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Molecular Structures of Carbonyl-Linked Bis(dioxolene) Complexes: Can a Carbonyl Group Act as an Effective Ferromagnetic Coupler?

David A. Shultz,*,§ Scot H. Bodnar,§ R. Krishna Kumar,§ Hyoyoung Lee,§,† and Jeff W. Kampf‡

Departments of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, and University of Michigan, Ann Arbor, Michigan 48109-1055

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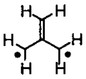
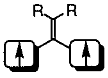
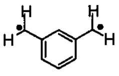
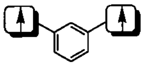
Molecular structures of two bis(Zn^{II}dioxolene) complexes are described: **(Tp^{Cum,Me}Zn)$_2$1-H$_2$** ($C_{106}H_{123.50}B_2N_{12}O_{10}Zn_2$), tetragonal, *P*4/*ncc*, $a = 25.1810(2)$ Å, $b = 25.1810(2)$ Å, $c = 34.7744(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $Z = 8$; **(Tp^{Cum,Me}Zn)$_2$1-H** ($C_{101}H_{120}B_2N_{12}O_6Zn_2$), triclinic, $P\bar{1}$, $a = 13.6624(2)$ Å, $b = 13.80920(10)$ Å, $c = 26.62340(10)$ Å, $\alpha = 96.6910(10)°$, $\beta = 91.8560(10)°$, $\gamma = 109.0190(10)°$, $Z = 2$. One of the complexes, **(Tp^{Cum,Me}Zn)$_2$1-H$_2$**, has two protonated catecholate ligands, while the other complex, **(Tp^{Cum,Me}Zn)$_2$1-H**, has one protonated catecholate and one semiquinone ligand. When reacted with PbO_2, a labile $S = 1$, bis(Zn^{II}-semiquinone) complex is formed in which the two semiquinones are attached to a common carbonyl group.

The major theme in the design of high-spin ($S \geq 1$) organic molecules and ligands is covalent attachment of paramagnetic functional groups to a fragment that promotes ferromagnetic coupling of the spins.[1−3] There are only two readily accessible π-type functional groups that can act as ferromagnetic couplers, vinylidene and *m*-phenylene. These couplers are present in the prototypical biradicals trimethylenemethane (TMM) and *m*-xylylene, respectively. Both theory and experiment agree on the ferromagnetic coupling ability of *m*-phenylene[4−7] and vinylidene.[8−18]


TMM

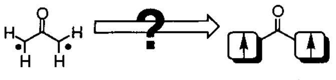

Generalized TMM-type Biradical


***meta*-Xylylene**


Generalized *meta*-Phenylene-type Biradical

On the other hand, oxallyl, formed conceptually by replacing one CH_2 of TMM with an oxygen atom, has not been synthesized. Computational studies on oxallyl have revealed that the singlet−triplet gap is ca. 10-fold less than the corresponding gap in TMM.[16,19−21] To the best of our knowledge, the only open-shell molecule having a carbonyl coupler (C═O) is a matrix-isolated dinitrene, prepared by Lahti's group, that was shown to exhibit a linear Curie plot, a result that is inconclusive evidence of a triplet ground state.[21] Due to the reactivity of nitrenes, further experimental study of this interesting molecule would be difficult, and is therefore unlikely.

The reason for the predicted smaller singlet−triplet gap in oxallyl is that the singly occupied MOs are nondegenerate due to the lower symmetry (C_{2v}) compared to TMM (D_{3h}). This lower symmetry combined with the strength of the C═O bond results in a small singlet−triplet gap.[1] Thus, the electron-withdrawing C═O has been predicted to be a weak exchange coupler.[16,19−21]


Oxallyl
C═O: A Weak Ferromagnetic Coupler (At Best)
Generalized Oxallyl-type Biradical

However, we reason that if C═O couples two radical *anions*, rather than two neutral radicals, stronger ferromagnetic coupling would exist. Our reasoning is based on the greater expected

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* To whom correspondence should be addressed. Voice: (919) 515-6972. E-mail: shultz@chemdept.chem.ncsu.edu. Fax: (919) 515-8920. Web: http://www2.ncsu.edu/ncsu/chemistry/das.html.

§ North Carolina State University.

‡ University of Michigan.

† Current address: Organic Materials Device Team, Telecommunication Basic Research, Electronics and Telecommunications Research Institute (ETRI), 161 Kajong-dong, Yusong-Gu, Taejon, 305-350, Korea.

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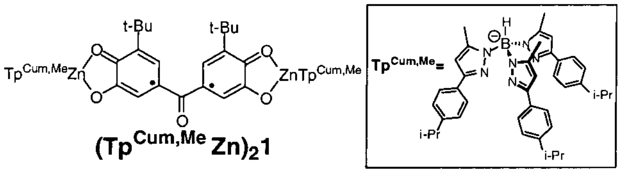
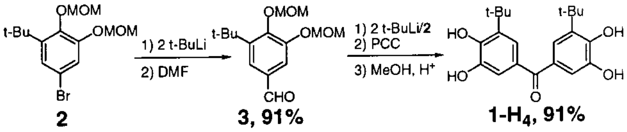
10.1021/ic000956a CCC: $20.00

charge/spin delocalization into the coupler (compared to spin delocalization in oxallyl) for a negatively charged spin carrier that should lead to a larger exchange integral and more effective ferromagnetic coupling.[22] Thus, C=O might prove to be useful for preparing high-spin molecules despite the predictions for oxallyl itself. To explore this important structure−property relationship, we wished to synthesize **($Tp^{Cum,Me}Zn$)$_2$1**.



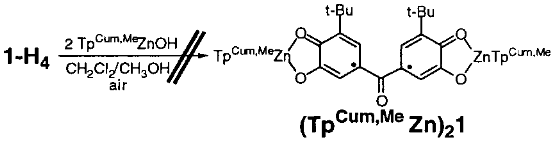
($Tp^{Cum,Me}Zn$)$_2$1

Our synthesis begins with the preparation of bis(catechol) **1-H$_4$** as shown below. Bromide **2**,[23] is converted to the corresponding aldehyde, which is subsequently reacted with lithiated **2** to yield a carbinol. Oxidation of the intermediate carbinol with pyridinium chlorochromate followed by deprotection of the methoxymethyl ethers gives the bis(catechol) in excellent yield.



2 **3, 91%** **1-H$_4$, 91%**

However, the reaction of **1-H$_4$** with 2 equiv of $Tp^{Cum,Me}ZnOH$, following a standard procedure,[24−27] does not yield the desired complex, **($Tp^{Cum,Me}Zn$)$_2$1**. Evidence in support of this conclusion includes (1) the lack of fine structure in the 77 K EPR spectrum, (2) the appearance of OH stretching in the IR spectrum (the bis(semiquinone) complex should lack OH groups), (3) the appearance of a strong IR peak at 1619 cm^{-1} (C−O stretching for a semiquinone is expected at 1420−1480 cm^{-1}),[28] and (4) a room-temperature magnetic moment that is less that 1.7 μ_B.[29]



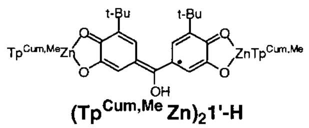
($Tp^{Cum,Me}Zn$)$_2$1

From the IR, EPR, and magnetic moment data, we considered the formation of either one or all of the complexes below. Complex **($Tp^{Cum,Me}Zn$)$_2$1′-H** contains a quinonemethide-type ligand, similar to a ligand we reported recently.[26,27] Complexes **($Tp^{Cum,Me}Zn$)$_2$1-H** and **($Tp^{Cum,Me}Zn$)$_2$1-H$_2$** have known protonated catecholates.[25]

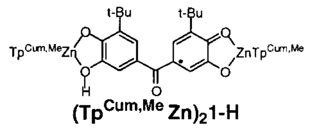
Table 1. Crystal Data and Structure Refinement for **($Tp^{Cum,Me}Zn$)$_2$1-H$_2$** and **($Tp^{Cum,Me}Zn$)$_2$1-H**

empirical formula	$C_{106}H_{123.50}B_2N_{12}O_{10}Zn_2$ (**($Tp^{Cum,Me}Zn$)$_2$1-H$_2$**)	$C_{101}H_{120}B_2N_{12}O_6Zn_2$ (**($Tp^{Cum,Me}Zn$)$_2$1-H**)
a/Å	25.1810(2)	13.6624(2)
b/Å	25.1810(2)	13.80920(10)
c/Å	34.7744(2)	26.62340(10)
α/deg	90	96.6910(10)
β/deg	90	91.8560(10)
γ/deg	90	109.0190(10)
V/Å^3	22049.8(3)	4703.15(8)
Z	8	2
formula weight	1878.03	1750.45
crystal system, space group	tetragonal, $P4/ncc$	triclinic, $P\bar{1}$
T/°C	−115	−115
λ/Å	0.71073	0.71073
δ_{calc}/g cm^{-3}	1.131	1.236
μ/cm^{-1}	4.93	5.70
final R indices [$I > 2\sigma(I)$]	R1 = 0.0693[a]	R1 = 0.0911[c]
	wR2 = 0.1762[b]	wR2 = 0.1651[d]

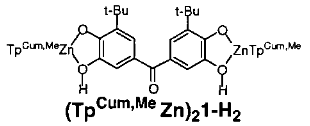
[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR = 1/[\sigma^2(F_o^2) + (0.0844P)^2 + 64.7100P]$, where $P = (F_o^2 + 2F_c^2)/3$. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 15.8468P]$, where $P = (F_o^2 + 2F_c^2)/3$.



($Tp^{Cum,Me}Zn$)$_2$1′-H



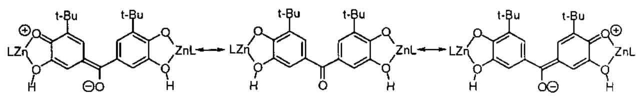
($Tp^{Cum,Me}Zn$)$_2$1-H



($Tp^{Cum,Me}Zn$)$_2$1-H$_2$

Fortunately, the solid that separates from the reaction mixture was crystallized by slow evaporation of a methylene chloride solution giving X-ray quality crystals. Upon inspection of the crystalline mass, two different crystal types were noted: pale green cubes and irregularly shaped blue crystals. Each crystal type was analyzed using X-ray crystallographic techniques, and crystal data are given in Table 1, while ORTEPs are shown in Figures 1 and 2, respectively. Important bond lengths and angles are given in Tables 2 and 3. A diagrammatic comparison of dioxolene bond lengths is given Figure 3.

The bond lengths for each complex are in accord with the structures for **($Tp^{Cum,Me}Zn$)$_2$1-H$_2$** and **($Tp^{Cum,Me}Zn$)$_2$1-H**. The diamagnetic complex, **($Tp^{Cum,Me}Zn$)$_2$1-H$_2$**, possesses crystallographic C_2 symmetry about the carbonyl C=O bond. The proton of each protonated catecholate group is situated on the less acidic oxygen atom, so that the oxygen para to the carbonyl group has a −1 formal charge. The Zn−O bond lengths also agree with this assessment, e.g., $r_{Zn(1)-O(1)} < r_{Zn(1)-O(2)}$. Delocalization of charge into the C=O group is evident from the quinoidal bond length pattern, and the short C(4)−C(11) bond length (1.475 Å) is consistent with the resonance structures shown below.



The bonding scheme is different for the $S = {}^1/_2$ complex, **($Tp^{Cum,Me}Zn$)$_2$1-H**. Here the geometric parameters of the

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(22) The exchange integral is the electron−electron repulsion in the overlap region shared by the magnetic orbitals. Therefore, increased delocalization from the spin carrier into the coupler will increase the exchange integral and selectively stabilize the high-spin state.

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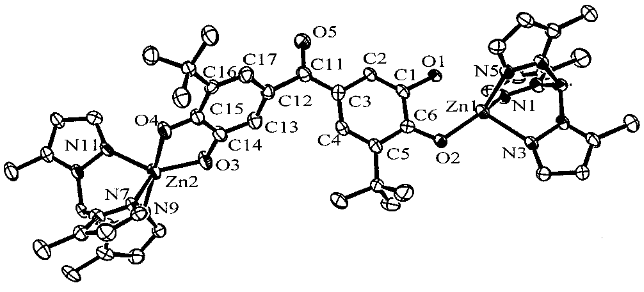


Figure 1. ORTEP of **(Tp^{Cum,Me}Zn)$_2$1-H**. Cumenyl groups have been omitted for clarity.

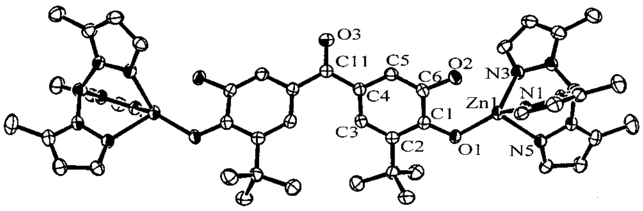


Figure 2. ORTEP of **(Tp^{Cum,Me}Zn)$_2$1-H$_2$**. Cumenyl groups have been omitted for clarity.

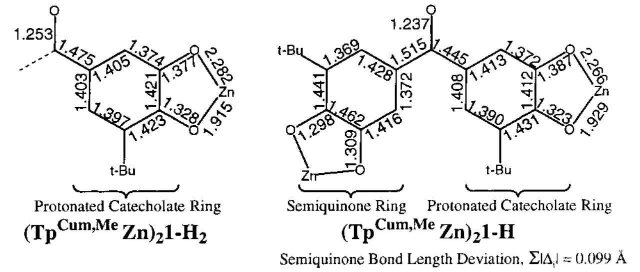


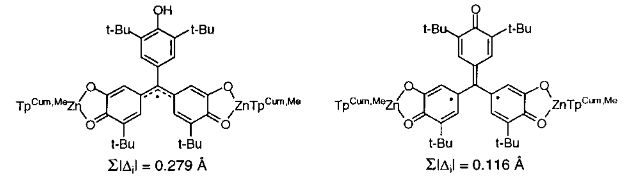
Figure 3. Comparison of important bond lengths for **(Tp^{Cum,Me}Zn)$_2$1-H$_2$** and **(Tp^{Cum,Me}Zn)$_2$1-H**.

Table 2. Important Bond Lengths (Å) and Angles (deg) for **(Tp^{Cum,Me}Zn)$_2$1-H$_2$**[a]

Zn(1)−O(1)	1.915(3)	Zn(1)−N(3)	2.047(3)
Zn(1)−N(1)	2.050(3)	Zn(1)−N(5)	2.134(3)
Zn(1)−O(2)	2.282(3)	O(1)−C(1)	1.328(5)
O(2)−C(6)	1.377(5)	O(3)−C(11)	1.253(7)
C(1)−C(6)	1.421(6)	C(1)−C(2)	1.423(5)
C(2)−C(3)	1.397(6)	C(3)−C(4)	1.403(6)
C(4)−C(5)	1.405(6)	C(4)−C(11)	1.475(5)
C(5)−C(6)	1.374(6)		
O(1)−Zn(1)−N(3)	128.47(13)	O(1)−Zn(1)−N(1)	129.68(12)
N(3)−Zn(1)−N(1)	98.22(13)	O(1)−Zn(1)−N(5)	108.44(12)
N(3)−Zn(1)−N(5)	88.65(13)	N(1)−Zn(1)−N(5)	87.71(13)
O(1)−Zn(1)−O(2)	77.14(11)	N(3)−Zn(1)−O(2)	86.13(12)
N(1)−Zn(1)−O(2)	90.20(12)	N(5)−Zn(1)−O(2)	174.05(12)
C(1)−O(1)−Zn(1)	120.4(2)	C(6)−O(2)−Zn(1)	108.8(2)
O(1)−C(1)−C(6)	119.2(3)	O(1)−C(1)−C(2)	123.0(4)
C(6)−C(1)−C(2)	117.9(3)	C(3)−C(2)−C(1)	118.6(4)
C(3)−C(2)−C(7)	121.4(4)	C(2)−C(3)−C(4)	122.6(4)
C(3)−C(4)−C(5)	118.7(4)	C(3)−C(4)−C(11)	122.5(4)
C(5)−C(4)−C(11)	118.8(4)	C(6)−C(5)−C(4)	119.5(4)
C(5)−C(6)−O(2)	123.2(4)	C(5)−C(6)−C(1)	122.7(4)
O(2)−C(6)−C(1)	114.1(3)	O(3)−C(11)−C(4)	120.0(2)

[a] Bond lengths and angles for cumenyl-methylpyrazole groups are omitted. See Supporting Information for a full list of parameters.

protonated catecholate group are very similar to those of **(Tp^{Cum,Me}Zn)$_2$1-H$_2$**, with the exception of the C(3)−C(11) bond length (1.445 Å), which is significantly shorter than the corresponding bond length of **(Tp^{Cum,Me}Zn)$_2$1-H$_2$**. This suggests moderate delocalization into the C=O group from the semiquinone group. Indeed, the C(12)−C(11) bond length (1.515 Å) is significantly longer than the corresponding bond lengths for the protonated catecholate groups. Moreover, the difference between semiquinone bond lengths of **(Tp^{Cum,Me}Zn)$_2$1-H** and reference semiquinone bond lengths,[24] represented as a structural deviation parameter[30] $\sum|\Delta_i| = 0.099$ Å, is less than either the structural deviation parameter for the quinonemethide-semiquinone ligand, below left, or the bis(semiquinone) ligand, below right.[30] Therefore, semiquinone-carbonyl delocalization in **(Tp^{Cum,Me}Zn)$_2$1-H** appears to be weak.



Both samples were subjected to PbO$_2$ in an EPR tube with the same results. Prior to exposure of the sample to the oxidant, a single EPR signal is observed at 77 K and $g \approx 2$; this is consistent with a single unpaired electron. The paramagnetic complex, **(Tp^{Cum,Me}Zn)$_2$1-H$_2$**, is EPR inactive. Upon addition of the oxidant, fine structure grows in with $|D/hc| = 0.01077$ cm^{-1} and $|E/hc| = 0.0011$ cm^{-1}, from spectral simulation,[29] as shown in Figure 4. This D-value is similar to those of other TMM-type bis(semiquinone)s we have reported.[31,32] In addition, a $\Delta m_S = 2$ transition grows in near half-field. Both of these observations are consistent with the formation of the $S = 1$ bis(semiquinone). Unfortunately, after extended exposure of the sample to PbO$_2$, these signals disappear; this suggests that the $S = 1$ bis(semiquinone), **(Tp^{Cum,Me}Zn)$_2$1**, is unstable.

We conclude, therefore, that despite the −1 charge on a semiquinone, conjugation with a carbonyl group is minimal, and exchange coupling in **(Tp^{Cum,Me}Zn)$_2$1** might also be minimal. Of course, since we have not isolated **(Tp^{Cum,Me}Zn)$_2$1**, we cannot judge exchange coupling with confidence. In addition, the bis(semiquinone) appears to be unstable unlike other similar bis(semiquinone)s.[31]

Despite the present results, we feel that the possibility of preparing a stable oxallyl-type bis(semiquinone) is quite good. Therefore, it remains to be seen whether C=O can act as an effective exchange coupler. It seems likely that a more electron rich semiquinone could stabilize the biradical oxidation state and interact more strongly with a carbonyl group. Efforts along these lines are underway.

Experimental Section

3-*tert*-Butyl-4,5-bis-methoxymethoxy-benzaldehyde (3). A 25 mL Schlenk flask containing bromide **2** (0.72 g, 2.15 mmol) in THF (20 mL) was cooled to −78 °C, and *tert*-butyllithium (1.5 M, 2.8 mL, 4.3 mmol) was added dropwise. The reaction mixture was stirred for 1 h at −78 °C, and DMF (1.7 mL, 21.5 mmol) was added. The mixture was then stirred for 1 h at −78 °C and for 18 h at room temperature. Saturated brine solution was added, and the mixture was extracted three times with ether and was evaporated to dryness. The crude product was purified by radial chromatography (SiO$_2$, 2% ether:petroleum ether) to give **3** (0.552 g, 91%). ^{1}H NMR (CDCl$_3$) δ (ppm): 9.87 (s, 1H), 7.55 (s, 2H), 5.31 (s, 2H), 5.23 (s, 2H), 3.65 (s, 3H), 3.52 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (CDCl$_3$) δ (ppm): 191.3, 151.8, 150.3, 143.9, 131.4, 123.7, 114.5, 99.3, 95.4, 57.8, 56.5, 35.3, 30.2. IR (film from CH$_2$Cl$_2$) ν (cm^{-1}): 1693.1. Anal. Calcd for C$_{15}$H$_{22}$O$_5$: C, 63.81; H, 7.85. Found: C, 63.78; H, 7.84.

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Table 3. Bond Lengths (Å) and Angles (deg) for **$(Tp^{Cum,Me}Zn)_2$1-H**[a]

Zn(1)−O(2)	1.929(4)	Zn(1)−N(1)	2.049(6)
Zn(1)−N(5)	2.068(6)	Zn(1)−N(3)	2.175(5)
Zn(1)−O(1)	2.266(5)	Zn(2)−O(3)	1.977(5)
Zn(2)−N(11)	2.035(6)	Zn(2)−N(7)	2.049(6)
Zn(2)−O(4)	2.149(5)	Zn(2)−N(9)	2.217(6)
O(1)−C(1)	1.387(8)	O(2)−C(6)	1.323(7)
O(3)−C(14)	1.309(8)	O(4)−C(15)	1.298(8)
O(5)−C(11)	1.237(8)	C(1)−C(2)	1.372(9)
C(1)−C(6)	1.412(9)	C(2)−C(3)	1.413(9)
C(3)−C(4)	1.408(9)	C(3)−C(11)	1.445(9)
C(4)−C(5)	1.390(9)	C(5)−C(6)	1.431(9)
C(11)−C(12)	1.515(9)	C(12)−C(13)	1.372(9)
C(12)−C(17)	1.428(9)	C(13)−C(14)	1.416(9)
C(14)−C(15)	1.462(10)	C(15)−C(16)	1.441(9)
C(16)−C(17)	1.369(9)		
O(2)−Zn(1)−N(1)	130.5(2)	O(2)−Zn(1)−N(5)	129.8(2)
N(1)−Zn(1)−N(5)	95.7(2)	O(2)−Zn(1)−N(3)	108.18(19)
N(1)−Zn(1)−N(3)	87.9(2)	N(5)−Zn(1)−N(3)	89.4(2)
O(2)−Zn(1)−O(1)	76.79(17)	N(1)−Zn(1)−O(1)	89.2(2)
N(5)−Zn(1)−O(1)	86.79(19)	N(3)−Zn(1)−O(1)	175.00(19)
O(3)−Zn(2)−N(11)	131.6(2)	O(3)−Zn(2)−N(7)	129.6(2)
N(11)−Zn(2)−N(7)	98.2(2)	O(3)−Zn(2)−O(4)	79.54(18)
N(11)−Zn(2)−O(4)	93.04(19)	N(7)−Zn(2)−O(4)	91.9(2)
O(3)−Zn(2)−N(9)	100.3(2)	N(11)−Zn(2)−N(9)	86.6(2)
N(7)−Zn(2)−N(9)	88.7(2)	O(4)−Zn(2)−N(9)	179.3(2)
C(1)−O(1)−Zn(1)	109.8(4)	C(6)−O(2)−Zn(1)	119.7(4)
C(14)−O(3)−Zn(2)	115.4(4)	C(15)−O(4)−Zn(2)	111.0(4)
C(2)−C(1)−O(1)	123.1(6)	C(2)−C(1)−C(6)	124.3(6)
O(1)−C(1)−C(6)	112.7(6)	C(1)−C(2)−C(3)	119.1(6)
C(4)−C(3)−C(2)	117.3(6)	C(4)−C(3)−C(11)	123.1(6)
C(2)−C(3)−C(11)	119.4(6)	C(5)−C(4)−C(3)	124.1(6)
C(4)−C(5)−C(6)	118.1(6)	C(4)−C(5)−C(7)	120.7(6)
C(6)−C(5)−C(7)	121.2(6)	O(2)−C(6)−C(1)	120.4(6)
O(2)−C(6)−C(5)	122.6(6)	C(1)−C(6)−C(5)	117.1(6)
O(5)−C(11)−C(3)	121.3(6)	O(5)−C(11)−C(12)	116.0(6)
C(3)−C(11)−C(12)	122.7(6)	C(13)−C(12)−C(17)	120.2(6)
C(13)−C(12)−C(11)	124.1(6)	C(17)−C(12)−C(11)	115.5(6)
C(12)−C(13)−C(14)	119.5(7)	O(3)−C(14)−C(13)	122.9(7)
O(3)−C(14)−C(15)	117.8(6)	C(13)−C(14)−C(15)	119.3(6)
O(4)−C(15)−C(16)	123.4(6)	O(4)−C(15)−C(14)	116.0(6)
C(16)−C(15)−C(14)	120.6(6)	C(17)−C(16)−C(15)	116.0(6)
C(16)−C(17)−C(12)	124.2(7)		

[a] Bond lengths and angles for cumenyl-methylpyrazole groups are omitted. See Supporting Information for a full list of parameters.

Di-(3,4-dimethoxymethoxy-5-*tert*-butylphenyl) methanol. A 100 mL Schlenk flask containing bromide **2** (1.45 g, 4.36 mmol) in THF (50 mL) was cooled to −78 °C, and *tert*-butyllithium (1.5 M, 5.8 mL, 8.7 mmol) was slowly added. The reaction mixture was stirred for 2 h at −78 °C. A solution of aldehyde **3** (1.03 g, 3.63 mmol) in THF (15 mL) was added via cannula, and the mixture was stirred for 1 h at −78 °C and for 19 h at room temperature. Saturated brine solution was added, and the mixture was extracted three times with ether and was evaporated to dryness. The crude product was purified by radial chromatography (SiO_2, 5−20% ether containing 5% CH_2Cl_2/petroleum ether) to give the alcohol as a colorless oil (1.85 g, 95%). ^1H NMR ($CDCl_3$) δ (ppm): 7.07 (s, 2H), 7.02 (s, 2H), 5.66 (d, 1H, $J = 2.79$ Hz), 5.18 (s, 4H), 5.13 (s, 4H), 3.63 (s, 6H), 3.47 (s, 4H), 2.59 (d, 1H, $J = 3.27$ Hz), 1.40 (s, 18H). ^{13}C NMR ($CDCl_3$) δ (ppm): 150.0, 145.2, 143.2, 138.6, 118.9, 113.1, 99.0, 95.4, 76.2, 57.5, 56.3, 35.3, 30.5. IR (film from CH_2Cl_2) ν (cm^{-1}): 3458. Anal. Calcd for $C_{29}H_{44}O_9$: C, 64.90; H, 8.26. Found: C, 65.04; H, 8.25.

Di-(3,4-dimethoxymethoxy-5-*tert*-butylphenyl)methanone (1-(MOM)$_4$). A 100 mL Schlenk flask containing CrO_3 (1.729 g, 17.30 mmol) and pyridine (2.80 mL, 34.6 mmol) in distilled CH_2Cl_2 (50 mL) was stirred for 15 min. A solution of the carbinol from the previous reaction was added by cannulation, and the reaction mixture was stirred for 1 h at room temperature. To work up, 1 M NaOH (10 mL) was added, and the organic layer was separated. Saturated brine solution was added, and the organic layer was extracted three times with CH_2Cl_2 and then was evaporated to dryness. The crude product was purified by column chromatography (SiO_2, 20−40% ether/petroleum ether) and recrystallized from ether/petroleum ether to give **1-(MOM)$_4$** as a white solid (1.49 g, 97%). ^1H NMR ($CDCl_3$) δ (ppm): 7.51 (s, 4H), 5.31 (s, 4H), 5.21 (s, 4H), 3.66 (s, 6H), 3.50 (s, 6H), 1.43 (s, 18H). ^{13}C NMR ($CDCl_3$) δ (ppm): 194.6, 149.9, 149.5, 142.8, 132.2, 123.5, 116.2, 99.2, 95.3, 57.7, 56.5, 35.4, 30.4. IR (film from CH_2Cl_2) ν (cm^{-1}): 1650. Anal. Calcd for $C_{29}H_{42}O_9$: C, 65.14; H, 7.91. Found: C, 64.87; H, 7.85.

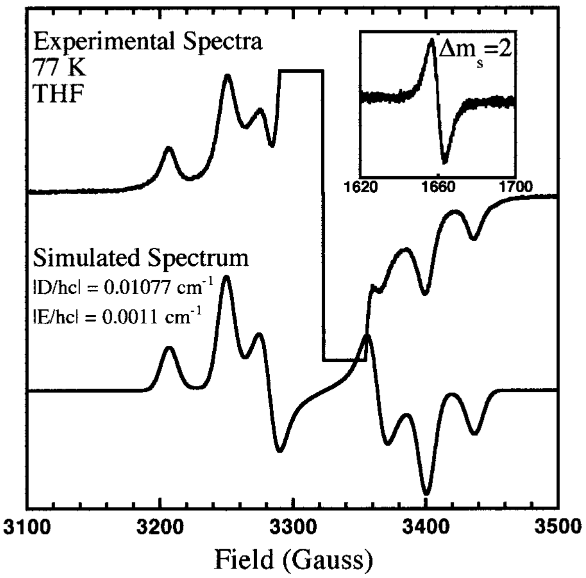

Figure 4. Upper line: 77 K EPR spectrum after oxidation of **$(Tp^{Cum,Me}Zn)_2$1-H** with PbO_2. Inset: $\Delta m_s = 2$ transition. Lower line: spectral simulation with $|D/hc| = 0.01077\ cm^{-1}$ and $|E/hc| = 0.0011\ cm^{-1}$.

Di-(3,4-dihydroxy-5-*tert*-butylphenyl)methanone (1-H$_4$). A 25 mL Schlenk flask containing **1-(MOM)$_4$** (0.2 g, 0.37 mmol) in methanol (10 mL) and 4 drops of 12 M HCl was pump-purged 5 times under nitrogen gas. The reaction mixture was refluxed for 15 h. After removal of the solvent by rotary evaporation, ether and $NaHCO_3$ solutions were added, and the mixture was extracted with ether. The combined organic extracts were dried over $NaSO_4$, filtered, and evaporated. The crude product was washed with CH_2Cl_2 to give **1-H$_4$** as a white solid (0.13 g, 99%). ^1H NMR (CD_3OD) δ (ppm): 7.24 (d, 2H, $J = 1.86$ Hz), 7.16 (d, 2H, $J = 1.68$ Hz), 4.86 (s, 4H), 1.40 (s, 18H). ^{13}C NMR ($CDCl_3$) δ (ppm): 198.4, 150.4, 145.9, 136.3, 129.6, 123.0, 115.2, 35.7, 29.9. IR (film from CH_2Cl_2) ν (cm^{-1}): 3495 (br), 3225 (br), 1603. Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.20; H, 7.35.

Complex Formation. A 25 mL Schlenk flask containing **1-H$_4$** (0.05 g, 0.14 mmol) and **$Tp^{Cum,Me}ZnOH$** (0.19 g, 0.28 mmol) in a mixture of methanol (5 mL) and CH_2Cl_2 (5 mL) was stirred overnight in air. The reaction mixture was concentrated to one-third volume by rotary evaporation, and the green precipitate was collected by filtration. IR (film from CH_2Cl_2) ν (cm^{-1}): 3352, 1619, 1574, 1550.9, 1520, 1424, 1314, 1186.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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