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Effects of cation–anion interactions on the structures and photophysical properties of anionic d^0 tungsten–benzylidyne complexes

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Dedicated to Professor Richard R. Schrock

Abstract

The structures and photophysical properties of anionic tungsten–benzylidyne complexes of the type $[Na(L)][W(\equiv CPh)(OBu^t)_4]$ ($[Na(L)]\mathbf{1}$; L = blank, 15-crown-5, crypt-2,2,2) are strongly dependent on the nature of the $[Na(L)]^+$ ion. The structures of the $\mathbf{1}^-$ ions are qualitatively similar, consisting of square-pyramidal tungsten centers with short W≡C bonds, but differ as a function of cation in the extent of their $Na-OBu^t$ interactions, the geometries of their OBu^t ligands, and their W–O bond distances. The $\mathbf{1}^-$ ions exhibit long-lived luminescence ($\tau > 1$ μs) in fluid solution and the solid state at room temperature. The emission lifetimes and energies are cation dependent even in polar solvents, indicating the presence of $[Na(L)]^+/\mathbf{1}^-$ ion pairs in solution for some L. The emissive state is a spin triplet of either $[\pi(W\equiv CPh)]^1[d_{xy}]^1$ or $[\pi(W\equiv CPh)]^1[\pi^*(W\equiv CPh)]^1$ configuration.

Keywords: Alkylidyne complexes; Luminescence; Ion pairing

1. Introduction

The discovery by Schrock two decades ago of high-oxidation-state metal–alkylidyne complexes was a milestone in organometallic chemistry that opened a number of new and still evolving areas of research [1]. Much of this research has been motivated by Schrock's discovery that certain derivatives of this class of complexes catalyze alkyne-metathesis reactions [1]. The ease with which alkyne metathesis and related triple-bond (M≡M, C≡E) metathesis reactions [2] allow the formation of C≡C and M≡C (M = Mo [3], W) bonds has encouraged the application of this chemistry to the synthesis of organic molecules [4] and conjugated organic [5] and organometallic [6] polymers.

In contrast to the extensively developed thermal chemistry of high-oxidation-state metal–alkylidyne complexes, little is known about their electronic excited states and photophysics [7]. Our interest in this aspect of their chemistry was motivated by a proposal that (pseudo)tetragonal d^0 complexes with multiple metal–ligand (ME) bonds are good candidates for luminescent LMCT chromophores [8], of which derivatives that luminesce in fluid solution are rare [8,9] compared to the ubiquitous MLCT chromophores. The basis for this proposal is that the $\pi(ME)\rightarrow M(d_{xy})$ (denoted $\pi\rightarrow n$) electronic transition of d^0 complexes (which, in many such compounds, should produce the lowest-energy excited state) is qualitatively similar, in terms of symmetry and expected excited-state distortion, to the $M(d_{xy})\rightarrow\pi^*(ME)$ ($n\rightarrow\pi^*$) transition [10] of the well established class of emissive d^2 multiply bonded com-

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plexes. In this context, the reports by Floriani and coworkers on the chemistry of square-pyramidal d^0 tungsten–alkylidyne calix[4]arene complexes of the type $[\{p\text{-Bu}^t\text{-calix}[4]\text{–(O)}_4\}W(CR)]^-$ (R = Ph, $SiMe_3$) attracted our attention [11–17]. Theoretical calculations by these workers on $[W(CMe)(OR)_4]^-$ model ions [14,16] indicate that the HOMO and LUMO are $\pi(W\equiv C)$ and $W(d_{xy})$, respectively. Thus, a study of the photophysical properties of complexes of the $[W(CR)(OR')_4]^-$ type would afford an opportunity to further test whether lowest-lying $\pi \rightarrow n$ excited states are, in general, luminescent.

We report here the syntheses, structures, and photophysical properties of salts of the anionic tungsten–benzylidyne complex $[W(CPh)(OBu^t)_4]^-$ ($\mathbf{1}^-$) with several sodium counterions (Na^+, $[Na(15\text{-crown-}5)]^+$, $[Na(\text{crypt-}2,2,2)]^+$). Complexes of the type $[W(CR)(OR')_4]^-$, with monodentate alkoxide ligands, are potentially advantageous for the purpose of studying excited-state energies and properties compared to calixarene derivatives because the electronic properties of these ligands are more broadly tunable. We have discovered that the $\mathbf{1}^-$ ion is strongly luminescent in both fluid solution and the solid state at room temperature, and that its structure and photophysical properties are significantly dependent on the nature of the counterion.

2. Experimental

2.1. General procedures

All syntheses and manipulations were performed under dinitrogen atmosphere using standard glovebox or standard Schlenk techniques. HPLC-grade solvents, stored under dinitrogen in stainless-steel cylinders, were purified by passing them under dinitrogen pressure through a stainless-steel system consisting of either two 4.5 in. × 24 in. (1 gal) columns of activated A2 alumina (MeCN, Et_2O, CH_2Cl_2, and THF) or one column of activated A2 alumina and one column of activated BASF R3-11 catalyst ($C_6H_5CH_3$, C_5H_{12}) [18]. Deuteriated NMR solvents were sparged with dinitrogen and stirred over CaH_2 (CD_2Cl_2) or Na/K (1:2) alloy (C_6D_6, THF-d_8), from which they were transferred under vacuum. Solvents used for photophysical measurements were purified by stirring for two days over Na/K (1:2) alloy (C_5H_{12}, dimethoxyethane and THF) or CaH_2 (CH_2Cl_2), from which they were transferred in vacuo. The compound $W(CPh)(OBu^t)_3$ [19] was prepared from the reaction between $W_2(OBu^t)_6$ [20] and diphenylacetylene at room temperature (r.t.) in C_5H_{12} solution in the presence of a small amount of 3-hexyne, and isolated using standard procedures. All other reagents were obtained from commercial sources and used as received.

NMR spectra were recorded at ambient temperature. Chemical shifts are referenced to Me_4Si using residual ^1H or natural abundance ^{13}C resonances of the solvent. Electronic-absorption spectra were recorded of samples contained in sealed cuvettes [21]. Emission and emission-excitation spectra were recorded using a Spex Fluorolog II spectrometer equipped with a Xenon lamp and an R406 photomultiplier tube. Emission spectra were corrected for instrument response using standard methods [22]. Emission-excitation spectra were corrected for instrument response using the internal correction hardware and software of the instrument. Emission quantum yields were measured relative to $[Ru(bpy)_3][PF_6]_2$ in water [23] and corrected for solvent refractive index [24]. Emission lifetimes were measured using the 355-nm (third harmonic) line of a Spectra Physics GCR-11 Nd:YAG laser operating at 10 Hz as the excitation source. Samples for lifetime measurements were placed in sealed quartz cuvettes (solution samples) or epr tubes (solid samples). A Hamamatsu R928 photomultiplier tube attached to an ISA 0.22 m monochromator was used to detect emission. Emission decay traces were recorded on a Tektronix 2431L digital oscilloscope, downloaded to a computer, and fit to exponential functions. Plots of $\ln(I_{em})$ versus t were linear over at least three lifetimes for all samples except $[Na(\text{crypt-}2,2,2)]\mathbf{1}$ in the solid state; this sample contained two structural forms of the compound that possess different emission lifetimes.

Elemental analyses were performed either by Micro-lytics (South Deerfield, MA) or by Midwest Microlabs (Indianapolis, IN). Despite multiple attempts the results of the carbon analyses are, in general, in borderline agreement with expectation. The complex $[Na(15\text{-crown-}5)]\mathbf{1}$ was noted to darken over time in the solid state at r.t. in a glovebox, undoubtedly accounting for its particularly poor analysis.

2.2. Synthesis of the complexes

2.2.1. $[Na][W(CPh)(OBu^t)_4]$ ($[Na]\mathbf{1}$)

To a stirred suspension of $NaOBu^t$ (0.10 g, 1.0 mmol) in C_5H_{12} (10 ml) was added $W(CPh)(OBu^t)_3$ (0.52 g, 1.1 mmol) in C_5H_{12} (5 ml). This resulted in the immediate precipitation of a bright yellow solid. The mixture was allowed to stand at −40 °C for 4 h, after which the solid was collected by filtration, washed with C_5H_{12} (approximately 25 ml), and dried under vacuum to give $[Na]\mathbf{1}$ (0.58 g, 95% yield). Yellow crystals of $[Na]\mathbf{1}\text{-}d_5\cdot 1/2C_5H_{12}$ (in which the benzylidyne ligand is deuterium labeled) suitable for X-ray diffraction measurements were obtained by layering a suspension of $NaOBu^t$ in $C_6H_5CH_3$ with a solution of $W(CPh\text{-}d_5)(OBu^t)_3$ in

$C_6H_5CH_3$ and C_5H_{12} (1:1) and allowing the resulting mixture to stand at −40 °C for 1 day.

Anal. Calc. (Found) for $C_{23}H_{41}O_4NaW$: C, 46.95 (47.42); H, 7.02% (6.97). ^1H NMR (300.1 MHz, CD_2Cl_2): δ 7.24 (t, 2H, *m*-Ph), 6.99 (d, 2H, *o*-Ph), 6.78 (t, 1H, *p*-Ph), 1.46 (s, 36H, OBu^t). ^1H NMR (400.1 MHz, THF-d_8): δ 7.09 (t, 2H, *m*-Ph), 6.88 (d, 2H, *o*-Ph), 6.55 (t, 1H, *p*-Ph), 1.38 (s, 36H, OBu^t). $^{13}C\{^1H\}$ NMR (100.6 MHz, THF-d_8): δ 258.7 (W≡C), 149.2 (Ph), 133.8 (Ph), 127.0 (Ph), 123.7 (Ph), 75.79 (O*C*(CH_3)$_3$), 33.61 (OC(*C*H_3)$_3$).

2.2.2. [Na(15-crown-5)][W(CPh)(OBu^t)$_4$] ([Na(15-crown-5)]**1**)

To [Na]**1** (0.58 g, 0.99 mmol) in THF (10 ml) was added 15-crown-5 (0.22 g, 1.0 mmol) in THF (5 ml). The resulting solution was shaken, cooled to −35 °C, layered with Et_2O and C_5H_{12}, and allowed to stand at −35 °C for 2 days. Yellow crystals of [Na(15-crown-5)]**1** (0.65 g, 82% yield) suitable for X-ray diffraction measurements were collected.

Anal. Calc. (Found) for $C_{33}H_{61}O_9NaW$: C, 49.01 (47.90); H, 7.60% (7.42). ^1H NMR (300.1 MHz, CD_2Cl_2): δ 7.17 (t, 2H, *m*-Ph), 6.93 (d, 2H, *o*-Ph), 6.61 (t, 1H, *p*-Ph), 3.71 (s, 20H, 15-crown-5), 1.36 (s, 36H, OBu^t). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 260.2 (W≡C), 148.9 (Ph), 134.2 (Ph), 126.8 (Ph), 122.6 (Ph), 75.48 (O*C*(CH_3)$_3$), 69.52 (15-crown-5), 33.70 (OC(*C*H_3)$_3$).

2.2.3. [Na(crypt-2,2,2)][W(CPh)(OBu^t)$_4$] ([Na(crypt-2,2,2)]**1**)

To [Na]**1** (0.16 g, 0.27 mmol) in THF (5 ml) was added a solution of crypt-2,2,2 (0.10 g, 0.27 mmol) in THF (5 ml). The solution was shaken, layered with Et_2O, and cooled to −80 °C for 2 days, giving yellow crystals of α-[Na(crypt-2,2,2)]**1**·THF (0.23 g, 82% yield). (The α designation refers to the structural type of the $\mathbf{1}^-$ ion.) If the reaction mixture is instead cooled to −35 °C, orange crystals of the THF-free polymorph β-[Na(crypt-2,2,2)]**1** are obtained. Both types of crystals were suitable for X-ray diffraction studies.

Anal. Calc. (Found) for $C_{41}H_{77}N_2NaO_{10}W$: C, 51.04 (50.52); H, 8.04 (8.11); N, 2.90% (2.86). ^1H NMR (300.1 MHz, CD_2Cl_2): δ 7.14 (t, 2H, *m*-Ph), 6.94 (d, 2H, *o*-Ph), 6.58 (t, 1H, *p*-Ph), 3.62 (s, 12H, crypt), 3.58 (t, 12H, crypt), 2.65 (t, 12H, crypt), 1.38 (s, 36H, OBu^t). ^1H NMR (300.1 MHz, C_6D_6): δ 7.59 (d, 2H, *o*-Ph), 7.38 (t, 2H, *m*-Ph), 6.72 (t, 1H, *p*-Ph), 3.22 (s, 12H, crypt), 3.16 (t, 12H, crypt), 2.19 (t, 12H, crypt), 1.96 (s, 36H, OBu^t). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 257.1 (W≡C), 149.7 (Ph), 133.1 (Ph), 126.7 (Ph), 121.8 (Ph), 74.55 (O*C*(CH_3)$_3$), 68.96 (crypt), 68.10 (crypt), 53.25 (crypt), 33.48 (OC(*C*H_3)$_3$).

2.3. Crystal structure determinations

X-ray crystal structures were determined using a Siemens R3m/V (for [Na]**1**-d_5·1/2C_5H_{12}) or a Bruker AXS SMART APEX diffractometer (for [Na(15-crown-5)]**1**, α-[Na(crypt-2,2,2)]**1**·THF, and β-[Na(crypt-2,2,2)]**1**) with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Crystals were attached to fine glass fibers with Fluorolube and placed in a cold N_2 stream for data collection. All computer programs used in the structure solution and refinement are contained in the SHELXTL (v 5.1) program suite [25]. Crystal data and data collection and refinement parameters are set out in Table 1. For [Na(15-crown-5)]**1**, α-[Na(crypt-2,2,2)]**1**·THF, and β-[Na(crypt-2,2,2)]**1**, initial cell constants were calculated using approximately 1000 reflections taken from data frames collected at three values of ϕ (0, 90, 180°). The data were processed using SAINT (v 6.02) and were corrected for X-ray absorption using SADABS (v 2.01). For [Na]**1**-d_5·1/2C_5H_{12} lattice parameters were determined from a least-squares fit of the angular settings of 24 reflections in the range $20^\circ \leq 2\theta \leq 25^\circ$. The intensities of three representative reflections were measured every 197 reflections during the data collection to ascertain that the sample did not decay. An empirical absorption correction, based on the azimuthal (ψ) scans of six reflections, was applied.

Direct methods were employed to determine the positions of heavy atoms. Remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses and refined using full-matrix least-squares methods. Idealized hydrogen-atom positions and thermal parameters were derived from the atoms to which they are bonded (except for those of the interstitial C_5H_{12} molecule of [Na]**1**-d_5·1/2C_5H_{12}, vide infra). The final cycles of refinement for each structure used anisotropic thermal parameters for all non-hydrogen atoms, with the following two exceptions. For β-[Na(crypt-2,2,2)]**1**, attempts to refine the *para* carbon atom (C(5)) of the benzylidyne ligand with anisotropic thermal displacement parameters led to poor refinement, so this atom was refined isotropically. (This problem was observed for data from two different crystals). For α-[Na(crypt-2,2,2)]**1**·THF, all non-hydrogen atoms except those of THF were refined anisotropically. The THF molecule was disordered; assignment of the oxygen atom was based on geometric considerations.

Two details concerning the refinement of the crystal structure of [Na]**1**·1/2C_5H_{12} should be noted. Successive refinements revealed that one *t*-butyl group is rotationally disordered about the C–O bond; two orientations were observed that are 60° out of phase. The methyl carbon atom positions were refined using a shared free variable that relates site occupancies of the two conformations to the observed electron density (with total

Table 1
Crystallographic data for [Na(L)][W(CPh)(OBu^t)$_4$]·([Na(L)]**1**) complexes

Parameter	[Na]**1**-d$_5$·1/2C$_5$H$_{12}$	[Na(15-crown-5)]**1**	α-[Na(crypt-2,2,2)]**1**·THF	β-[Na(crypt-2,2,2)]**1**
Empirical formula	$C_{25.5}H_{42}D_5NaO_4W$	$C_{33}H_{61}NaO_9W$	$C_{45}H_{85}N_2NaO_{11}W$	$C_{41}H_{77}N_2NaO_{10}W$
Formula weight	629.47	808.66	1036.99	964.89
T (K)	213	173	100	100
Crystal system	triclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)	*Pbca* (No. 61)	*Pcca* (No. 54)
Unit cell dimensions				
a (Å)	9.931(2)	10.818(3)	21.395(9)	19.680(8)
b (Å)	11.784(2)	15.553(4)	19.143(8)	19.396(7)
c (Å)	13.848(3)	11.930(3)	24.571(11)	23.974(9)
α (°)	66.70(2)	90	90	90
β (°)	78.59(2)	112.870(4)	90	90
γ (°)	78.87(2)	90	90	90
V (Å^3)	1447.1(5)	1849.4(9)	10063(8)	9151(6)
Z	2	2	8	8
Crystal size (mm)	0.24 × 0.26 × 0.34	0.30 × 0.30 × 0.25	0.20 × 0.12 × 0.10	0.15 × 0.15 × 0.15
ρ_{calc} (g cm^{-3})	1.433	1.452	1.369	1.401
μ (cm^{-1})	40.31	31.82	23.60	25.88
$F(000)$	634	832	4336	4015
θ Range (°)	2.11–26.02	2.04–25.04	1.65–28.28	1.70–25.07
Reflections collected	5973	9399	59 878	44 109
Independent reflections (R_{int})	5683 (0.0507)	5308 (0.0234)	12 108 (0.0317)	8106 (0.0580)
Index ranges	$-12 \leq h \leq 12$	$-11 \leq h \leq 12$	$-27 \leq h \leq 27$	$-21 \leq h \leq 23$
	$0 \leq k \leq 14$	$-15 \leq k \leq 18$	$-15 \leq k \leq 25$	$-23 \leq k \leq 22$
	$-15 \leq l \leq 17$	$-13 \leq l \leq 14$	$-29 \leq l \leq 32$	$-28 \leq l \leq 23$
R_1 [$I > 2\sigma(I)$]	0.0281	0.0198	0.0293	0.0543
wR_2 [$I > 2\sigma(I)$]	0.0671	0.0506	0.0761	0.1417
R_1 (all data)	0.0366	0.0200	0.0393	0.0652
wR_2 (all data)	0.0705	0.0507	0.0790	0.1463
Data/restraints/parameters	5683/0/324	5308/1/397	12 108/0/516	8106/0/492
Max/min transmission	1.00/0.712	1.00/0.776	1.00/0.819	1.00/0.599
Goodness-of-fit	1.011	1.038	0.984	1.165
Largest difference peak/hole (e Å^{-3})	1.419/−0.814	1.088/−0.598	2.167/−0.778	2.937/−2.017

occupancy constrained to unity); site-occupancy factors of 0.638 and 0.362 were found for the two orientations. In addition, the interstitial pentane molecule is disordered, residing on a $\bar{1}$ site.

3. Results and discussion

3.1. Synthesis and characterization of [Na(L)][W(CPh)(OBu^t)$_4$] complexes

The complex [Na][W(CPh)(OBu^t)$_4$] ([Na]**1**) can be prepared in >90% yield from the reaction between equimolar amounts of W(CPh)(OBu^t)$_3$ and NaOBu^t at 25 °C in pentane, from which it precipitates as a yellow solid. The compound is air sensitive in the solid state and in solution. This salt is slightly soluble in dichloromethane and more so in acetonitrile, tetrahydrofuran and 1,2-dimethoxyethane, but shows evidence of slow decomposition in solution (vide infra). Compound [Na]**1** was characterized by elemental analysis, ^{1}H and ^{13}C NMR spectroscopy, and X-ray crystallography (vide infra).

Derivatives of [Na]**1** in which the sodium ion is coordinated by 15-crown-5 or crypt-2,2,2 were prepared in >80% yield by treatment of [Na]**1** with one equivalent of these ligands in THF. The reaction between [Na]**1** and 15-crown-5 at −35 °C provides crystals of the salt [Na(15-crown-5)]**1**. The reaction between [Na]**1** and crypt-2,2,2 provides the salt [Na(crypt-2,2,2)]**1**. At −35 °C the crystalline product is predominantly a morphology that lacks interstitial solvent, while at −80 °C the main crystalline form is [Na(crypt-2,2,2)]**1**·THF; the structures of the **1**$^-$ ions in these salts differ significantly (vide infra). In addition to X-ray crystallography, these salts were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The [Na(L)]**1** salts are generally more soluble in polar organic solvents than is [Na]**1**; [Na(crypt-2,2,2)]**1** is even slightly soluble in benzene and toluene.

The ^{1}H and ^{13}C NMR spectra of [Na]**1**, [Na(15-crown-5)]**1**, and [Na(crypt-2,2,2)]**1** are consistent with the formulation of the **1**$^-$ ions, exhibiting resonances attributable to the benzylidyne ligand and 4 equiv. tert-butoxide ligands. Principally diagnostic for the presence of the benzylidyne ligand is the characteristic ^{13}C NMR resonance of the triply bonded carbon at approximately δ 260. This and the other resonances are shifted downfield from those of the starting material $W(CPh)(OBu^t)_3$. In CD_2Cl_2 solution, the resonances of [Na]**1** are shifted from those of [Na(15-crown-5)]**1** and [Na(crypt-2,2,2)]**1**, suggesting that the former is (more strongly) ion paired in this solvent.

The NMR spectra of freshly prepared solutions of [Na(L)]**1** in CD_2Cl_2 and THF-d_8 also show weak resonances attributable to $W(CPh)(OBu^t)_3$, which slowly increase in intensity over time. Since this starting material is easily removed from [Na(L)]**1** during purification of the product (by washing with pentane), the presence of these signals is attributed to decomposition of $\mathbf{1}^-$ in these solvents. In contrast, the ^{1}H-NMR spectrum of [Na(crypt-2,2,2)]**1** in C_6D_6 does not exhibit resonances due to $W(CPh)(OBu^t)_3$. It is not certain whether [Na(L)]**1** decomposes to form $W(CPh)(OBu^t)_3$ via dissociation of t-butoxide or by the reaction between $\mathbf{1}^-$ and the solvent.

The [Na(L)]**1** compounds are members of the general class of $[W(CR)X_4]^-$ ions, of which the prior examples are $[W(CBu^t)Cl_4]^-$ [26] and the calixarene derivatives $[\{p\text{-Bu}^t\text{-calix[4]–(O)}_4\}W(CR)]^-$ noted above [11–17]. The $\mathbf{1}^-$ ion is also the conjugate base of the alkylidene complex $W(CHPh)(OBu^t)_4$, of which related $W(CHR)(OR')_4$ derivatives have been prepared from the reaction between $W(CR)(OR')_3$ and HOR′ [27]. It is probable that $\mathbf{1}^-$ could also be prepared by deprotonation of the conjugate-acid benzylidene complex, but this has not been investigated given the simplicity and high yield of the present synthetic procedure.

3.2. Crystal structures of $[Na(L)][W(CPh)(OBu^t)_4]$ complexes

The crystal structures of [Na]**1**·1/2C_5H_{12}, [Na(15-crown-5)]**1**, α-[Na(crypt-2,2,2)]**1**·THF, and β-[Na(crypt-2,2,2)]**1** were determined through single-crystal X-ray diffraction studies. The structures of these complexes are shown in Figs. 1–4 and selected bond distances and bond angles are set out in Table 2.

The structures of the $\mathbf{1}^-$ ions of the [Na(L)]**1** complexes are qualitatively similar in several respects. The geometry about the tungsten center is roughly square-pyramidal, with an apical benzylidyne ligand and equatorial alkoxide ligands. As expected for metal–alkylidyne complexes, the W≡C bonds are short (1.755(4)–1.780(4) Å), similar to those for $W(CPh)(OBu^t)_3$ ($d(W{\equiv}C) = 1.758(5)$ Å) [28] and $[\{p\text{-Bu}^t\text{-calix[4]–(O)}_4\}W(CPh)]^-$ ($d(W{\equiv}C) = 1.728(7)$ Å) [14], and the W≡C–C linkages are approximately linear ($\angle WCC \geq 175°$). As is generally observed for the equatorial ligands of square-pyramidal complexes with multiple metal–ligand bonds [29], the WO_4 fragment is pyramidal ($\angle C{\equiv}W{-}O = 99–110°$). The W–O bond distances (1.90–2.04 Å) are similar to those found for $[\{p\text{-Bu}^t\text{-calix[4]–(O)}_4\}W(CPh)]^-$ (1.96–2.00 Å) [14], although there are some significant differences among W–O bond lengths within individual compounds that result from specific features of the structures (vide infra). In general, the W–O bond distances are longer than those for $W(CPh)(OBu^t)_3$ (1.86–1.87 Å) [28], which presumably reflects the stronger trans influence of these ligands in $\mathbf{1}^-$ than in the trigonal WO_3 geometry of $W(CPh)(OBu^t)_3$.

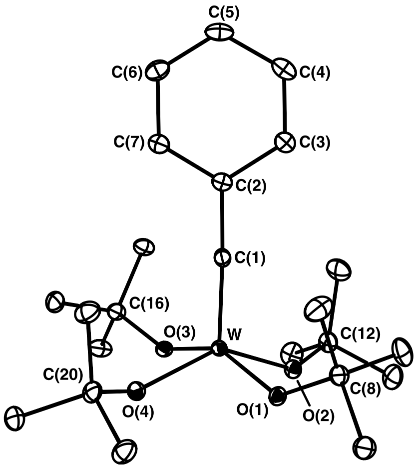


Fig. 1. ORTEP drawing (30% probability ellipsoids) of the structure of the $[W(CPh)(OBu^t)_4]^-$ ion of α-[Na(crypt-2,2,2)][W(CPh)$(OBu^t)_4$]·THF. Hydrogen atoms are omitted for clarity.

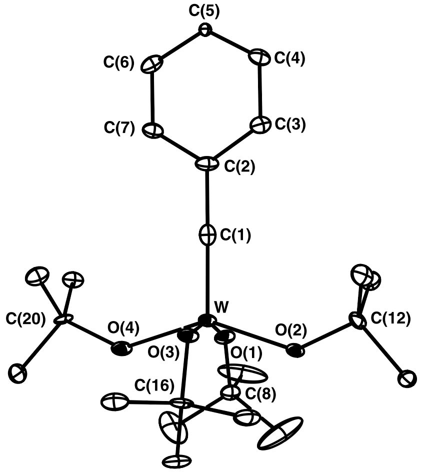


Fig. 2. ORTEP drawing (30% probability ellipsoids) of the structure of the $[W(CPh)(OBu^t)_4]^-$ ion of β-[Na(crypt-2,2,2)][W(CPh)$(OBu^t)_4$]. Hydrogen atoms are omitted for clarity.

Several structural features of the $\mathbf{1}^-$ ions are sensitive functions of the nature of the counter ion and crystal morphology. The structures of these ions in α-[Na(crypt-2,2,2)]**1**·THF and β-[Na(crypt-2,2,2)]**1** are considered first because they lack the close anion–cation contacts found for [Na]**1** and [Na(15-crown-5)]**1** (vide infra). In α-[Na(crypt-2,2,2)]**1**·THF (Fig. 1) the t-butyl groups of $\mathbf{1}^-$ lie on the same side of the approximate O_4 plane as the alkylidyne ligand. This orientation of alkoxide

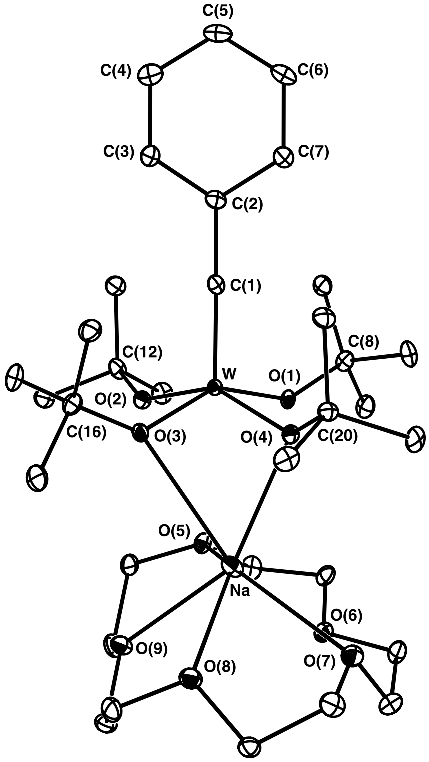


Fig. 3. ORTEP drawing (30% probability ellipsoids) of the structure of [Na(15-crown-5)][W(CPh)(OBu^{t})$_4$]. Hydrogen atoms are omitted for clarity.

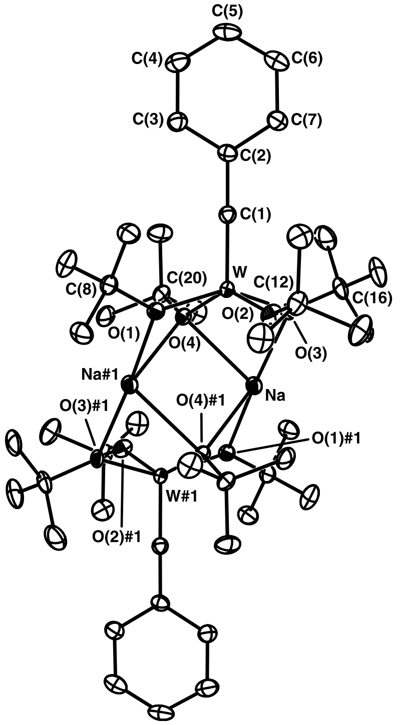


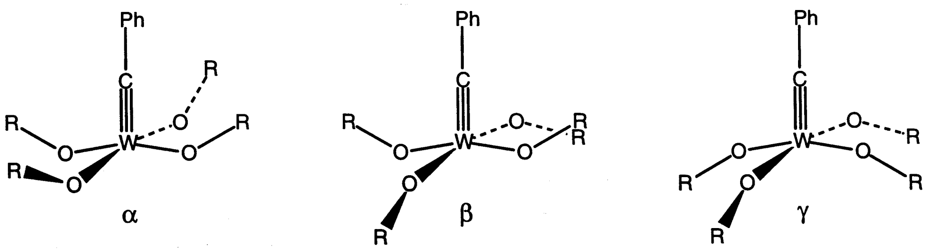
Fig. 4. ORTEP drawing (20% probability ellipsoids) of the structure of a dimer of [Na][W(CPh-d$_5$)(OBu^{t})$_4$]·1/2C$_5$H$_{12}$. Hydrogen atoms and the interstitial pentane are omitted for clarity.

Table 2
Selected bond distances and bond and torsion angles for [Na(L)][W(CPh)(OBu^{t})$_4$] ([Na(L)]**1**) complexes

	[Na]**1**	[Na(15-crown-5)]**1**	α-[Na(crypt-2,2,2)]**1**	β-[Na(crypt-2,2,2)]**1**
Bond distances (Å)				
W–C(1)	1.755(4)	1.780(4)	1.772(3)	1.756(8)
W–O(1)	1.985(3)	1.950(3)	1.971(2)	1.980(5)
W–O(2)	1.899(3)	1.944(2)	1.9533(19)	1.961(5)
W–O(3)	1.985(3)	1.994(3)	1.9652(19)	1.979(5)
W–O(4)	2.037(3)	2.019(2)	1.952(2)	1.945(5)
Na–O(1)	2.313(3) [a]			
Na–O(2)				
Na–O(3)	2.272(3)	2.746(3)		
Na–O(4)	2.387(3) [a], 2.505(3)	2.426(3)		
Bond angles (°)				
W–C(1)–C(2)	177.5(4)	175.3(3)	177.0(2)	178.5(6)
C(1)–W–O(1)	104.68(17)	102.67(15)	104.27(10)	99.9(2)
C(1)–W–O(2)	106.67(18)	104.10(15)	108.85(11)	108.0(2)
C(1)–W–O(3)	105.50(17)	105.49(16)	102.75(10)	99.1(2)
C(1)–W–O(4)	110.05(17)	105.16(14)	108.67(10)	107.3(2)
W–O(1)–C(8)	139.8(3)	141.0(2)	135.74(17)	131.7(4)
W–O(2)–C(12)	150.0(3)	143.3(2)	142.32(18)	137.2(4)
W–O(3)–C(16)	138.3(3)	136.2(3)	138.88(17)	126.6(4)
W–O(4)–C(20)	137.9(3)	136.6(2)	142.25(18)	137.6(4)
Torsion angles (°)				
C(1)–W–O(1)–C(8)	−6.3(5)	16.9(4)	−24.8(3)	−179.3(6)
C(1)–W–O(2)–C(12)	21.3(7)	40.6(6)	−34.0(3)	−2.0(7)
C(1)–W–O(3)–C(16)	25.8(5)	26.3(4)	−26.3(3)	−179.2(5)
C(1)–W–O(4)–C(20)	11.6(4)	22.4(4)	−40.0(3)	1.0(7)

[a] Distance to Na(#1).

ligands, denoted structure type α (see in-text figure) is similar to that seen for W(CPh)(OBu^t)$_3$ [28] but inverted from that observed for [{p-Bu^t-calix[4]–(O)$_4$}W(CR)]$^-$ [14], for which the R groups are constrained to lie opposite the benzylidyne ligand relative to the O$_4$ plane. This latter arrangement of alkoxide R groups is denoted structure type γ (see in-text figure). The benzylidyne phenyl group approximately bisects the *cis* W(OBu^t)$_2$ linkages. The W(OBu^t)$_4$ fragment is slightly puckered, with the two *trans* OBu^t ligands that are distorted downward (O(2) and O(4): ∠C≡W–O = 108.85(11), 108.67(10)°) exhibiting larger internal bond angles (∠W–O–C = 142.32(18), 142.35(18)°) than those that are higher (O(1) and O(3): ∠C≡W–O = 104.27(10), 102.75(10)°; ∠W–O–C = 135.74(17), 138.88(17)°). None of the t-butyl groups are eclipsed with the W≡C bond, exhibiting C≡W–O–C torsion angles of 25–40°. These differences in bond and torsion angles are reflected in the W–O bond distances, which fall into two statistically distinguishable ($\sigma \geq 2.58$) sets: the W–O(1) and W–O(3) bonds (1.971(2), 1.9652(19) Å) are longer than the W–O(2) and W–O(4) bonds (1.9533(19), 1.952(2) Å).



The structure of β-[Na(crypt-2,2,2)]**1** (Fig. 2) differs from that of α-[Na(crypt-2,2,2)]**1** principally in that the t-butyl groups are oriented alternately above (*Z*: O(2) and O(4)) and below (*E*: O(1) and O(3)) the O$_4$ plane, relative to the benzylidyne ligand, instead of all lying above the plane. This orientation of alkoxide ligands is denoted as structure type β (see in-text figure). As observed for α-[Na(crypt-2,2,2)]**1** there is puckering of the WO$_4$ unit, with similar trends in bond distances and angles. Specifically, the *Z* t-butoxy ligands have larger C≡W–O angles (108.0(2), 107.3(2)°) than do the *E* ligands (99.9(2), 99.1(2)°) as well as larger W–O–C angles (*Z*: 137.2(4), 137.6(4)°; *E*: 131.7(4), 126.6(4)°) and shorter W–O bonds (*Z*: 1.961(5), 1.945(5) Å; *E*: 1.980(5), 1.979(5) Å), although the comparatively low quality of the crystal structure reduces the confidence level of this latter observation. The benzylidyne phenyl group is oriented over the *E* t-butoxy ligands; this orientation is similar to that found for [{p-Bu^t-calix[4]–(O)$_4$}W(CPh)]$^-$ [14] but rotated approximately 45° from α-[Na(crypt-2,2,2)]**1**.

The structures of [Na(15-crown-5)]**1**, shown in Fig. 3, and [Na]**1**, shown in Fig. 4, exhibit strong interactions between the Na$^+$ ion and oxygen atoms of **1**$^-$. The **1**$^-$ ions of [Na]**1** and [Na(15-crown-5)]**1** are of structural type α, although, as for α-[Na(crypt-2,2,2)]**1**, the t-butyl groups are not rigorously eclipsed with the W≡C bond (C≡W–O–C torsion angles = 6–41°). In both [Na(15-crown-5)]**1** and [Na]**1** the Na$^+$ ions coordinate to the oxygen atoms on the O$_4$ face opposite the t-butyl groups: for [Na(15-crown-5)]**1**, a single Na$^+$ ion coordinates to two oxygen atoms (O(3) and O(4)), while for [Na]**1**, which crystallizes as a dimer with bridging sodium ions, each Na$^+$ ion is four coordinate, bonding to O(3) and O(4) of one **1**$^-$ ion and to O(1) and O(4) of the other **1**$^-$ ion. Neither **1**$^-$ ion exhibits puckering of the WO$_4$ unit to the same extent as do the α- and β-[Na(crypt-2,2,2)]**1** structures (although O(4) of [Na]**1** has an unusually large C≡W–O bond angle, 110.05(17)°, due to the fact that it is the only t-butoxide ligand that is coordinated to two Na$^+$ ions).

In general, the length of a given W–O bond in [Na(15-crown-5)]**1** and [Na]**1** depends on the strengths of its Na–O interactions and those of the t-butoxide ligand *trans* to it. Taking the average W–O bond distance of the α- and β-[Na(crypt-2,2,2)]**1** complexes (1.963 Å) as normal for the **1**$^-$ ion, the W–O bonds of t-butoxide ligands with coordinated Na$^+$ ions are 0.022–0.074 Å longer than normal. For both complexes, the W–O bonds that lack coordinated Na$^+$ ions are trans to the elongated W–O bonds; these bonds are 0.013–0.064 Å shorter than normal. The structure of [Na]**1** provides the extreme example of this phenomenon: the W–O(4) bond, which is coordinated by two Na$^+$ ions, exhibits the longest distance (2.037(3) Å) among the four [Na(L)]**1** structures, while the W–O(2) bond that is *trans* to it is the shortest (1.899(3) Å).

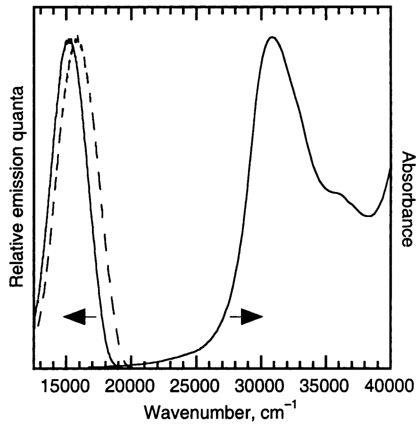


Fig. 5. Electronic-absorption and -emission spectra of [Na(15-crown-5)][W(CPh)(OBu^t)$_4$] at room temperature: (—) THF solution; (---) microcrystalline sample.

3.3. Photophysical properties of [Na(L)][W(CPh)(OBu^t)$_4$] complexes

The complexes [Na]**1**, [Na(15-crown-5)]**1**, and [Na(crypt-2,2,2)]**1** are luminescent in fluid solution and the solid state at room temperature. These complexes constitute one of the few classes of d^0 transition-metal complexes that luminesce in fluid solution [9]. The electronic-absorption and -emission spectra of [Na(15-crown-5)]**1**, which are representative of those of the other [Na(L)]**1** complexes, are shown in Fig. 5 and photophysical data for the [Na(L)]**1** complexes are set out in Table 3 [30].

The electronic-absorption spectra of [Na(L)]**1** complexes are dominated by an intense band in the near-UV that maximizes at 323 nm (30 960 cm^{-1}) for [Na(15-crown-5)]**1** (Fig. 5) and [Na]**1** and at 332 nm (30 120 cm^{-1}) for [Na(crypt-2,2,2)]**1** in THF solution. To the red of this band the absorption slowly tails off without revealing additional distinct bands. Assignments for these absorption features can be contemplated on the basis of the molecular-orbital diagrams shown in Fig. 6.

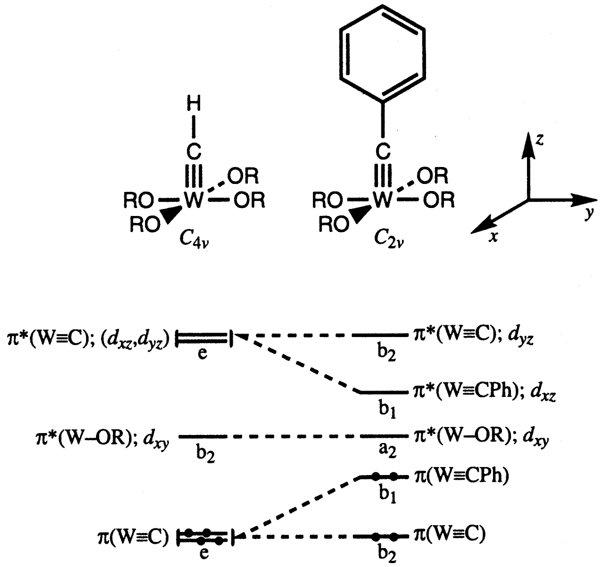


Fig. 6. Molecular-orbital diagrams for [W(CR)(OR′)$_4$]$^-$ (R = H, Ph) ions.

Theoretical calculations on γ-[W(CMe)(OR)$_4$]$^-$ [14,16] and simple symmetry considerations indicate that the HOMO of a complex with strict C_{4v} symmetry is the degenerate π(W≡C) level and that the LUMO is d$_{xy}$; the degenerate π*(W≡C) orbital, of d$_{xz}$, d$_{yz}$ parentage, should lie next highest in energy. The d$_{xy}$ orbital is nonbonding (δ symmetry) with respect to the alkylidyne ligand and π*(W–OR) in character for structure types α, β, and γ, with the W–O π-overlap being a function ($|\cos\theta|$) of the C≡W–O–R torsion angles. Replacement of a cylindrically symmetric alkylidyne R group with phenyl, as for **1**$^-$, should significantly split the π(W≡C) and π*(W≡C) orbitals due to π conjugation between the W≡C and C_6H_5 moieties. In view of these considerations, the strong absorption band in the spectra of the **1**$^-$ ions is undoubtedly attributable to the dipole- and spin-allowed ^{1}[π(W≡CPh) → π*(W≡CPh)] transition. The absorption tail to lower energy of this band may arise from ^{3}[π(W≡CPh) → π*(W≡CPh)] and/or π(W≡

Table 3
Photophysical data for [Na(L)][W(CPh)(OBu^t)$_4$] ([Na(L)]**1**) complexes at room temperature

Solvent	[Na]**1** $\tilde{\nu}_{max}$ (cm^{-1})	τ (μs)	$\phi \times 10^4$	[Na(15-crown-5)]**1** $\tilde{\nu}_{max}$ (cm^{-1})	τ (μs)	$\phi \times 10^4$	[Na(crypt-2,2,2)]**1** $\tilde{\nu}_{max}$ (cm^{-1})	τ (μs)	$\phi \times 10^4$
Solid	16 350	6.8		15 850	10.2		14 000 [a]; 15 625 [b]	~ 0.30 [c]	
Acetonitrile	~ 14 700	1.6		14 900	2.1		[d]	[d]	
Dichloromethane	14 900	3.3		15 000	4.6				
Tetrahydrofuran	14 850	3.0	2.1	15 200	3.7	1.4	14 800	2.8	0.7
1,2-Dimethoxyethane	15 700	7.7		15 200	4.3		14 800	4.6	
Toluene	[e]	[e]		[e]	[e]		14 400	4.0	

[a] Microcrystals grown from THF/ether at −80 °C, which provided mostly α-[Na(crypt-2,2,2)]**1**; some β form is present.
[b] Microcrystals grown from THF/ether at −35 °C, which provided mostly β-[Na(crypt-2,2,2)]**1**; some α form is present.
[c] Excited-state decay is biexponential.
[d] Emission is too weak to measure.
[e] Compound is insoluble in this solvent.

CPh) → d_{xy} transitions. The relative energies of these transitions will depend on the geometry of the alkoxide ligands, and should be tunable by changing the alkylidyne and alkoxide R groups. Definitive assignments will require polarized single-crystal spectroscopic measurements; the initial experiments of this type have not yet resolved this question [31].

Photoexcitation of the [Na(L)]**1** complexes in fluid solution and the solid state produces easily visible orange–red luminescence. The blue tail of the emission band overlaps the end of the red tail of the absorption spectrum (Fig. 5), suggesting that the absorption band that produces the emissive state is very weak. Consistent with this, the photophysical data indicate that the emission is a spin-forbidden process. Specifically, the emission lifetimes of the [Na(L)]**1** complexes in both the solid state and solution exceed 1 μs (with the exception of [Na(crypt-2,2,2)]**1** in the solid state), and the emission quantum yields in tetrahydrofuran solution are on the order of 10^{-4}. From these data, the radiative-decay rate constants are in the range $k_r = 25–70\ s^{-1}$ and the nonradiative decay rate constants are $k_{nr} = 2.7–3.6 \times 10^5\ s^{-1}$. Because of the uncertainty regarding the transition responsible for the absorption tail, it is not yet established whether the emission originates from a triplet $[\pi(W{\equiv}CPh)]^1[d_{xy}]^1$ or $[\pi(W{\equiv}CPh)]^1[\pi^*(W{\equiv}CPh)]^1$ state. Preliminary measurements of emission spectra at low temperature reveal complicated vibronic structure, with particularly intense progressions with approximately 1200 cm^{-1} spacings being evident. Although definitive assignment of these modes is difficult due to the complexity of the W≡CPh oscillator [32], the high frequencies are consistent with modes that have significant contributions from phenyl coordinates. Vibronic activity of such modes would be expected for electronic transitions involving either excited state.

The emission properties of the $\mathbf{1}^-$ complexes are a function of the nature of the $[Na(L)]^+$ ion. The emission of [Na(L)]**1** in the solid state shows modest variations in band maximum with cation, with a range of 14 000–16 350 cm^{-1} (612–712 nm), and, qualitatively, in intensity, with the emission of [Na]**1** and [Na(15-crown-5)]**1** appearing considerably stronger to the eye than that of [Na(crypt-2,2,2)]. This latter observation is consistent with the trend in emission lifetimes in the solid state (τ [Na]**1** = 6.8 μs, τ [Na(15-crown-5)]**1** = 10.2 μs, τ [Na(crypt-2,2,2)]**1** ≅ 0.3 μs). The fact that the emission properties of [Na]**1** and [Na(15-crown-5)]**1** also differ from those of [Na(crypt-2,2,2)]**1** in solution is strong evidence that the former two complexes maintain some cation–anion interactions in solution. It is also noteworthy that the emission band maxima of α- and β-[Na(crypt-2,2,2)]**1** differ by > 1500 cm^{-1} in the solid state [33]. A plausible case can be made that the blue shift of the emission band of β-[Na(crypt-2,2,2)]**1** relative to that of α-[Na(crypt-2,2,2)]**1** supports assignment of the emission to the triplet $[\pi(W{\equiv}CPh)]^1[d_{xy}]^1$ state, on the basis that the d_{xy} orbital should be higher in energy for the β form than the α form as a result of the signficantly larger C≡W–O–C torsion angles of the latter.

4. Conclusion

Anionic square-pyramidal tungsten–benzylidyne complexes of the type $[Na(L)][W(CPh)(OBu^t)_4]$ constitute rare examples of d^0 complexes that luminesce in fluid solution. The structures and photophysical properties of the $[W({\equiv}CPh)(OBu^t)_4]^-$ ions in these complexes are strongly dependent on the nature of the $[Na(L)]^+$ counterion. The long emission lifetimes (≥ 1 μs) of the $\mathbf{1}^-$ ions open the way for studying the bimolecular photochemistry of high-oxidation-state metal–alkylidyne complexes, which has not previously been explored. Although the present data do not allow the two plausible candidates for the emissive state, $[\pi(W{\equiv}CPh)]^1[d_{xy}]^1$ and $[\pi(W{\equiv}CPh)]^1[\pi^*(W{\equiv}CPh)]^1$, to be distinguished, both should be amenable to tuning through counterion and alkylidyne and alkoxide R group variation. Indeed, preliminary investigations of the related ions $[W(CBu^t)(OBu^t)_4]^-$ and $[\{p\text{-}Bu^t\text{-}calix[4]\text{–}(O)_4\}W({\equiv}CR)]^-$ indicate that they are strongly luminescent as well.

5. Supplementary material

CIF format crystallographic files for $[Na][W(CPh\text{-}d_5)(OBu^t)_4]\cdot 1/2C_5H_{12}$, $[Na(15\text{-}crown\text{-}5)][W(CPh)(OBu^t)_4]$, $\alpha\text{-}[Na(crypt\text{-}2,2,2)][W(CPh)(OBu^t)_4]\cdot THF$, and $\beta\text{-}[Na(crypt\text{-}2,2,2)][W(CPh)(OBu^t)_4]$ have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 187044–187047. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[30] It must be noted that the interpretation of the photophysical data for solution samples is complicated by the fact that the **1**$^-$ ion decomposes in polar solvents to give W(CPh)(OBu^t)$_3$ as the main identifiable product, as described in Section 3.1. Consistent with the NMR spectroscopic measurements, monitoring of solution samples of [Na(L)]**1** by electronic-absorption spectroscopy before and after photophysical measurements indicated that features attributable to **1**$^-$ decreased in intensity by 1–10%, depending on the sample concentration and the duration of the experiment. However, two lines of evidence argue against the possibility that the photophysical data in solution are strongly perturbed by the decomposition products. First, the decomposition product W(CPh)(OBu^t)$_3$ does not luminesce in solution or the solid state at temperatures above 100 K [T.P. Pollagi, Ph.D. Thesis, University of Pittsburgh (1985)]; thus, it can be excluded as the source of the emission. Moreover, emission-excitation spectra of solution samples of [Na(L)]**1** exhibit the same features as the

electronic-absorption spectra, indicating that the emission arises from these chromophores. Nonetheless, the possibility that unidentified decomposition products quench the emissive state of the [Na(L)]**1** complexes cannot be excluded; emission lifetimes and quantum yields in solution should be considered to be lower limits.

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[33] It is likely that the solid α- and β-[Na(crypt-2,2,2)]**1** samples are each contaminated with the other isomer, based on the shapes of their emission bands and the fact that the emission does not decay according to a single-exponential function. Unfortunately, the emission from single crystals of α- and β-[Na(crypt-2,2,2)]**1** was not sufficiently strong to allow the emission spectra and lifetimes of the pure isomers to be measured.