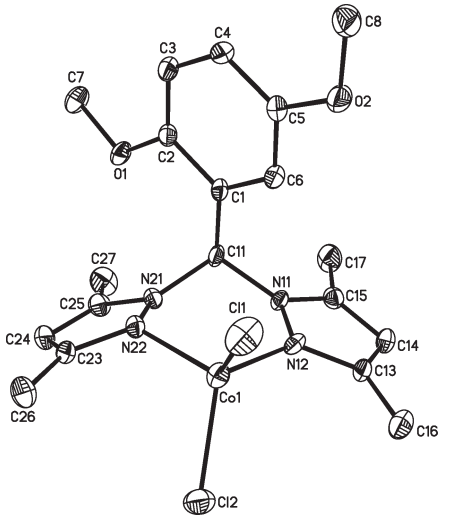


Figure 7. Molecular structure and numbering scheme of compound $[Cl_2Co(\mathbf{L2^{Me2}})]$ (50% displacement ellipsoids; H atoms omitted for clarity). Selected bond lengths [Å], bond angles [deg], and dihedral angles [deg]: Co1−Cl1 = 2.218(1), Co1−Cl2 = 2.240(1), Co1−N12 = 2.015(2), Co1−N22 = 2.023(2), C11−N11 = 1.468(3), C11−N21 = 1.456(3), C1−C11 = 1.509(4), C2−O1 = 1.372(3), C5−O2 = 1.384(3); Cl1−Co1−Cl2 = 113.8(1), Cl1−Co1−N12 = 114.2(1), Cl1−Co1−N22 = 120.0(1), Cl2−Co1−N12 = 108.2(1), Cl2−Co1−N22 = 105.3(1), N12−Co1−N22 = 93.0(1), N11−C11−N21 = 110.1(2); HQ//pz(N11) = 76.5, HQ//pz(N21) = 89.7, pz(N11)//pz(N21) = 43.4.

nitrate donor occupying the axial position (for more details, see the Supporting Information).

Thus, the solid-state structures of $[Cl_2Co(\mathbf{L2^{Me2}})]$ and $[(NO_3)_2Co(\mathbf{L2^{Me2}})]$ show the aimed-for 1:1 ratio between the Co^{II} ions and the respective bis(3,5-dimethylpyrazol-1-yl)methane ligand. However, electrospray mass spectra of MeCN solutions of these complexes reveal peaks at m/z = 370 ($[Co(\mathbf{L2^{Me2}})_2]^{2+}$), which indicates that in solution also the homoleptic 1:2 complexes are apparent.

Investigations into the Formation of the *ortho*-Quinone Ligand $\mathbf{L5^{Me2}}$. Only scattered examples are known for the transformation of phenol or *para*-hydroquinone derivatives into *ortho*-quinones. In most cases, Frémy's salt has been employed as an oxidizing agent.[29−33] Thus, the unexpected Ce^{IV}-induced formation of the *ortho*-quinone ligand $\mathbf{L5^{Me2}}$ posed a number of questions regarding the factors governing this reaction.

At first, we investigated whether the source of the newly introduced oxygen atom is dioxygen or water. To this end, we repeated the reaction between $\mathbf{L3^{Me2}}$ and $[Ce(NH_4)_2(NO_3)_6]$, which had previously been carried out in the presence of air, under an atmosphere of nitrogen in deaerated solvents (H_2O/MeCN). As a consequence, the isolated yield of $\mathbf{L5^{Me2}}$ dropped from previously 59% to now < 10%. We take this result as an indication that the semiquinone intermediate of the first Ce^{IV}-induced one-electron oxidation step reacts with triplet oxygen, which is the entry to *ortho*-quinone formation.

In order to elucidate what effect the steric demand of the bis(pyrazol-1-yl) substituent has on the outcome of the oxidation reaction, we treated also the derivative $\mathbf{L2^{Me2}}$ with $[Ce(NH_4)_2(NO_3)_6]$ in H_2O/MeCN (in this case and in all following experiments, air was admitted to the reaction mixture). As shown in Scheme 4, the reaction of $\mathbf{L2^{Me2}}$ took the usual course and gave the *para*-benzoquinone derivative $\mathbf{L6^{Me2}}$ in 64% yield.[34]

Given that Ce^{IV} oxidation of $\mathbf{L3^{Ph}}$ and $\mathbf{L3^{tBu}}$ also leads to *para*-benzoquinones ($\mathbf{L4^{Ph}}$/$\mathbf{L4^{tBu}}$; Scheme 2), it is safe to conclude that *both* the methyl substituent at the aliphatic bridge *and* the methyl groups in the 5- positions of the pyrazolyl rings are required to enforce *ortho*-quinone formation.

In the next step, we studied the influence of the π-electron density within the six-membered ring on the reaction outcome with the help of two model systems: the *ortho*-isomer **M1**[34] and the *meta*-isomer **M2**[34] (Scheme 4). Both compounds underwent almost quantitative hydrolysis to the corresponding methoxyphenylketone upon the addition of $[Ce(NH_4)_2(NO_3)_6]$ in H_2O/MeCN. This observation is revealing in two respects: (i) it becomes clear that both MeO substituents are required for the Ce^{IV}-induced oxidation to take place, even though only one of the methoxy groups is finally transformed and incorporated into the *ortho*-benzoquinone moiety; (ii) hydrolysis of our bis(pyrazol-1-yl)methane ligands is obviously retarded when the redox-active unit is in its BQ state. The latter result can be rationalized by taking into account that a cationic hydrolysis intermediate $[(HQ)C(H,Me)pz^{R,R'}]^+$ should be mesomerically stabilized, whereas the oxidized congener $[(BQ)C(H,Me)pz^{R,R'}]^+$ is not. We therefore conclude that the oxidative demethylation of ligands $\mathbf{L3^{Me2}}$, $\mathbf{L3^{Ph}}$, and $\mathbf{L3^{tBu}}$ must be significantly faster than the competing hydrolysis reaction.

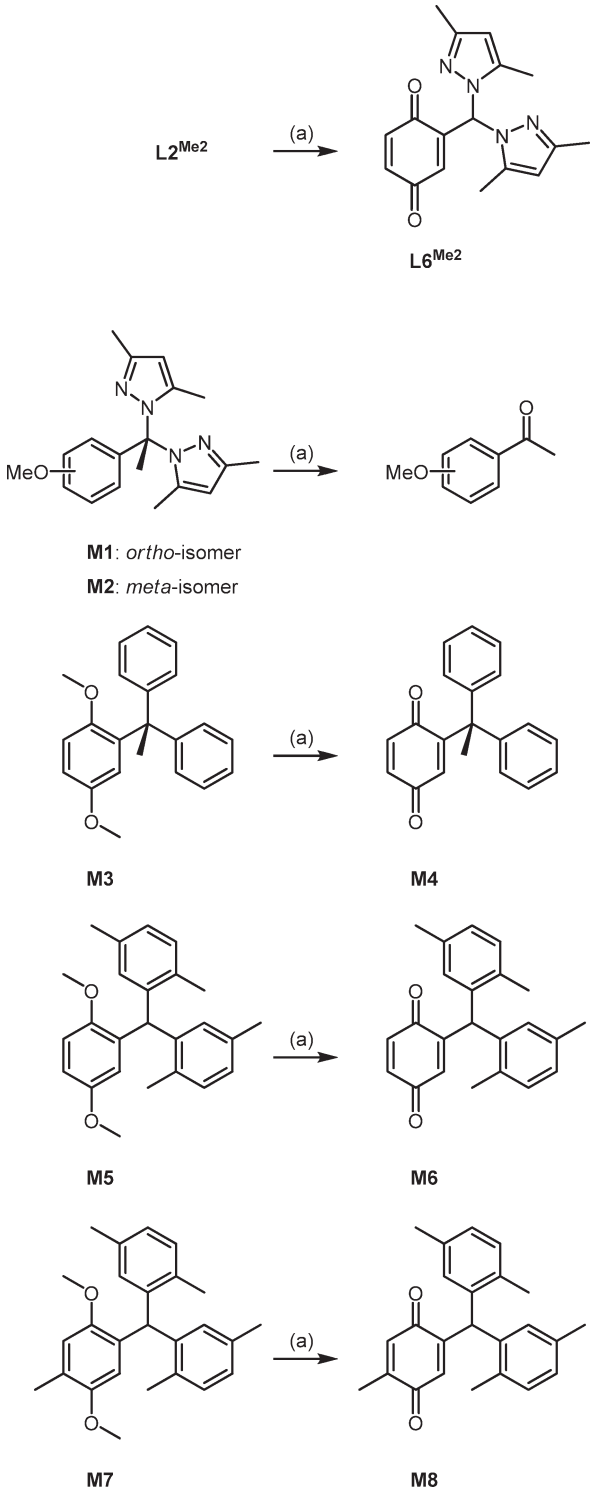
Molecular modeling studies on the various bis(pyrazol-1-yl)methane ligands indicate that the presence of the methyl substituents in $\mathbf{L3^{Me2}}$ has a pronounced effect on the preferred conformation of the molecule. If we assume that coordination of Ce^{IV} to the pyrazolyl rings precedes the metal-mediated oxidation event(s), a unique orientation of the metal ion with respect to the *para*-dimethoxybenzene ring in the $[Ce^{IV}(\mathbf{L3^{Me2}})]$ fragment may well explain the unique product selectivity. Given this background, we prepared the noncoordinating model systems **M3**[34] and **M5**[34] (Scheme 4) in order to evaluate whether *ortho*-benzoquinone formation just requires a sterically demanding diarylmethyl substituent or whether Ce^{IV} precoordination is also likely to play a role.

In both cases, *para*-benzoquinone derivatives (i.e., **M4**[34] and **M6**[34]) were isolated after the oxidation reaction was completed. It has, however, to be taken into account that a realistic noncoordinating mimic of $\mathbf{L3^{Me2}}$ would have to bear one methyl substituent (as in **M3**) and at the same time two *para*-xylyl groups (as in **M5**) on the exocyclic carbon atom. Unfortunately, all attempts to methylate **M5** at its alkyl bridge resulted in methylation of the

(29) Zimmer, H.; Lankin, D. C.; Horgan, S. W. *Chem. Rev.* **1971**, *71*, 229–246.
(30) Barton, D. H. R.; Finet, J.-P.; Thomas, M. *Tetrahedron* **1988**, *44*, 6397–6406.
(31) Krohn, K.; Rieger, H.; Khanbabaee, K. *Chem. Ber.* **1989**, *122*, 2323–2330.
(32) Krohn, K.; Rieger, H.; Brüggmann, K. *Synthesis* **1990**, 1141–1143.
(33) Nebois, P.; Cherkaoui, O.; Benameur, L.; Fillion, H.; Fenet, B. *Tetrahedron* **1994**, *50*, 8457–8464.

(34) For details of the synthesis procedure(s) and the characterization of this (these) compound(s), see the Supporting Information.

Scheme 4. Reactivities of $\mathbf{L2^{Me2}}$ and the Model Systems **M1**, **M2**, **M3**, **M5**, and **M7** toward $[Ce(NH_4)_2(NO_3)_6]$[a]



[a] (a) + exc. $[Ce(NH_4)_2(NO_3)_6]$, H_2O/MeCN, rt, 3 h.

para-dimethoxybenzene fragment (cf. **M7**;[34] Scheme 4). At the present stage, it is therefore not possible to fully evaluate the impact that Ce^{IV} precoordination may have on the formation of $\mathbf{L5^{Me2}}$.

We note in passing that we have also treated **M7** with $[Ce(NH_4)_2(NO_3)_6]$ in H_2O/MeCN and again obtained a *para*-benzoquinone derivative **M8**[34] (Scheme 4).

Moreover, we want to emphasize that the reduced parent system $((HO)_2C_6H_3)C(H)(pz^{H,H})_2$ of $\mathbf{L5^{Me2}}$ is readily available from 3,4-dihydroxybenzaldehyde and $(pz^{H,H})_2SO$/pyridine.[34]

Conclusion

This work aimed at the preparation of *para*-quinone-containing redox-active bis(pyrazol-1-yl)methane ligands **L** for applications in bioinorganic chemistry and homogeneous catalysis. One major focus was on the development of derivatives bearing bulky substituents at the 3- positions of their pyrazolyl rings in order to stabilize 1:1 transition metal complexes $[M(\mathbf{L})]^{n+}$ and to avoid the formation of less reactive $[M(\mathbf{L})_2]^{n+}$ species.

To this end, two series of sterically demanding *para*-dimethoxyphenyl-substituted bis(pyrazol-1-yl)methane ligands have been synthesized, i.e., $\mathbf{L2^{R,R'}}$ = $((MeO)_2C_6H_3)C(H)(pz^{R,R'})_2$ and $\mathbf{L3^{R,R'}}$ = $((MeO)_2C_6H_3)C(Me)(pz^{R,R'})_2$ (R,R′ = 3-Me,5-Me; 3-Ph,5-H; 3-*t*Bu,5-H).

Complexation studies with Co^{II} as the transition metal ion showed that already the derivative $\mathbf{L2^{Me2}}$ is able to stabilize complexes of the form $[X_2Co(\mathbf{L2^{Me2}})]$ (X = Cl, NO_3) in the solid state. In MeCN solution, however, these complexes are at an equilibrium with the 1:2 species $[Co(\mathbf{L2^{Me2}})_2]^{2+}$.

Oxidative demethylation of $\mathbf{L3^{Ph}}$ and $\mathbf{L3^{tBu}}$ with $[Ce(NH_4)_2(NO_3)_6]$ leads to the corresponding *para*-benzoquinonyl-substituted bis(pyrazol-1-yl)methanes $\mathbf{L4^{Ph}}$ and $\mathbf{L4^{tBu}}$ so that these ligands can now operate at their full redox capacity.

Under similar reaction conditions, the methyl derivative $\mathbf{L3^{Me2}}$ is transformed into the *ortho*-benzoquinone species $\mathbf{L5^{Me2}}$, which still contains one methoxy substituent while one carbonyl oxygen atom has been newly introduced. We have repeated the reaction under an inert gas atmosphere in deaerated solvents, and we have investigated numerous model systems with different substitution patterns. These experiments led to the conclusion that $\mathbf{L5^{Me2}}$ formation requires (i) the admission of O_2, (ii) the presence of both methoxy substituents of $\mathbf{L3^{Me2}}$, and (iii) the presence of (methyl) substituents both at the exocyclic carbon atom and at the 5- positions of the pyrazolyl rings.

We have also prepared a selection of noncoordinating analogs of **L2** and **L3** in which the pyrazolyl rings are replaced by phenyl or *para*-xylyl groups. Our motivation was to find out whether Ce^{IV} coordination is important in the product-determining step. In all cases, the Ce^{IV}-induced oxidation went the usual course and gave the respective *para*-benzoquinone derivatives. It has, however, to be mentioned that the most realistic analog of $\mathbf{L3^{Me2}}$ (i.e., $((MeO)_2C_6H_3)C(Me)(C_6H_3Me_2)_2$) was synthetically not accessible. Thus, at the present stage, it is not possible to fully exclude that Ce^{IV} precoordination may have an impact on the formation of $\mathbf{L5^{Me2}}$.

The redox-active fragment in $\mathbf{L5^{Me2}}$ resembles the enzyme cofactor topaquinone, which makes $\mathbf{L5^{Me2}}$ an interesting ligand for the development of Cu-dependent amine oxidase model systems. $\mathbf{L5^{Me2}}$ (in its hydroquinone form) can also act as a ditopic bridging unit in (hetero)oligonuclear complexes. Here, coordination of transition metal ions to the *ortho*-hydroquinone unit will not only modify the redox behavior of the entire system but also decouple electron transfer from proton transfer.

Experimental Section

General. All reactions and manipulations of air-sensitive compounds were carried out under dry, oxygen-free nitrogen by using standard Schlenk ware. Where appropriate, THF was freshly distilled under argon from Na/benzophenone. NaH was used as a 60% per weight suspension in mineral oil (commercially available); however, throughout the Experimental Section, all weight-out quantities refer to neat NaH.

NMR spectra were recorded with Bruker AM-250, Bruker Avance-300, and Bruker Avance-400 spectrometers. Chemical shifts are referenced to residual solvent signals ($^1H/^{13}C\{^1H\}$, C_6D_6: 7.16/128.00; $CDCl_3$: 7.26/77.16; CD_2Cl_2: 5.32/53.8; d^6-DMSO: 2.50/39.52). Abbreviations: s = singlet; d = doublet; dd = doublet of doublets; m = multiplet; br = signal broadened; n.r. = multiplet expected in the ^1H NMR spectrum, but not resolved; pz = pyrazol-1-yl; HQ = hydroquinone core; BQ = benzoquinone core.

Elemental analyses were performed by the Microanalytical Laboratory of the University of Frankfurt. Mass spectra were recorded with a VG PLATFORM II mass spectrometer.

Synthesis of [Co(L1)$_2$]. A solution of H**L1** (189 mg, 0.40 mmol) in MeOH (15 mL) was treated at room temperature with a solution of NaOMe in MeOH (0.5 M, 1 mL). Neat $Co(OAc)_2$ (35 mg, 0.20 mmol) was added, and the reaction mixture was stirred at room temperature for 12 h. All volatiles were removed under reduced pressure, and the solid residue was recrystallized from CH_2Cl_2. Yield: 158 mg (73%). ESI-MS: m/z 995 $[M]^+$. Anal. Calcd for $C_{52}H_{78}CoN_8O_4Si_2$ [994.34] × CH_2Cl_2 [84.93]: C, 58.98; H, 7.47; N, 10.38. Found: C, 58.86; H, 7.49; N, 10.65.

Synthesis of L2^{Me}. In a representative procedure, neat methylpyrazole (0.98 mL, 1.00 g, 12.2 mmol) was added at 0 °C to a stirred suspension of NaH (0.29 g, 12.1 mmol) in THF (75 mL). Stirring was continued for 30 min. Neat $SOCl_2$ (0.44 mL, 0.72 g, 6.1 mmol) was added in one portion via syringe, and the resulting mixture was allowed to warm to room temperature. After treatment with *para*-dimethoxybenzaldehyde (1.01 g, 6.1 mmol) and pyridine (0.49 mL, 0.48 g, 6.1 mmol), the reaction mixture was kept at the reflux temperature for 12 h. H_2O (40 mL) was added and the aqueous phase extracted into CH_2Cl_2 (3 × 100 mL). The combined organic extracts were dried over $MgSO_4$ and filtered, and the filtrate was evaporated to dryness under a vacuum. The crude product of **L2^{Me}** was purified by column chromatography (silica gel; hexane/EtOAc 1:1). Yield: 1.07 g (56%). The pure product was obtained as a colorless oil, which solidified upon standing. It was composed of a mixture of the 3,3′- and the *rac*-3,5′-isomers in a stoichiometric ratio of 4:1. The isomeric ratio could be raised to 10:1 by repeated recrystallizations from hexane. R_f = 0.40 (silica gel; hexane/EtOAc 1:1). **3,3′-Isomer.** ^1H NMR (250.1 MHz, C_6D_6): δ 2.16 (s, 6 H; pz-CH_3), 3.09, 3.28 (2 × s, 2 × 3 H; OCH_3), 5.83 (d, $^3J_{HH}$ = 2.3 Hz, 2 H; pz-H4), 6.36 (d, $^3J_{HH}$ = 8.9 Hz, 1 H; HQ-H3), 6.67 (dd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 3.1 Hz, 1 H; HQ-H4), 7.08 (d, $^4J_{HH}$ = 3.1 Hz, 1 H; HQ-H6), 7.21 (d, $^3J_{HH}$ = 2.3 Hz, 2 H; pz-H5), 8.14 (s, 1 H; CH). ^{13}C NMR (62.9 MHz, C_6D_6): δ 13.8 (pz-CH_3), 55.2, 55.7 (OCH_3), 73.2 (Cpz_2), 105.7 (pz-C4), 112.1, 115.0, 115.2 (HQ-C3,4,6), 127.9 (HQ-C1), 130.1 (pz-C5), 149.6 (pz-C3), 151.3, 154.4 (HQ-C2,5). **3,5′-Isomer.** ^1H NMR (300.0 MHz, C_6D_6): δ 2.07, 2.18 (2 × s, 2 × 3 H; pz-CH_3), 3.13, 3.30 (2 × s, 2 × 3 H; OCH_3), 5.79, 5.88 (n.r., d, $^3J_{HH}$ = 2.3 Hz, 2 × 1 H; pz-H4,4′), 6.40 (d, $^3J_{HH}$ = 8.9 Hz, 1 H; HQ-H3), 6.70 (dd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 3.1 Hz, 1 H; HQ-H4), 7.17 (n.r., 1 H; HQ-H6), 7.42, 7.62 (n.r., d, $^3J_{HH}$ = 2.3 Hz, 2 × 1 H; pz-H3′,5), 8.14 (s, 1 H; CH). ESI-MS: m/z (%) 231 $[M - pzMe]^+$ (100), 313 $[M + H]^+$ (26). Anal. Calcd for $C_{17}H_{20}N_4O_2$ [312.37]: C, 65.37; H, 6.45; N, 17.94. Found: C, 65.29; H, 6.40; N, 18.05.

Synthesis of L2^{Me2}. The compound was prepared as described for **L2^{Me}** from 3,5-dimethylpyrazole (10.00 g, 104.0 mmol), NaH (2.50 g, 104.2 mmol), $SOCl_2$ (3.80 mL, 6.22 g, 52.3 mmol), *para*-dimethoxybenzaldehyde (8.64 g, 52.0 mmol), and pyridine (4.20 mL, 4.12 g, 52.0 mmol). The yellow oily crude product was dissolved in EtOAc and the resulting solution evaporated to dryness under a vacuum. The solid residue was recrystallized from Et_2O to obtain colorless pure **L2^{Me2}**. Yield: 14.20 g (80%). Single crystals were obtained by gas-phase diffusion of pentane into a dilute Et_2O solution of **L2^{Me2}**. R_f = 0.32 (silica gel; hexane/EtOAc 1:1). ^1H NMR (400.1 MHz, $CDCl_3$): δ 2.12, 2.20 (2 × s, 2 × 6 H; pz-CH_3), 3.65, 3.67 (2 × s, 2 × 3 H; OCH_3), 5.83 (s, 2 H; pz-H4), 6.35 (d, $^4J_{HH}$ = 2.1 Hz, 1 H; HQ-H6), 6.83 (m, 2 H; HQ-H3,4), 7.72 (s, 1 H; CH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 11.4, 13.7 (pz-CH_3), 55.6, 56.5 (OCH_3), 70.0 (Cpz_2), 106.5 (pz-C4), 112.0, 114.0 (HQ-C3,4), 115.2 (HQ-C6), 126.2 (HQ-C1), 140.4, 147.8 (pz-C3,5), 151.1, 153.6 (HQ-C2,5). ESI-MS: m/z (%) 245 $[M - pzMe_2]^+$ (78), 341 $[M + H]^+$ (100). Anal. Calcd for $C_{19}H_{24}N_4O_2$ [340.42]: C, 67.04; H, 7.11; N, 16.46. Found: C, 67.20; H, 7.21; N, 16.46.

Synthesis of L2^{Ph}. The compound was prepared as described for **L2^{Me}** from phenylpyrazole (1.00 g, 6.9 mmol), NaH (0.17 g, 7.1 mmol), $SOCl_2$ (0.25 mL, 0.41 g, 3.5 mmol), *para*-dimethoxybenzaldehyde (0.57 g, 3.4 mmol), and pyridine (0.28 mL, 0.27 g, 3.5 mmol). Recrystallization of the crude product from MeCN gave a colorless solid. Yield: 0.79 g (52%). To grow single crystals of **L2^{Ph}**, a MeCN solution was layered with hexane. ^1H NMR (300.0 MHz, d^6-DMSO): δ 3.65, 3.72 (2 × s, 2 × 3 H; OCH_3), 6.71 (d, $^4J_{HH}$ = 2.9 Hz, 1 H; HQ-H6), 6.83 (d, $^3J_{HH}$ = 2.5 Hz, 2 H; pz-H4), 7.02 (dd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 2.9 Hz, 1 H; HQ-H4), 7.09 (d, $^3J_{HH}$ = 8.9 Hz, 1 H; HQ-H3), 7.31 (m, 2 H; Ph-H_p), 7.40 (m, 4 H; Ph-H_m), 7.80 (m, 4 H; Ph-H_o), 7.85 (d, $^3J_{HH}$ = 2.5 Hz, 2 H; pz-H5), 8.02 (s, 1 H; CH). ^{13}C NMR (75.5 MHz, d^6-DMSO): δ 55.3, 56.3 (OCH_3), 72.2 (Cpz_2), 103.3 (pz-C4), 112.7 (HQ-C3), 114.4, 114.5 (HQ-C4,6), 124.6 (HQ-C1), 125.2 (Ph−C_o), 127.8 (Ph−C_p), 128.6 (Ph−C_m), 131.8 (pz-C5), 132.6 (Ph−C_i), 150.4, 151.2, 152.9 (pz-C3, HQ-C2,5). ESI-MS: m/z (%) 293 $[M - pzPh]^+$ (100), 437 $[M + H]^+$ (41). Anal. Calcd for $C_{27}H_{24}N_4O_2$ [436.51]: C, 74.29; H, 5.54; N, 12.84. Found: C, 74.24; H, 5.61; N, 13.05.

Synthesis of L2^{tBu}. The compound was prepared as described for **L2^{Me}** from *tert*-butylpyrazole (0.50 g, 4.0 mmol), NaH (0.10 g, 4.1 mmol), $SOCl_2$ (0.15 mL, 0.25 g, 2.0 mmol), *para*-dimethoxybenzaldehyde (0.33 g, 2.0 mmol), and pyridine (0.16 mL, 0.16 g, 2.0 mmol). **L2^{tBu}**, which is a colorless solid, was purified by column chromatography (silica gel, hexane/EtOAc 1:2). However, recrystallization from hexane is more advisable for a large-scale synthesis. Yield: 0.60 g (76%). Single crystals were grown by slow evaporation of a dilute hexane solution of **L2^{tBu}**. R_f = 0.83 (silica gel; hexane/EtOAc 1:2). ^1H NMR (400.1 MHz, C_6D_6): δ 1.32 (s, 18 H; CCH_3), 3.04, 3.31 (2 × s, 2 × 3 H; OCH_3), 6.00 (d, $^3J_{HH}$ = 2.4 Hz, 2 H; pz-H4), 6.34 (d, $^3J_{HH}$ = 8.9 Hz, 1 H; HQ-H3), 6.68 (dd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 3.0 Hz, 1 H; HQ-H4), 6.88 (d, $^4J_{HH}$ = 3.0 Hz, 1 H; HQ-H6), 7.18 (d, $^3J_{HH}$ = 2.4 Hz, 2 H; pz-H5), 8.18 (s, 1 H; CH). ^{13}C NMR (100.6 MHz, C_6D_6): δ 30.8 (CCH_3), 32.5 (CCH_3), 55.2, 55.7 (OCH_3), 73.5 (Cpz_2), 102.3 (pz-C4), 112.4 (HQ-C3), 114.5 (HQ-C6), 115.4 (HQ-C4), 127.0 (HQ-C1), 129.6 (pz-C5), 151.3, 154.2 (HQ-C2,5), 162.9 (pz-C3). ESI-MS: m/z (%) 273 $[M - pztBu]^+$ (100), 397 $[M + H]^+$ (13). Anal. Calcd for $C_{23}H_{32}N_4O_2$ [396.53]: C, 69.67; H, 8.13; N, 14.13. Found: C, 69.81; H, 8.17; N, 14.17.

Synthesis of L3^{Me2}. In a representative procedure, *n*BuLi (1.52 M in hexane; 1.93 mL, 2.9 mmol) was added at 0 °C via syringe to a stirred solution of **L2^{Me2}** (1.00 g, 2.9 mmol) in THF (40 mL). After 30 min, the bright red reaction mixture was allowed to warm to room temperature, and neat MeI (0.18 mL, 0.41 g, 2.9 mmol) was added via syringe, whereupon the red color vanished rapidly. Stirring was continued for another 30 min. The reaction mixture was poured into H_2O (30 mL), and **L3^{Me2}** was extracted into CH_2Cl_2 (3 × 20 mL). The combined extracts were dried over $MgSO_4$ and filtered, and the filtrate was evaporated to dryness. The crude product was triturated with hexane and recrystallized from hot hexane to obtain colorless crystals. Yield: 0.73 g (71%). R_f = 0.69 (silica gel; hexane/EtOAc 1:1).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ 1.68, 2.19 (2 × s, 2 × 6 H; pz-CH_3), 2.70 (s, 3 H; CH_3), 3.60, 3.72 (2 × s, 2 × 3 H; OCH_3), 5.42 (d, $^4J_{HH}$ = 3.0 Hz, 1 H; HQ-H6), 5.86 (s, 2 H; pz-H4), 6.81 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 3.0 Hz, 1 H; HQ-H4), 6.91 (d, $^3J_{HH}$ = 8.8 Hz, 1 H; HQ-H3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 11.9, 13.6 (pz-CH_3), 28.2 (CH_3), 55.3, 56.6 (OCH_3), 83.0 (Cpz_2), 108.3 (pz-C4), 112.9 (HQ-C6), 113.3, 114.1 (HQ-C3,4), 132.6, 141.2, 145.9 (HQ-C1, pz-C3,5), 152.1, 153.5 (HQ-C2,5). ESI-MS: *m*/*z* (%) 259 [M − $pzMe_2$]$^+$ (100). Anal. Calcd for $C_{20}H_{26}N_4O_2$ [354.45]: C, 67.77; H, 7.39; N, 15.81. Found: C, 68.00; H, 7.43; N, 15.81.

Synthesis of L3^{Ph}. The compound was prepared as described for **L3^{Me2}** from **L2^{Ph}** (0.44 g, 1.0 mmol), *n*BuLi (1.60 M in hexane; 0.63 mL, 1.0 mmol), and MeI (0.06 mL, 0.14 g, 1.0 mmol). The crude product was purified by column chromatography (silica gel; hexane/EtOAc 3:1). In order to obtain X-ray quality crystals, a sample of **L3^{Ph}** was dissolved in boiling hexane and the clear solution stored in an oven at +50 °C overnight. Yield: 0.37 g (82%). R_f = 0.55 (silica gel; hexane/EtOAc 3:1). ^{1}H NMR (400.1 MHz, d^6-DMSO): δ 2.75 (s, 3 H; CH_3), 3.55, 3.58 (2 × s, 2 × 3 H; OCH_3), 5.39 (d, $^4J_{HH}$ = 3.0 Hz; HQ-H6), 6.84 (d, $^3J_{HH}$ = 2.3 Hz, 2 H; pz-H4), 6.98 (dd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 3.0 Hz, 1 H; HQ-H4), 7.09 (d, $^3J_{HH}$ = 8.9 Hz, 1 H; HQ-H3), 7.31 (m, 2 H; Ph-H_p), 7.40 (m, 4H; Ph-H_m), 7.52 (d, $^3J_{HH}$ = 2.3 Hz, 2 H; pz-H5), 7.81 (m, 4 H; Ph-H_o). ^{13}C NMR (100.6 MHz, d^6-DMSO): δ 24.5 (CH_3), 55.1, 56.3 (OCH_3), 81.5 (Cpz_2), 103.4 (pz-C4), 113.5, 114.0, 114.2 (HQ-C3,4,6), 125.3 (Ph−C_o), 127.8 (Ph−C_p), 128.7 (Ph−C_m), 131.0 (pz-C5), 131.4, 132.9 (Ph−C_i, HQ-C1), 150.3, 150.4, 152.8 (pz-C3, HQ-C2,5). ESI-MS: *m*/*z* (%) 307 [M − pzPh]$^+$ (58). Anal. Calcd for $C_{28}H_{26}N_4O_2$ [450.55]: C, 74.65; H, 5.82; N, 12.44. Found: C, 74.62; H, 5.96; N, 12.40.

Synthesis of L3^{tBu}. The compound was prepared as described for **L3^{Me2}** from **L2^{tBu}** (1.00 g, 2.5 mmol), *n*BuLi (1.52 M in hexane; 1.66 mL, 2.5 mmol), and MeI (0.16 mL, 0.36 g, 2.5 mmol). The crude product was purified by column chromatography (silica gel; hexane/EtOAc 2:1). **L3^{tBu}** was obtained as a colorless oil and a mixture of isomers (3,3′-isomer/3,5′-isomer ≈ 8:1). Yield: 0.82 g (80%). R_f = 0.75 (silica gel; hexane/EtOAc 2:1). **3,3′-Isomer.** ^{1}H NMR (300.0 MHz, C_6D_6): δ 1.37 (s, 18 H; CCH_3), 3.05 (s, 3 H; CH_3), 3.06, 3.28 (2 × s, 2 × 3 H; OCH_3), 5.80 (d, $^4J_{HH}$ = 3.1 Hz, 1 H; HQ-H6), 6.03 (d, $^3J_{HH}$ = 2.4 Hz, 2 H; pz-H4), 6.45 (d, $^3J_{HH}$ = 8.9 Hz, 1 H; HQ-H3), 6.72 (dd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 3.1 Hz, 1 H; HQ-H4), 7.01 (d, $^3J_{HH}$ = 2.4 Hz, 2 H; pz-H5). ^{13}C NMR (75.5 MHz, C_6D_6): δ 25.1 (CH_3), 30.8 (CCH_3), 32.5 (CCH_3), 55.0, 55.8 (OCH_3), 82.5 (Cpz_2), 102.1 (pz-C4), 113.4, 114.1, 115.3 (HQ-C3,4,6), 129.6 (pz-C5), 133.0 (HQ-C1), 151.2, 154.2 (HQ-C2,5), 162.1 (pz-C3). **3,5′-Isomer.** ^{1}H NMR (300.0 MHz, C_6D_6): δ 1.35, 1.39 (2 × s, 2 × 9 H; CCH_3), 3.08, 3.11, 3.29 (3 × s, 3 × 3 H; CH_3, OCH_3), 5.84 (n.r., 1 H; HQ-H6), 5.90, 6.01 (2 × d, $^3J_{HH}$ = 3.1 Hz, 2.4 Hz, 2 × 1 H; pz-H4,4′), 6.17 (n.r., 2 H; HQ-H3,4), 6.97 (d, $^3J_{HH}$ = 2.4 Hz, 1 H; pz-H5 or 5′), n.o. (pz-H5 or 5′). ESI-MS: *m*/*z* (%) 287 [M − pz*t*Bu]$^+$ (100), 411 [M + H]$^+$ (9). Anal. Calcd for $C_{24}H_{34}N_4O_2$ [410.55]: C, 70.21; H, 8.35; N, 13.65. Found: C, 70.26; H, 8.61; N, 13.58.

Synthesis of L4^{Ph}. In a representative procedure, $[Ce(NH_4)_2(NO_3)_6]$ (2.63 g, 4.8 mmol) in H_2O (20 mL) was added at 0 °C to a stirred solution of **L3^{Ph}** (0.72 g, 1.6 mmol) in MeCN (20 mL). The mixture was allowed to warm to room temperature, and stirring was continued for 3 h. The product was extracted into CH_2Cl_2 (3 × 50 mL). The combined extracts were dried over $MgSO_4$ and filtered, and the filtrate was evaporated to dryness under reduced pressure. **L4^{Ph}** was purified by column chromatography (silica gel; hexane/EtOAc 3:1) and obtained as a yellow solid. Yield: (0.55 g, 82%). X-ray quality crystals of the compound were obtained from a saturated solution in Et_2O at −20 °C. R_f = 0.39 (silica gel; hexane/EtOAc 3:1). ^{1}H NMR (250.1 MHz, CD_2Cl_2): δ 2.76 (s, 3 H; CH_3), 5.68 (d, $^4J_{HH}$ = 1.9 Hz, 1 H; BQ-H6), 6.70 (d, $^3J_{HH}$ = 2.6 Hz, 2 H; pz-H4), 6.78 (m, 2 H; BQ-H3,4), 7.38 (m, 6 H; Ph-H_p,H_m), 7.52 (d, $^3J_{HH}$ = 2.6 Hz, 2 H; pz-H5), 7.81 (m, 4 H; Ph-H_o). ^{13}C NMR (62.9 MHz, d^6-DMSO): δ 24.3 (CH_3), 79.8 (Cpz_2), 104.4 (pz-C4), 125.4 (Ph−C_o), 128.1, 128.3 (Ph−C_m,C_p), 128.7 (Ph−C_i), 131.1 (pz-C5), 132.5 (BQ-C6), 136.0, 137.8 (BQ-C3,4), 146.9 (BQ-C1), 150.9 (pz-C3), 184.7, 187.2 (BQ-C2,5). ESI-MS: *m*/*z* (%) 277 [M − pzPh]$^+$ (100), 421 [M + H]$^+$ (13). Anal. Calcd for $C_{26}H_{20}N_4O_2$ [420.46]: C, 74.27; H, 4.79; N, 13.33. Found: C, 74.36; H, 4.84; N, 13.44.

Synthesis of L4^{tBu}. The compound was prepared as described for **L4^{Ph}** from **L3^{tBu}** (1.04 g, 2.5 mmol; 8:1 mixture of isomers) and $[Ce(NH_4)_2(NO_3)_6]$ (2.77 g, 5.1 mmol). **L4^{tBu}** was purified by column chromatography (silica gel; hexane/EtOAc 2:1) and obtained as a red oil (8:1 mixture of regioisomers). Yield: 0.86 g (90%). R_f = 0.68 (silica gel; hexane/EtOAc 2:1). **3,3′-Isomer.** ^{1}H NMR (400.1 MHz, C_6D_6): δ 1.32 (s, 18 H; CCH_3), 2.54 (s, 3 H; CH_3), 5.59 (d, $^4J_{HH}$ = 2.0 Hz, 1 H; BQ-H6), 6.00 (m, 4 H; pz-H4, BQ-H3,4), 7.00 (d, $^3J_{HH}$ = 2.5 Hz, 2 H; pz-H5). ^{13}C NMR (62.9 MHz, C_6D_6): δ 24.7 (CH_3), 30.6 (CCH_3), 32.4 (CCH_3), 79.9 (Cpz_2), 103.4 (pz-C4), 128.6 (pz-C5), 132.5, 135.4, 137.0 (BQ-C3,4,6), 149.0 (BQ-C1), 162.5 (pz-C3), 184.7, 186.9 (BQ-C2,5). ESI-MS: *m*/*z* (%) 257 [M − pz*t*Bu]$^+$ (100), 381 [M + H]$^+$ (67). Anal. Calcd for $C_{22}H_{28}N_4O_2$ [380.48]: C, 69.45; H, 7.42; N, 14.73. Found: C, 69.25; H, 7.44; N, 14.74.

Synthesis of L5^{Me2}. $[Ce(NH_4)_2(NO_3)_6]$ (1.55 g, 2.8 mmol) in H_2O (20 mL) was added at 0 °C to a stirred solution of **L3^{Me2}** (0.50 g, 1.4 mmol) in MeCN (20 mL). The mixture was warmed to room temperature, and stirring was continued for 3 h. The product was extracted into CH_2Cl_2 (3 × 50 mL). The combined organic extracts were dried over $MgSO_4$ and filtered, and the filtrate was evaporated to dryness under reduced pressure. **L5^{Me2}** was purified by column chromatography (silica gel; hexane/EtOAc 1:3; *note*: the column should be shorter than 5 cm, because prolonged contact with silica gel leads to product decomposition). **L5^{Me2}** was obtained as a red solid. Yield: (0.29 g, 59%). Single crystals of **L5^{Me2}** were obtained by storing a Et_2O solution at −20 °C. R_f = 0.56 (silica gel; hexane/EtOAc 1:3). ^{1}H NMR (300.0 MHz, C_6D_6): δ 1.51, 2.10 (2 × s, 2 × 6 H; pz-CH_3), 2.60 (s, 3 H; CH_3), 2.74 (s, 3 H; OCH_3), 5.06, 5.45 (2 × s, 2 × 1 H; BQ-H3,6), 5.56 (s, 2 H; pz-H4). ^{13}C NMR (75.5 MHz, d^6-DMSO): δ 10.8 (very br), 13.3 (pz-CH_3), 27.9 (CH_3), 57.1 (OCH_3), 81.4 (Cpz_2), 103.3 (BQ-C3 or 6), 108.7 (pz-C4), 124.2 (BQ-C3 or 6), 150.5, 168.8, n.o., n.o. (BQ-C1,2, pz-C3,5), 178.0, 180.8 (BQ-C4,5). ESI-MS: *m*/*z* (%) 259 [M − $pzMe_2$]$^+$ (26), 355 [M + H]$^+$ (100). IR (KBr, cm^{-1}): $\tilde{\nu}$ 1688 (m), 1648 (s), 1627 (m), 1570 (s), 1561 (s), 1449 (m), 1414 (m), 1371 (s), 1343 (m), 1251 (s). Anal. Calcd for $C_{19}H_{22}N_4O_3$ [354.40]: C, 64.39; H, 6.26; N, 15.81. Found: C, 64.46; H, 6.18; N, 15.81.

Synthesis of [Cl_2Co(L2^{Me2})]. $CoCl_2$ (23 mg, 0.18 mmol) was added at room temperature to a stirred solution of **L2^{Me2}** (60 mg, 0.18 mmol) in MeOH (10 mL). Stirring was continued for 30 min. The crude product was isolated by filtration, repeatedly washed with small portions of MeOH, and then recrystallized from MeCN. Yield: 80 mg (95%). Blue single crystals were obtained by slow evaporation of a dilute MeCN solution. ESI-MS: *m*/*z* (%) 245 [**L2^{Me2}** − $pzMe_2$]$^+$ (50), 341 [**L2^{Me2}** + H]$^+$ (49), 370 [Co(**L2^{Me2}**)$_2$]$^{2+}$ (100). Anal. Calcd for $C_{19}H_{24}Cl_2CoN_4O_2$ [470.25]: C, 48.53; H, 5.14; N, 11.91. Found: C, 46.11; H, 4.87; N, 11.76.

Synthesis of [$(NO_3)_2$Co(L2^{Me2})]. $Co(NO_3)_2 \times 6H_2O$ (171 mg, 0.59 mmol) was added at room temperature to a stirred solution of **L2^{Me2}** (200 mg, 0.59 mmol) in EtOH (10 mL). Stirring was continued overnight. The crude product was collected on a frit, washed with EtOH, and dried under reduced pressure. Yield: 168 mg (54%). Purple single crystals were grown by slow evaporation of a dilute EtOH solution. ESI-MS: *m*/*z* (%) 245 [**L2^{Me2}** − $pzMe_2$]$^+$ (83), 341 [**L2^{Me2}** + H]$^+$ (7), 370 [Co(**L2^{Me2}**)$_2$]$^{2+}$ (100), 461 [(NO_3)Co(**L2^{Me2}**)]$^+$ (21). Anal. Calcd for $C_{19}H_{24}CoN_6O_8$ [523.37]: C, 43.60; H, 4.62; N, 16.06. Found: C, 43.84; H, 4.62; N, 16.26.

X-Ray Crystallography of L2^{Me}, L2^{Me2}, L2^{Ph}, L2^{tBu}, L3^{Me2}, L3^{Ph}, L4^{Ph}, L5^{Me2}, S4, M3, M7, [Co(L1)$_2$], [Cl_2Co(L2^{Me2})], and [$(NO_3)_2$Co(L2^{Me2})]. Data collections were performed on a Stoe-IPDS-II two-circle diffractometer (**L2^{Me}**, **L2^{Me2}**, **L3^{Me2}**, **L3^{Ph}**,

L4^{Ph}, **M3**, [Cl_2Co(**L2^{Me2}**)], [$(NO_3)_2Co$(**L2^{Me2}**)]) or on a SIEMENS SMART CCD diffractometer (**L2^{Ph}**, **L2^{tBu}**, **L5^{Me2}**, **S4**, **M7**, [Co(**L1**)$_2$]) with graphite-monochromated Mo Kα radiation. In all cases, repeatedly, measured reflections remained stable. Empirical absorption corrections were performed using either the MULABS[35] option in PLATON[36] ([Cl_2Co(**L2^{Me2}**)] and [$(NO_3)_2Co$(**L2^{Me2}**)]) or the program SADABS[37] (**L2^{Ph}**, **S4**, **M7**, and [Co(**L1**)$_2$]). Equivalent reflections were averaged. The structures were solved by direct methods using the program SHELXS[38] and refined with full-matrix least-squares on F^2 using the program SHELXL-97.[39] Hydrogen atoms were generally placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model.

One ^{i}Pr group of compound [Co(**L1**)$_2$] was found to be seriously disordered and was refined with split atoms. One of the two independent CH_2Cl_2 solvate molecules in this structure has very large displacement parameters, showing this group to be disordered. It was not attempted to resolve this disorder.

The crystal lattice of [Cl_2Co(**L2^{Me2}**)] contains 0.5 equiv of MeCN solvate molecules. Each of these molecules is disordered over two equally occupied positions about a 2-fold rotation axis.

CCDC reference numbers: 773297 (**L2^{Me}**), 773293 (**L2^{Me2}**), 773305 (**L2^{Ph}**), 773302 (**L2^{tBu}**), 773295 (**L3^{Me2}**), 773300 (**L3^{Ph}**), 773298 (**L4^{Ph}**), 773303 (**L5^{Me2}**), 773306 (**S4**), 773299 (**M3**), 773307 (**M7**), 773301 ([Co(**L1**)$_2$]), 773294 ([Cl_2Co(**L2^{Me2}**)]), 773296 ([$(NO_3)_2Co$(**L2^{Me2}**)]).

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Supporting Information Available: Crystallographic data of **L2^{Me}**, **L2^{Me2}**, **L2^{Ph}**, **L2^{tBu}**, **L3^{Me2}**, **L3^{Ph}**, **L4^{Ph}**, **L5^{Me2}**, **S4**, **M3**, **M7**, [Co(**L1**)$_2$], [Cl_2Co(**L2^{Me2}**)], and [$(NO_3)_2Co$(**L2^{Me2}**)] in CIF format; synthesis and analytical data of **L6^{Me2}**, $((HO)_2C_6H_3)C(H)(pz^{H,H})_2$, and the model systems **M1**−**M8**; structure plots and selected crystallographic data/structure parameters of **L2^{Me}**, **L2^{Me2}**, **L2^{Ph}**, **L3^{Ph}**, [$(NO_3)_2Co$(**L2^{Me2}**)], **M3**, **S4**, and **M7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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