1 Thermodynamic and Structural Factors That Influence the Redox Properties of Tungsten–Alkylidyne Complexes

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Supporting Information

Abstract: The thermodynamic and structural factors that influence the redox properties of an extensive set of tungsten–alkylidyne complexes W(CR)L₄X are analyzed by combining synthesis, electrochemistry, and computational modeling based on free energy calculations of oxidation potentials at the density functional theory level. The observed linear correlations among oxidation potentials, HOMO energies, and gas-phase ionization energies are found to be consistent with the approximately constant solvation free energy dependence of the redox potential, HOMO energy, and gas-phase ionization energy differences between reduced and oxidized species over the complete set. The W−X bond length, trans to the alkylidyne ligand, is found to be a good descriptor of the positioning of the key frontier orbitals that regulate the redox properties of the complexes.

Keywords: redox potentials, tungsten–alkylidyne complex, density functional theory, photoredox chromophores, descriptor

Introduction

Understanding the electronic and structural factors that govern the redox properties of transition metal complexes is centrally important to much of inorganic chemistry. Computational approaches that accurately reproduce experimental redox potentials offer the possibility of both understanding these potentials in terms of underlying thermodynamic quantities and designing new complexes with specific properties.1,2 One of many areas where computational design could play an important role is in the development of new photoredox chromophores with applications in solar fuels and organic synthesis.3−6 The excited-state redox potential of a photoredox chromophore is governed by the ground-state redox potential and the excited-state energy; these quantities are independently computable, whereas empirical prediction of their sum can be difficult for new compounds because variations within the coordination sphere affect the energies in ways that are not straightforwardly separable.7

One family of photoredox chromophores with desirable properties is comprised of tungsten–alkylidyne complexes of the form W(CR)L₄X (L is a neutral ligand, and X is an anionic ligand).7,8 These luminescent d⁰ complexes have oxidation potentials that can be tuned over the unusually broad range of 2 V9 which suggests a corresponding level of control can be exercised over their excited-state redox potentials. In addition, the structures of these complexes are characterized by small distortions among their ground, excited, and oxidized (d¹) states, evincing correspondingly small inner-sphere reorganization energies for their redox reactions.10 Finally, the chromophore can be regenerated following oxidation via reaction with H₂, providing a means of closing a solar-fuel cycle with renewable reducing equivalents rather than conventional sacrificial donors.11 We reported an electrochemical study of the effects on the oxidation potentials of W(CR)L₄X compounds resulting from variation of the CR, L, and X ligands across 32 derivatives [1−32 (Chart 1)].9 It was observed that the oxidation potential is significantly more sensitive to the nature of the L ligands than to the CR and X ligands, consistent with the fact that the dₓ o redox orbital has π symmetry with respect to the equatorial L ligands and nonbonding (δ) symmetry with respect to the axial X and CR ligands. It was also found that there is a strong linear correlation (with a slope of ≅1) between the experimentally measured oxidation potential and the calculated energy [density functional theory (DFT)] of the redox orbital. There were notable outliers in this correlation, however, and it was further observed, surprisingly, that the potential is not correlated with the calculated relative dₓ o/L atomic parentage of the redox orbital. The application of more sophisticated computational methods for redox properties offers the possibility of understanding the positive and negative correlations among this broad range of complexes in terms of underlying structural and thermodynamic factors.

Here, we use the Born−Haber cycle1 theoretical framework that partitions calculated free energy contributions into the gas-phase free energy and solution energies of the d² (reactant) and d¹ (product) species of W(CR)L₄X oxidation reactions (Scheme 1). Values obtained from the free energy calculations can be directly correlated to experimental oxidation potentials through use of an oxidation potential standard. This methodology has been applied to the original set of 32 complexes and...
three new derivatives [33–35 (Chart 1)] that broaden the variation of the CR and X groups. In general, we find good agreement between theory and experiment. Further analysis of the partitioned free energy contributions shows that the net solvation energy spans a narrow range for these compounds, consistent with the previously observed linear correlation between oxidation potential and redox orbital energy. Spin density calculations on the d1 (product) complexes demonstrate that the SOMO is of metal-centered d_{xy} parentage. However, we observe only a very coarse overall correlation between the spin density and the energy of the d_{xy} redox orbital. Finally, we find that the W–X bond length is a reporter of the oxidation potential: complexes with longer W–X bonds are easier to oxidize, with the bond length and potential being linearly related. This relatively simple, low-level DFT method provides a convenient, accurate computational model that can be used to predict the oxidation potentials for new or previously unstudied tungsten–alkylidyne chromophores.

### METHODS

**Experimental Methods.** The new complexes W(CPh)−(dmpe)2F (33) and W(CC6H4-4-pyr)(dmpe)2Cl (35; pyr = N-pyrrolidyl) were synthesized using routes and procedures similar to those employed for related complexes and were characterized by multinuclear nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, elemental analyses, and X-ray crystallography; full details of their preparation and characterization are provided in the Supporting Information. The compound W(CMes)(dmpe)2Cl (34; Mes = 2,4,6-C6H2Me3) was prepared according to the standard procedure. Electrochemical measurements [cyclic voltammetry (CV) and differential pulse voltammetry (DPV)] were performed at room temperature in a nitrogen-filled glovebox using a Bioanalytical Systems 100 B/W Electrochemical Workstation. A three-electrode configuration was used, which consisted of a working electrode (platinum disk), an auxiliary electrode (platinum disk), and a quasi-reference electrode (silver wire). Samples ranged in concentration from 0.3 to 2.0 mM analyte in a tetrahydrofuran (THF) solution with 0.1 M [Bu4N][PF6]. The electrochemical reversibility of redox couples was established via Randles−Sevcik plots of CV data. Electrode potentials are referenced to FeCp20+/+. Full experimental details and data pertaining to the electrochemical measurements are provided in the Supporting Information.

Single-crystal X-ray diffraction measurements of 12, 34, and 35 were performed using a Bruker D8 VENTURE with
PHOTON 100 CMOS detector system equipped with a Mo target X-ray tube (λ = 0.71073 Å). Full details regarding data acquisition and structure refinement are provided in the Supporting Information.

**RESULTS AND DISCUSSION**

**Electrochemical Properties of W(CR)L₄X Complexes**

To investigate the effects on oxidation potentials of R and X substituents not encompassed by the original set of 32 W(CR)L₄X compounds [1–32 (Chart 1)], the oxidation potentials of three additional tungsten–alkylidyne complexes were measured [33–35 (Chart 1)]. The effects of incorporat-
electron-donating groups on the commonly employed benzylidyne CR ligand were probed via a study of the methyl- and amine-substituted derivatives W(CMes)(dmpe)2Cl (34; Mes = 2,4,6-C6H2Me3) and W(CC6H4-4-pyr)(dmpe)2Cl (35; pyr = N-pyrrolidyl). In addition, the effect of a fluoro X ligand was assessed via a study of complex W(CPh)(dmpe)2F (33); the only fluoro derivative in the original set [W(CH)(dmpe)2F (1)] exhibited a quasi-reversible oxidation, which was unusual because chloro, bromo, and iodo derivatives generally exhibit reversible oxidations. The reference compound for evaluating the effects of these substituents is W(CPh)(dmpe)2Cl (12). To determine whether these substituents significantly perturb the molecular structures of the compounds, which would complicate comparisons of their redox properties, the structures of 12 (Figure S14), 33 (Figure S15), and 35 (Figure 1) were determined by single-crystal X-ray diffraction studies. The core bond distances and angles of the three compounds are essentially identical, with the W−C and W−P bond lengths differing from each other by less than 3σ (Table S7). Of note for pyrrolidyl derivative 35 (Figure 1) are the facts that this substituent exhibits a planar geometry at the nitrogen atom [sum of C−N−C angles of 359° (Table S6)] and is approximately coplanar with the phenyl ring (dihedral angle of ≈6°), consistent with maximal electron donation by the pyrrolidyl group.

The oxidation potentials of W(CPh)(dmpe)2F (33), W(CMes)(dmpe)2Cl (34; Mes = 2,4,6-C6H2Me3), and W(CC6H4-4-pyr)(dmpe)2Cl (35) were determined by cyclic (CV) and differential pulse (DPV) voltammetry (Table 1 and Figures S20–S22). The compounds display a reversible WIV/V couple. The oxidation potentials of 34 (E1/2 = −0.87 V) and 35 (E1/2 = −0.93 V) are lower than those of parent benzylidyne complex W(CPh)(dmpe)2Cl (12; E1/2 = −0.82 V) and lie in the order consistent with the electron-donating ability of the phenyl substituent (Ph > Mes > C6H4-4-pyr). These results demonstrate the possibility of fine-tuning the redox potential via benzylidyne substituents despite the orthogonality of alkylidyne−ligand orbitals to the dxy redox orbital. The reversible oxidation exhibited by fluoro derivative W(CPh)−(dmpe)2F (33; E1/2 = −0.91 V) contrasts with the quasi-reversible process noted above for W(CH)(dmpe)2F (1) but is in line with the reversibility observed for all other halide derivatives with phosphine ligands (X = Cl, Br, or I; 2−4, 9−14, 17−21, 23, and 24). The negative shift of the oxidation potentials...
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264 W(CR)L4X complexes
265 equatorial ligands (267 W(CR)L4X compounds that have exclusively phosphine
266 (265 calculated thermodynamic quantities that contribute to
267 imental measured and computed oxidation potentials of
268 tions of the oxidation potentials for this set of compounds.
269 DPV potentials and CV peak potentials is only 0.02
270 suitable for comparison to theoretically computed values, the
271 are close enough to the actual oxidation potentials to be
272 potential of 33 relative to that of the chloro analogue 12 (ΔE1/2
273 0.09 V) is close to the difference between W(CH)(dmpe)2F
274 (1) and W(CH)(dmpe)2Cl (2) (ΔE1/2 = 0.07 V).9
275 Within the original set of 32 compounds, complex
276 W(CPb)(POMe3)4Cl (26) and all those of the form
277 W(CPb)L2(CO)2X (L = 1/2dppe, X = Cl, 27; L = 1/2tmeda,
278 X = Cl, 28; L = 1/2tmeda, X = Br, 29; L = CNBu3, X = Br, 30; L = py, X = Br, 31) were observed to exhibit quasi-reversible or
279 irreversible oxidations in CV experiments at room temperature.
280 To determine whether the reported CV peak potentials
281 are close enough to the actual oxidation potentials to be
282 suitable for comparison to theoretically computed values, the
283 oxidation potentials (E1/2) of 26–28 were measured by DPV21
284 (Table 1 and Figures S18 and S19). The difference between the
285 DPV potentials and CV peak potentials is only 0.02–0.04 V,
286 suggesting that the CV peak potentials are good approxima-
287 tions of the oxidation potentials for this set of compounds.
288 Correlation between Calculated and Experimental
289 Oxidation Potentials. The relationship between the exper-
290 imently measured and computed oxidation potentials of
291 W(CR)L4X complexes 1–35 is shown in Figure 2, and the
292 calculated thermodynamic quantities that contribute to E1/2
293 (ΔG_reac,olv, ΔG_exp, and ΔG_prod,olv) are set out in Table S10.
294 The complexes fall into two broad classes with regard to the
295 agreement between theoretical and experimental values.
296 W(CR)L4X compounds that have exclusively phosphine
297 equatorial ligands (1–21 and 33–35), which exhibit reversible
298 oxidations with E1/2 values of less than −0.5 V, show good
299 agreement between the theoretical and experimental oxidation
300 potentials: most lie near the line of perfect agreement (slope = 1, intercept = 0). Compounds of the form W(CR)L4X (27–31), which exhibit quasi-reversible or irreversible
301 oxidations with E1/2 values of >0.3 V, clearly lie above the
302 line of ideal agreement. Three compounds with singular
303 compositions lie between these two clusters of complexes: 278
304 [W(Cp)](dppe)2(NCMe)(22), which is the only cationic
305 compound in the set; phosphite derivative W(Cp)[P(OMe3)3]Cl (26), which exhibits a quasi-reversible oxidation
306 at room temperature and, similar to 27–31, lies above the line;281
307 and W[CpCH(C=C6H4)](triphos)(CO)Cl (25),32 which is the sole monocarbonyl derivative.
308
309 A statistical evaluation of the agreement between theory and
310 experiment was performed using the subset of 21 complexes
311 286 that have fully reversible oxidations in THF solution at room
312 temperature. The experimental and computed potentials for
313 this set of compounds (2–6, 9–11, 13–15, 17–21, 23, 24, and
314 33–35) can be fit to a linear relationship (r2 = 0.76) with a
315 slope of 0.97 and an intercept of −0.04, which is close to the
316 case of ideal agreement with a slope of 1 and an intercept of 0 (Figure S23). The agreement between theory and experiment
317 was evaluated by examination of the distribution of values of
318 294 ΔE = E_theory − E_exp (Figure S24); this provides the mean
319 standard deviation μ = −4 mV [μ = (ΣΔE)/n] and standard deviation
320 σ = 46 mV. The distribution of binned mean deviation values
321 was observed to be approximately Gaussian (Figure S24); the
322 parameters obtained from a Gaussian fit [μ = −8 mV, σ = 299
323 50 mV (Figure S24)] are in close agreement with the values
324 obtained above, confirming that μ and σ are appropriate statistical
325 parameters for evaluating the concordance of theoretical and
326 experimental potentials. Over the 0.35 V range of measured
327 oxidation potentials for this subset of compounds, the line of
328 ideal agreement lies within the 1σ limits. The mean and
329 standard deviations compare well with those derived in the
330 earlier study1 (μ = −2 mV, and σ = 64 mV), which employed a
331 similar level of theory using a redox couple in the same row of
332 the periodic table.
333 Although for the majority of compounds the computed and
334 experimental oxidation potentials differ by less than one
335 standard deviation, there are several others for which this is not the case. Among the subset of 21 complexes noted above
336 used to determine the statistical metrics, the calculated
337 oxidation potentials of complexes W(CBu3)(PMe3)2Cl (10), W(CBu3)(PMe3)Cl (11), W(Cp)(PMe3)2Cl (17), W(Cp)(PMe3)Br (18), and W(Cp)(depe)2Cl (20) differ from
338 experiment by |E_theory − E_exp| = 60–80 mV. These outliers do not share obvious common chemical features apart from the
339 fact that they have multiple methyl groups on the L and/or R
340 substituents. It is possible that these compounds have multiple
341 structural minima with similar energies; a more accurate
342 calculation of their oxidation potentials may require a Monte
343 Carlo average over thermally accessible configurations. The
344 largest deviations (>2σ) between theoretical and experimental
345 potentials are found for W(Cp)(dppe)2Cl (21), W(Cp)[P(OMe3)3]Cl (26), and compounds of the form W(Cp)Cl
346 L1(CO)X (27–31). As discussed below, these compounds
347 share the same dppe redox orbital as those compounds for which the experimental and computed potentials are in close
348 agreement. All but 21 exhibit quasi-reversible or irreversible
349 oxidations; whether this is related to the deviation between
350 theory and experiment is unclear. Except for compound 28, 333

Figure 3. (a) Correlation between theoretical oxidation potentials and the DFT energy of the frontier orbital with d_n character for all complexes except 12, 22, and 32, with an expansion (b) of the region between −4.3 and −3.9 eV (area within the red dashed-line box, top).
which shows the largest deviation between theory and experiment, the DFT methodology nevertheless correctly predicts the trend in oxidation potential for these compounds. To probe whether higher levels of theory would improve the agreement with experiment, a calculation that accounts for dispersion [Grimme’s D3 empirical dispersion factor with Becke–Johnson damping (GD3BJ)] was performed on 21, which is the one outlier in this group that exhibits an electrochemically reversible oxidation. This calculation decreased the difference between theory and experiment to 50 mV ($\sigma$).

The fact that DFT methodology allows accurate (1–20, 22–25, and 33–35) and semiquantitative (21 and 26–31) prediction of the oxidation potential allows analysis of the trends in redox properties over the series of complexes by examination of the partitioned thermodynamic quantities ($\Delta G_{\text{reag,prod}}, \Delta G_{\text{ox,red}}$, and $\Delta G_{\text{prod,solv}}$ (Scheme 1 and Table S10). In our prior report, it was noted that the measured oxidation potentials of these compounds are correlated linearly with the calculated energy of the $d_{xy}$ orbital of the $d^2$-configured reactant. This result is reproduced by the calculations employed in the study presented here (Figure 3 and Figure S25). In addition, calculation of the symmetry of the total spin densities of the frontier orbitals for the oxidized ($d^1$) products (Table S11) confirms that the frontier orbital with $d_{xy}$ character is the redox orbital for all complexes except W(CCCPh)$_2$Cl (32), for which the $d_{xy}$ orbital is HOMO−2. As one might expect, a corresponding relationship is also found between the experimental oxidation potential and the calculated ionization energy ($\Delta G_{\text{ox,red}}$) (Figure S26). As was suggested for the case of the correlation with the $d_{xy}$ orbital energy, this result indicates that the solvation energy differences associated with oxidation are roughly constant across the series. Indeed, analysis of the solvation energies for the 32 complexes with experimental electrochemical data in THF (Figure S27) shows that $\Delta G_{\text{prod,solv}} - \Delta G_{\text{reac,solv}}$ varies only from −23 to −35 kcal/mol, indicating that the factors that control the energies of the frontier orbitals, summarized in Figure S28, are most responsible for the observed trends in oxidation potentials. The complexes that show the largest differences between computed and experimental oxidation potential (21 and 26–27, 31, >$\sigma$) also tend to be outliers in the correlation between $E_{\text{1/2}}$ and $\Delta G_{\text{reag}}$ (Figure S26) and have solvation energies that are clustered toward the edges of the overall range (Figure S27) but do not exhibit a systematic positive or negative skew in these quantities.

Electronic and Structural Factors Relevant to Oxidation Potentials. It was noted in the earlier report that the oxidation potentials of W(CR)L$_4$X compounds vary more strongly with substitution of the equatorial L ligands than with that of the CR and X ligands. This observation was rationalized by noting that the $d_{xy}$ redox orbital is nonbonding ($\delta$ symmetry) relative to the CR and X ligands and $\pi$ symmetry with respect to the L ligands, thus allowing stronger electronic interactions between the $d_{xy}$ orbital and the L ligands. Consistent with this expectation, comparison of the redox frontier orbitals of W(CPh)(dmpe)$_2$Cl (12) and W(CPh)$_2$O$_2$(tmeya)Cl (28), using data from the study presented here (Figure 4), shows that the orbital with $d_{xy}$ character is more localized on W in 12 (−4.19 eV) than in 28 (−5.45 eV).

Figure 4. (a) Isosurface of the frontier orbital with $d_{xy}$ character for 12 (isovalue = 0.04). (b) Mulliken spin population for 12$^+$ (the oxidized form of 12), where red indicates $\beta$ spin density (<−0.10), green indicates a very large $\alpha$ spin density (>0.5), maroon indicates slight $\beta$ spin density (∼0.03), and black indicates a negligible spin density. Panels c and d show analogous results for 28 and 28$^+$, respectively. Color key for isosurfaces in panels a and c: green and brown isosurfaces indicate positive and negative phases, respectively, of the frontier orbital. In panels a and c, atoms are represented as follows: white for H, blue for N, turquoise for W, orange for P, gray for C, and green for Cl.
where there is significant delocalization on the carbonyl ligands due to π-backbonding interactions. It is intuitively reasonable to expect, therefore, that the strong correlation between the oxidation potential and d$_{xy}$ orbital energy would be paralleled by correlations between the d$_{xy}$ orbital energy and measures of d$_{xy}$–L delocalization. However, it was found in the prior study that this correlation is not quantitative when calculated atomic orbital parentages of the d$_{xy}$ redox orbital are used as the measure of delocalization. For example, among the 27 W(CR)₄Lₓ derivatives with phosphine or phosphite R groups (1−21, 23, 24, 26, and 33−35), the oxidation potential spans a range of 0.74 V (from −0.98 V for 8 to −0.24 V for 26) and the calculated d$_{xy}$ orbital energy varies by ~1 V, yet the tungsten atomic parentage of the redox orbital ranges only from 72 to 77%. In the work presented here, we probed these relationships further by examining the spin density on the W center in the oxidized complexes (Table S11). As shown in Figure 5, there is a very coarse overall correlation between the energy of the d$_{xy}$ frontier orbital and the spin density on W, with the CO-containing complexes (25 and 27−31) showing a reasonable linear correlation but the phosphine-containing W(CR)₄Lₓ complexes (1−21, 23, 24, and 33−36) appearing as a scatter plot. This result is very similar to that found for the correlation with the d$_{xy}$ atomic parentage for the d$^2$ complexes. That these two calculated measures of delocalization (redox orbital tungsten parentage for the reduced compound and tungsten spin density for the oxidized compound) represent complimentary probes of the redox orbital as reflected in the fact that they exhibit a reasonable linear correlation with each other (Figure S29). This plot would be predictive for complexes with very different spin densities [e.g., 12 vs 28 (Figure 4)] but could not differentiate very well between similar complexes [e.g., the W(CR)(phosphine)₄X derivatives in the inset of Figure 5].

In contrast to the ambiguous relationships of redox orbital parentage and spin density with redox orbital energy and oxidation potential, a relationship was observed between calculated oxidation potentials and W−X bond lengths for complexes with a given X ligand, for both reduced (d$^2$) reactants and oxidized (d$^1$) products. For the chloro derivatives of type W(CR)₄Cl (2, 10−12, 17, 20, 21, 23, 24, 26, and 34−36) and W(CR)₄(CO)$_n$Cl (25, 27, 28, and 32), it is found that the longer the W−Cl bond, the more negative the oxidation potential (Figure 6). The correlation is due to the effect of metal–ligand interactions on the relative energies of frontier orbitals and the resulting geometry change, analogous to the correlation between octahedral and square planar d orbital splittings. Equatorial ligands typically stabilize the

Figure 5. (a) Correlation between the energy of the d$_{xy}$ frontier orbital and the spin density on W (omitting 22 and 32) with an expansion (b) of the region with the red dashed-line box of the top figure. W spin densities of >1 reflect spin polarization of the alkylidyne group and antiferromagnetic coupling.

Figure 6. Correlation between oxidation potentials and W−Cl bond lengths for W−alkylidyne complexes, with Cl axial ligands, excluding 22, for (a) reactants and (b) products.
Scheme 2. Illustration of the Stabilization through Backbonding of the Frontier Orbitals of Tungsten—Alkylidyne Complexes

We note that the W−X bond length is unique with regard to correlations with the redox properties of these complexes. Other bond lengths in the complexes do not show significant correlation with the oxidation potential of the complex. For example, the W−P bond lengths for complexes with phosphine ligands vary within only a narrow range from 2.47 Å (8) to 2.53 Å (27) and the W≡C(R) bond lengths for all complexes vary within only a narrow range from 1.79 Å (5) to 1.83 Å (33). As has been noted elsewhere, W−X bond lengths of tungsten−alkylidyne complexes tend to be unusually long compared to those of non-alkylidyne−tungsten compounds because of the strong trans influence of the alkylidyne ligand. This may also make them especially sensitive to subtle electronic structural effects that are important to physical properties such as redox potentials.

## CONCLUSIONS

We have demonstrated the ability of a combined electrochemical and computational analysis of tungsten−alkylidyne complexes to provide a basis for understanding their redox properties on the basis of the symmetries of metal−ligand interactions and the relative contributions of ionization and solvation energies. Good agreement between theory and experiment can be achieved with comparatively standard levels of theory [B3LYP/(LANL2DZ,6-311G*)], suggesting that these approaches can be readily applied to the design of new complexes with specific redox potentials. It is striking that the strong linear correlation between the oxidation potential and energy of the redox orbital is not mirrored by broad correlations with measures of redox orbital delocalization, such as the local spin density of the oxidized product. However, the orbital−energy correlation is manifest in the W−X bond length, which serves as a structural descriptor for the redox properties of the complex. The observed correlations should be particularly valuable for the design of new tungsten−alkylidyne complexes with specific redox properties, which is of interest for their applications as photoreductants and for the activation of H2.11

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b01636.

Figure 7. Correlation between the $E(\text{LUMO}) - E(\text{d}_{\pi})$ gap and the W−Cl bond length for all complexes for which R = Ph for (a) reactants and (b) products.

HOMO with $d_{xz}$ symmetry through $\pi$-backbonding interactions. The stabilization increases the energy gap between the HOMO and orbitals of $d_{xz}$ and $d_{yz}$ character (mainly the LUMO), which in turn reduces the W−X bond length. The change in bond length thus correlates with the increase in oxidation potential. This effect is related to the energy pattern of the frontier orbitals as opposed to either the steric and inductive cis influences found in cobaloximes and cobalamin, or the conservation of bond order about the W. The axial W−X bond length is thus a descriptor of equatorial bond lengths in the complexes with specific oxidation potentials. The observed correlations confirm that the W−X bond length reports on the energy gap between frontier orbitals that determine the oxidation potential of the complexes, as illustrated in Scheme 2. A similar correlation is found for complexes for which X = Br, as shown in Figure S30. Therefore, the W−X bond length could be used as a structural marker for designing complexes with specific oxidation potentials. The effect in the oxidized products is even more evident as the W−Cl bond length differences are slightly larger.
Synthesis and characterization (13C, 31P, 1H, and 19F NMR, mass spectrometry, and elemental analysis) of 33, 35, and their precursor complexes, single-crystal X-ray diffraction studies of 12, 33, and 35, electrochemistry (CV and DPV), oxidation potentials for all complexes studied along with partitioned contributions, comparison and discussion of the theoretical and experimental geometric parameters for 12, 21, 21*, 33, and 35, computed free energies and redox potentials, analysis of the error between theory and experiment, comparison of $E(d_{\sigma})$ values to those in previous work with these complexes, calculated HOMO reactant energies, calculated spin densities and their symmetries, correlation between gas-phase ionization potentials and experimental oxidation potentials in solution, differences in solvation energy between the reactant and product, overall comparison of orbital energies with potentials, correlation between atomic parentage and oxidized W spin density, correlation between the $E(LUMO) - E(d_{\sigma})$ gap and W–Br bond lengths, analysis of results obtained upon optimization in solution, and additional references (PDF)

Theoretical coordinates in the form of .xyz files labeled by the SCF energy given by Gaussian (PDF)

Details of the X-ray crystal structure (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

V.S.B. acknowledges support from AFOSR Grant FA9550-13-1-0020 and supercomputing time from NERSC and from the high-performance computing facilities at Yale University. M.D.H. acknowledges financial support from the U.S. Department of Energy, Office of Basic Energy Sciences, Solar Photochemistry Program (Grant DE-FG02-07-ER15910). B.R. acknowledges support from a National Science Foundation Graduate Research Fellowship under Grant DGE-1122492. We thank Prof. Robert H. Crabtree, Dr. Junming Ho, and Dr. Andreas Markmann for helpful comments and Dr. Alexander Filatov for determining the crystal structure.

■ REFERENCES


24. In the following discussion, the cationic compound [W(Cp)]2(dppe)(NCMe)]+(22) is excluded, because of the difference in charge relative to the otherwise neutral compounds in this study.


