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Oxidation-Potential Tuning of Tungsten−Alkylidyne Complexes over a 2 V Range

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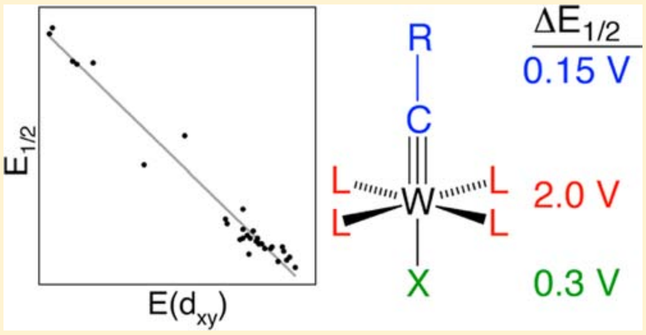
Supporting Information



ABSTRACT: The electrochemistry and electronic structures of over 30 tungsten−alkylidyne compounds of the form $W(CR)L_nL'_{4-n}X$ (R = H, Bu^t, Ph, p-C_6H_4CCH, p-$C_6H_4CCSiPr^i_3$; X = F, Cl, Br, I, OTf, Bu^n, CN, $OSiMe_3$, OPh; L/L′ = PMe_3, 1/2 dmpe, 1/2 depe, 1/2 dppe, 1/2 tmeda, $P(OMe)_3$, CO, $CNBu^t$, py), in which the alkylidyne R group and L and X ligands are systematically varied, have been investigated using cyclic voltammetry and density functional theory calculations in order to determine the extent to which the oxidation potential may be tuned and its dependence on the nature of the metal−ligand interactions. The first oxidation potentials are found to span a range of ~2 V. Symmetry considerations and the electronic-structure calculations indicate that the highest occupied molecular orbital (and redox orbital) is of principal d_{xy} orbital parentage for most of the compounds in this series. The dependence of the oxidation potential on ligand is a strong function of the symmetry relationship between the substituent and the d_{xy} orbital, being much more sensitive to the nature of the equatorial L ligands (π symmetry, with respect to d_{xy}, $\Delta E_{1/2} \cong 0.5$ V/L) than to the axial CR and X ligands (nonbonding with respect to d_{xy}, $\Delta E_{1/2} < 0.3$ V/L). The oxidation potential is linearly correlated with the calculated d_{xy} orbital energy (slope ≅ 1, $R^2 = 0.97$), which thus provides a convenient computational descriptor for the potential. The strength of the correlation and slope of unity are proposed to be manifestations of the small inner-sphere reorganization energy associated with one-electron oxidation.

■ INTRODUCTION

The descriptive chemistry of compounds containing metal−carbon triple bonds is generally organized according to the formal oxidation state of the metal center, as embodied in the familiar classification of these compounds as being "low-oxidation-state" Fischer carbyne or "high-oxidation-state" Schrock alkylidyne complexes.[1] It is unsurprising, then, that there have been numerous studies of the electrochemistry of metal−alkylidyne (−carbyne) complexes aimed at determining the redox potentials that characterize the metal oxidation states and elucidating the processes that connect them.[2−22] The understanding of redox processes and potentials gleaned from these studies is important in many contexts, including elucidating the nature of ground-state[23] and photochemical[4,5,24] redox-induced reactions of the alkylidyne ligand, the development of oxidation and reduction reactions that interconvert high- and low-oxidation-state metal−alkylidyne complexes,[25] and designing and understanding the properties of luminescent photoredox chromophores[5,6,11,26−43] 43 and π-conjugated compounds and materials[7,15−21,35,39,44−46] based on metal−alkylidyne compounds.

In order to guide the rational design of new substances for which the control of electron-transfer properties is central to their function, it is important to develop theoretical methods or empirical relationships that enable the prediction of their redox potentials. Within a set of related metal−alkylidyne complexes of a given metal, it is reasonable to expect that the electrode potential of a particular metal-centered redox process should vary in a systematic way as a function of the electronic properties of the supporting ligands and alkylidyne R group. Such relationships have been codified more generally for transition-metal compounds in empirical ligand-additivity models developed by Lever,[47,48] Pickett,[49] and Bursten,[50] in which the redox potential is expressed as a sum of ligand electrochemical parameters whose magnitudes reflect the relative electron donor/acceptor properties of the ligands. Pombeiro and co-workers have reported extensive analyses within the Pickett model of the first oxidation potentials of rhenium and tungsten−alkylidyne compounds of the types $[Re(CCH_2R)(dppe)_2X]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane; X = F, Cl; R = H, Bu^t, CO_2Me, CO_2Et, Ph, 4-C_6H_4Me),[3] W{CCH=(*cyclo*-$C(CH_2)_n$)}$(CO)_2$(dppe)X (X = F, Cl, SCN, OCN, $S_2P(OEt)_2$; n = 1, 4),[9] and [W{CCH=(*cyclo*-$C(CH_2)_n$)}$(CO)_2$(dppe)(CNR)$]^+$ (R = Bu^n, Bu^t, Cy, $PhCH_2$, C_6H_3-2,6-Me_2).[12] Because of the variety of

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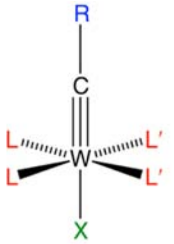
supporting ligands possessed by these compounds, it was possible to determine values of the electrochemical parameter P_L for their specific alkylidyne ligands ($P_L = 0.21-0.24$); these could be used to predict the oxidation potentials of new derivatives. It was also proposed that the large values of P_L indicate that the alkylidyne ligand is a stronger net π-acceptor than CO, based on the description of the P_L parameter as a measure of the net σ-donor minus π-acceptor ability of the ligand.[51]

For some applications of metal−alkylidyne complexes, including as photoredox chromophores and building blocks for π-conjugated materials, the ability to tune the redox potential over a wider range than can be predicted from available empirical parameters is desirable. In order to understand the extent of redox-potential tuning that can be achieved by ligand variation, we have investigated the electrochemistry of the broad class of d^2-configured tungsten−alkylidyne compounds of the form $W(CR)L_nL'_{4-n}X$ (L/L' = neutral ligand, X = anionic ligand). One motivation for studying this class of compounds is that their synthetic chemistry enables the electronic properties of the alkylidyne R group and supporting X and L ligands to be systematically varied over a wide range. The compounds studied in the present report, shown in Chart 1, include derivatives with saturated and unsaturated alkylidyne R groups, L ligands that include soft donors and π-acceptors, and X ligands that include σ and π donors and electron-withdrawing ligands. An additional consideration is that there have not yet been electrochemical studies of metal−alkylidyne complexes that examine how the symmetry relationship between ligand and redox orbital influences redox-potential tuning. Addressing this question is facilitated for d^2 $W(CR)L_nL'_{4-n}X$ complexes because previous structural and EPR studies of chemically oxidized, d^1 redox congeners have allowed assignment of the redox-active orbital for oxidation as being of metal d_{xy} parentage.[10,14,41] Finally, understanding the redox potentials of $W(CR)L_nL'_{4-n}X$ compounds is of interest because several of these complexes have been employed as luminescent photoredox chromophores[5,6,11,26,27,34,35,38−42] and in π-conjugated materials.[7,16,19−21,35,39,45]

Chart 1. Tungsten−Alkylidyne Complexes of the Type $W(CR)L_nL'_{4-n}X$ ($L = L'$, $n = 4$; $L \neq L'$, $n = 2$)



R = H, Bu^t, Ph, C_6H_4-4-CCR′

L/L′ = PMe_3, 1/2 dmpe, 1/2 depe, 1/2 dppe, CO, py, $CNBu^t$, 1/2 tmeda

dmpe = $Me_2PCH_2CH_2PMe_2$
depe = $Et_2PCH_2CH_2PEt_2$
dppe = $Ph_2PCH_2CH_2PPh_2$
tmeda = $Me_2NCH_2CH_2NMe_2$

X = F, Cl, Br, I, OTf, Bu^n, CN, $OSiMe_3$, OPh, $NCCH_3$

Here, we report the dependence of the first oxidation potentials of $W(CR)L_nL'_{4-n}X$ complexes on the nature of the alkylidyne R group and X and L ancillary ligands. The electrochemical data reveal that the oxidation potential can be tuned over a 2 V range through ligand variation. Density functional theory calculations show that the highest occupied molecular orbital (HOMO) and redox-active orbital is the metal-centered d_{xy} orbital for nearly all compounds in this series. The extent to which the oxidation potential varies with the CR, L, and X ligands is found to be a strong function of their symmetry relationship to the d_{xy} orbital, with the equatorial L ligands affecting the potential more than the axial CR and X ligands. The oxidation potential does not vary systematically with the calculated ligand parentage of the HOMO but does exhibit a linear correlation with the HOMO energy (slope ≅ 1), from which it may inferred that inner-sphere reorganization energies associated with one-electron oxidation are constant or small across this series. This simple Koopmans-Theorem-like relationship provides a convenient computational descriptor for predicting the redox potentials of new or unstudied metal−alkylidyne compounds of this class.

RESULTS

Electrochemistry of $W(CR)L_nL'_{4-n}X$ Complexes. Compounds of the general form $W(CR)L_nL'_{4-n}X$ were studied by cyclic voltammetry in order to characterize the nature and potentials of their redox processes. The cyclic voltammogram of $W(CPh)(depe)_2Cl$ in THF, shown in Figure 1, is illustrative of the redox processes that are usually observed for these complexes: it exhibits an electrochemically reversible one-electron oxidation ($E_{1/2}^{0/+} = -0.84$ V vs $FeCp_2^{0/+}$); an irreversible second oxidation ($E_p = 0.19$ V); and an irreversible reduction near the cathodic limit of the THF solvent ($E_p = -3.35$ V). The electrode potentials for the first oxidations of the $W(CR)L_nL'_{4-n}X$ compounds are set out in Table 1;[52] those for reductions and second oxidations are reported in the Supporting Information (Table S1). The first oxidation is assigned to a one-electron process, based on prior work that demonstrated that $W(CR)L_4X$ compounds (L = phosphine) may be chemically oxidized by one electron to form stable $[W(CR)L_4X]^+$ ions.[7,10,14,41] Furthermore, for those compounds for which the first oxidation is reversible or quasi-reversible, the splitting between anodic and cathodic peaks (ΔE_p) is essentially the same as that for the $FeCp_2$ internal reference. The second oxidation, when observed (see Table S1 in the Supporting Information), is irreversible for all compounds except $W(CPh)(dmpe)_2(OPh)$ (**16**), which exhibits a reversible second oxidation (Figure S1 in the Supporting Information). The irreversible reduction (Table S1 in the Supporting Information) is observed for $W(CR)L_nL'_{4-n}X$ derivatives with unsaturated R

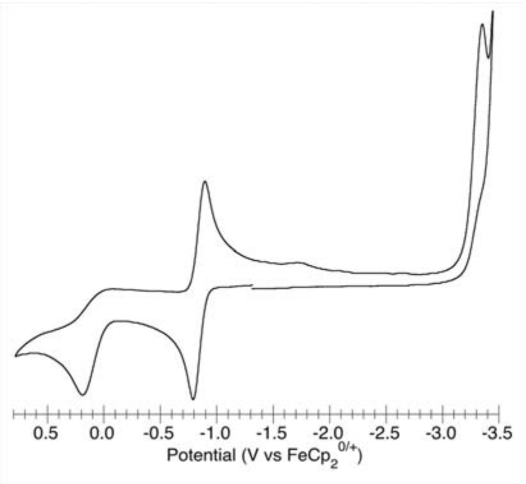


Figure 1. Cyclic voltammogram of $W(CPh)(depe)_2Cl$ (**20**) in THF solution at room temperature ($\nu = 0.1$ V s^{-1}, 0.3 M $[NBu^n_4][PF_6]$).

Table 1. Oxidation Potentials and Calculated Energies and Atomic Parentages of d_{xy}-Derived Orbitals of W(CR)L$_n$L′$_{4-n}$X Complexes

				Atomic Parentage (%)			
compound	compound number	$E_{1/2}^{0/+}$ (V)[a]	$E(d_{xy})$ (eV)	W	CR	L	X
W(CH)(dmpe)$_2$F	**1**	−0.91[b]	−4.58	73.3	0.0	26.7	0.0
W(CH)(dmpe)$_2$Cl	**2**	−0.84[c]	−4.70	74.3	0.1	25.6	0.0
W(CH)(dmpe)$_2$Br	**3**	−0.82	−4.77	74.7	0.1	25.3	0.0
W(CH)(dmpe)$_2$I	**4**	−0.73	−4.83	75.0	0.1	25.0	0.0
W(CH)(dmpe)$_2$(OTf)	**5**	−0.68[c]	−5.01	75.4	0.1	24.4	0.2
W(CH)(dmpe)$_2$(CN)	**6**	−0.78	−4.80	74.0	0.1	25.9	0.0
W(CH)(dmpe)$_2$(OSiMe$_3$)	**7**	−0.94[b,d]	−4.66	74.3	0.0	25.6	0.0
W(CH)(dmpe)$_2$(Bu^n)	**8**	−0.98[e]	−4.54	73.1	0.1	26.3	0.5
W(CH)(PMe$_3$)$_4$Cl	**9**	−0.85[c]	−4.71	76.1	0.0	23.9	0.0
W(CBu^t)(dmpe)$_2$Cl	**10**	−0.93	−4.60	73.7	0.1	26.2	0.0
W(CBu^t)(PMe$_3$)$_4$Cl	**11**	−0.87	−4.62	75.3	0.0	24.7	0.0
W(CPh)(dmpe)$_2$Cl	**12**	−0.82	−4.79	74.7	0.0	25.3	0.0
W(CPh)(dmpe)$_2$Br	**13**	−0.78	−4.85	75.0	0.0	25.0	0.0
W(CPh)(dmpe)$_2$I	**14**	−0.72	−4.90	75.3	0.0	24.7	0.0
W(CPh)(dmpe)$_2$(OTf)	**15**	−0.65	−5.02	75.4	0.1	24.4	0.2
W(CPh)(dmpe)$_2$(OPh)	**16**	−0.89[f]	−4.86	72.2	0.8	24.3	2.7
W(CPh)(PMe$_3$)$_4$Cl	**17**	−0.85	−4.75	76.3	0.1	23.6	0.0
W(CPh)(PMe$_3$)$_4$Br	**18**	−0.80	−4.81	76.5	0.1	23.4	0.0
W(CPh)(PMe$_3$)$_4$I	**19**	−0.76	−4.87	76.6	0.1	23.2	0.0
W(CPh)(depe)$_2$Cl	**20**	−0.84	−4.63	74.6	0.1	25.3	0.0
W(CPh)(dppe)$_2$Cl	**21**	−0.58	−4.90	74.2	0.0	25.7	0.1
[W(CPh)(dppe)$_2$(CH$_3$CN)][PF$_6$]	**22**	−0.24	−7.43	74.8	0.0	25.2	0.0
W(CC$_6$H$_4$-4-CCH)(dmpe)$_2$Cl	**23**	−0.79[g]	−4.92	75.0	0.0	25.0	0.0
W(CC$_6$H$_4$-4-CCSiPr$^i_3$)(dmpe)$_2$Cl	**24**	−0.78[g]	−4.90	75.0	0.0	25.0	0.0
W{CCHC(*c*-C$_4$H$_8$)}(triphos)(CO)Cl	**25**	−0.08[h]	−5.30	63.4	2.0	15.9 (CO), 15.8 (P$_3$)	2.8
W(CPh){P(OMe)$_3$}$_4$Cl	**26**	−0.28[b,i]	−5.58	77.4	0.0	22.7	0.0
W(CPh)(dppe)(CO)$_2$Cl	**27**	0.66[e]	−6.21	58.2	6.2	23.1 (CO), 6.7 (dppe)	5.7
W(CPh)(tmeda)(CO)$_2$Cl	**28**	0.41[b]	−6.04	63.0	2.5	30.4 (CO), 1.2 (tmeda)	2.9
W(CPh)(tmeda)(CO)$_2$Br	**29**	0.43[b]	−6.07	60.3	3.0	28.5 (CO), 1.2 (tmeda)	7.0
W(CPh)(CNBu^t)$_2$(CO)$_2$Br	**30**	0.62[b,j]	−6.23[k]	50.0	6.1	17.1 (CO), 11.5 (CNR)	15.4
W(CPh)(py)$_2$(CO)$_2$Br	**31**	0.42[b]	−5.93	58.9	2.3	26.7 (CO), 7.3 (py)	4.8
W(CCCPh)(CO)$_4$Cl	**32**	>1.1[l]	−7.83[m]	65.6	0.2	34.3	0.0

[a] Unless otherwise noted, data are reported for compounds in THF solution ((0.5−5.0) × 10^{-3} M analyte, 0.3 M [NBu$^n_4$][PF$_6$]) at 25 °C, ν = 0.1 V s^{-1}, and are referenced to FeCp$_2^{0/+}$. [b] Quasi-reversible. [c] Reference 10 reports $E_{1/2}^{0/+}$ = −0.91 V for W(CH)(dmpe)$_2$Cl, −0.68 V for W(CH)(dmpe)$_2$(OTf), −0.88 V for W(CH)(PMe$_3$)$_4$Cl in THF/0.1 M [NBu$^n_4$][PF$_6$]. [d] The compound formed a film on the electrode during the experiment. [e] Irreversible; E_{pa} reported. [f] Measured in CH$_2$Cl$_2$; reversible second oxidation observed at $E_{1/2}^{+/2+}$ = −0.46 V. [g] Reference 7. [h] Reference 9; measured in CH$_3$CN with 0.2 M [NBu$^n_4$][BF$_4$] electrolyte. [i] Sample temperature = −13 °C. [j] Measured in CH$_2$Cl$_2$ with Ag/Ag$^+$ reference electrode; all other conditions as in footnote [a]. [k] HOMO-1. [l] Reference 8. [m] HOMO-2; calculation on W(CPh)(CO)$_4$Cl.

groups (R = Ph, C$_6$H$_4$CCH, C$_6$H$_4$CCSiPr$^i_3$), but not for complexes with saturated alkylidyne R groups (R = H, Bu^t).

The W(CR)L$_n$L′$_{4-n}$X compounds set out in Table 1 can be partitioned into two groups, based on the reversibility and potential of the first oxidation. One group is comprised of derivatives with phosphine equatorial ligands (L = L′ = PMe$_3$, 1/2 dmpe, 1/2 depe, 1/2 dppe; **1**−**24**), for which the first oxidation is usually reversible and lies in the potential range −1.0 V < $E_{1/2}$ < −0.5 V vs FeCp$_2^{0/+}$. The only exceptions to reversible behavior within this group are W(CH)(dmpe)$_2$F (**1**) and W(CH)(dmpe)$_2$(OSiMe$_3$) (**7**), for which the first oxidation is quasi-reversible, and W(CH)(dmpe)$_2$(Bu^n) (**8**), which is irreversible. The single cationic derivative among these compounds, [W(CPh)(dppe)$_2$(NCMe)]$^+$ (**22**), also exhibits a reversible oxidation; its potential is shifted ca. +0.3 V relative to that of W(CPh)(dppe)$_2$Cl (**21**), its closest neutral analogue, as a result of the positive charge. The second group is comprised of W(CR)L$_n$L′$_{4-n}$X compounds with stronger π-acceptor equatorial ligands (L = L′ = P(OMe)$_3$; L′ = CO, CNBu^t; **26**−**32**). For these, the first oxidation is quasi-reversible or irreversible and occurs at more positive potentials than the phosphine derivatives (−0.3 V < E_p < 0.7 V). Measurements on selected compounds at low temperature showed that the cyclic voltammetric wave for the first oxidation approaches reversibility as the temperature decreases. For W(CPh){P(OMe)$_3$}$_4$Cl (**26**), the wave changes from quasi-reversible at room temperature (i_{pa}/i_{pc} = 0.36 at ν = 0.10 V s^{-1}) to reversible at −13 °C (i_{pa}/i_{pc} = 0.97). Similarly, the appearance of the oxidation wave for W(CPh)(dppe)(CO)$_2$Cl (**27**) changes from irreversible at room temperature to quasi-reversible at 2 °C.

Across all complexes in the present study, the first oxidation potential (including irreversible processes) is observed to vary over a 1.7 V range, from −0.98 V (W(CH)(dmpe)$_2$(Bu^n), **8**) to 0.66 V (W(CPh)(dppe)(CO)$_2$Cl, **27**). Inclusion of the lower bound on the oxidation potential reported for W(CCCPh)(CO)$_4$Cl (**32**, > 1.1 V)[8] extends this range to ~2 V.

Density Functional Theory Calculations on W(CR)L$_n$L′$_{4-n}$X Complexes. Density functional theory calculations

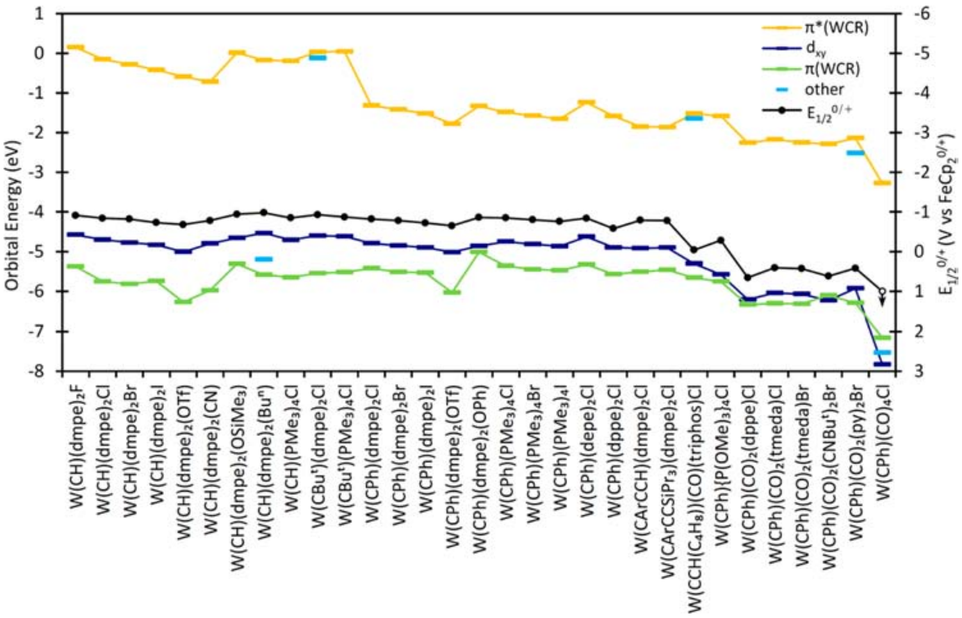


Figure 2. Oxidation potentials and calculated π*(W≡CR), d_{xy}, and π(W≡CR) orbital energies of W(CR)$L_4L'_{4-n}$X complexes (see Table 1 and Table S2 in the Supporting Information). Orbitals labeled "other" are indicated for compounds with additional orbitals in this energy space. The open circle for W(CPh)$(CO)_4$Cl represents the lower limit of the oxidation potential for W(CCCPh)$(CO)_4$Cl.

were performed on W(CR)$L_nL'_{4-n}$X complexes **1**−**32** in order to determine the energies and atomic parentages of their frontier orbitals, which include the redox-active orbitals. Based on symmetry arguments described in detail elsewhere[43] and prior computational studies of individual tungsten−alkylidyne compounds,[21,41,53] the frontier orbitals of d^2 W(CR)L_4X complexes are generally expected to be of metal t_{2g} parentage: the d_{xy} orbital is the principal basis for the HOMO and the d_{xz} and d_{yz} orbitals contribute substantially to the π(W≡CR) HOMO−1 and π*(W≡CR) lowest unoccupied molecular orbital (LUMO).[54] These frontier orbitals are analogous to those well-known for related d^2 M(≡E)L_5 metal−oxo and nitrido complexes.[55]

The frontier orbitals calculated for the W(CR)$L_nL'_{4-n}$X complexes conform to this expected pattern with few exceptions. The energy levels of the d_{xy}, π(W≡CR), and π*(W≡CR) orbitals are depicted in Figure 2, and orbital energies and atomic parentages are set out in Table 1 (for d_{xy}) and Table S2 in the Supporting Information (for π(W≡CR) and π*(W≡CR)). The π*(W≡CR) orbital is the LUMO for all compounds except W(CBu^t)$(dmpe)_2$Cl (**10**), W(CR)(triphos)(CO)Cl (**25**), and W(CPh)$(CO)_2(py)_2$Br (**31**), for which L-centered orbitals lie at slightly lower energy. Among pairs of compounds with constant X and L ligands, the LUMOs of derivatives with unsaturated alkylidyne R groups (R = Ph, C_6H_4CCR) lie >1 eV lower in energy than for those with saturated R groups (R = H, Bu^t) due to π conjugation within the WCPh unit.[41,43] These differences in LUMO delocalization and energy are reflected in the reduction properties of the compounds (vide infra).

The HOMO is found to be derived from the d_{xy} orbital for all compounds except W(CPh)$(CNBu^t)_2(CO)_2$Br (**30**) and W(CPh)$(CO)_4$Cl (**32**), for which the HOMO is π(W≡CR) (vide infra). The ligand contributions to the HOMO (Table 1) clearly reflect the symmetry properties of the d_{xy} orbital, which in the limit of C_{4v} symmetry is nonbonding (δ symmetry) relative to the axial CR and X ligands and π symmetry with respect to the equatorial L ligands. Accordingly, for W(CR)$L_nL'_{4-n}$X compounds that possess axial symmetry (L = L′: **1**−**15**, **17**−**24**, **26**, **32**) mixing of d_{xy} with X and CR orbitals is negligible (≤0.5%) while contributions from L range from 23%−34% (being highest for W(CPh)$(CO)_4$Cl). For lower-symmetry W(CR)$L_nL'_{4-n}$X compounds (L ≠ L′: **25**, **27**−**31**; L = L′, X = OPh: **16**), mixing of the d_{xy} and axial ligand orbitals is symmetry allowed and contributions from the X and CR ligands are higher, approaching a combined 22% for W(CPh)$(CNBu^t)_2(CO)_2$Br (**30**) and ranging from 3% to 12% for the other derivatives.

The energy of the d_{xy}-derived HOMO varies considerably according to the nature of the L/L′ ligands (Figure 2), as expected from the fact that it possesses substantial L parentage. The d_{xy} orbital energies span a fairly narrow range among phosphine derivatives (Δ*E*(HOMO) ≅ 0.5 eV for L/L′ = PMe_3, 1/2 dmpe, 1/2 depe, 1/2 dppe; **1**−**21**, **23**, **24**) despite their diverse CR and X ligands, but decrease significantly in compounds with stronger π-backbonding L ligand sets (Δ*E*(HOMO) ≅ 2.5 eV for L = $P(OMe)_3$, CO, $CNBu^t$; **25**−**32**). For W(CPh)$(CNBu^t)_2(CO)_2$Br (**30**) and W(CPh)$(CO)_4$Cl (**32**), which have the strongest π-backbonding L ligands, the d_{xy} orbital is sufficiently stabilized that π(W≡CR) is the HOMO; d_{xy} is the HOMO-1 for W(CPh)$(CNBu^t)_2(CO)_2$Br, for which it lies just below the HOMO (Δ*E*(HOMO/HOMO-1) = 0.13 eV), and HOMO-2 for W(CPh)$(CO)_4$Cl (Δ*E*(HOMO/HOMO-2) = 0.67 eV).

■ DISCUSSION

The first oxidation potential of W(CR)$L_nL'_{4-n}$X compounds is tunable over a 2 V range, and is observed to vary with the nature of the alkylidyne R group and X and L/L′ ligands in a manner consistent with assignment of the d_{xy} HOMO as the redox orbital. Based on the symmetry considerations outlined above, the oxidation-potential tuning should be more sensitive to the nature of L than to that of X and CR due to the equatorial π-symmetry and axial δ-symmetry of the d_{xy} orbital.

The observations are in strong accord with this expectation. The small effects on oxidation potential of changing the alkylidyne R group are illustrated by the set of W(CR)(dmpe)$_2$Cl compounds (R = H, Bu^t, Ph, C_6H_4-4-CCH, C_6H_4-4-CCSiMe$_3$; **2**, **10**, **12**, **23**, **24**), the potentials of which span a range of only 0.15 V ($E_{1/2}^{0/+}$ = −0.78 to −0.93 V). Similarly, variation of the X ligand within the series of compounds of type W(CH)(dmpe)$_2$X (X = F, Cl, Br, I, OTf, CN, Bu^n, OSiMe$_3$; **1**−**8**) shifts the oxidation potential across a range of 0.30 V ($E_{1/2}^{0/+}$ = −0.68 to −0.98 V). These narrow potential ranges are striking given the electronic diversity of the ligands within these sets—the alkylidyne ligands include saturated and unsaturated R groups, and the X ligands include hard π donors (F, OR), soft σ donors (Bu^n), and unsaturated (CN) and electron-withdrawing (OTf) ligands. In contrast, under variation of the equatorial L ligands the oxidation potentials of the W(CPh)L$_n$L′$_{4-n}$X complexes reported here (including both reversible and irreversible processes) span a range of 1.7 V (+0.66 to −0.98 V; **1**−**24**, **26**−**31**), and inclusion of the lower bound on the oxidation potential reported for W(CCCPh)(CO)$_4$Cl (>1.1 V; **32**)[8] extends this range to ~2 V. Normalizing this range for the fact that there are four equatorial ligands places the per-ligand contribution at 0.5 V/L, which exceeds those of the axial X ligands (0.30 V) and CR ligands (0.15 V). Qualitatively, the oxidation potential is observed to increase with the π-acceptor strength of the {L$_n$L′$_{4-n}$} equatorial ligand set, lying in the order (PMe$_3$)$_4$ ≅ (dmpe)$_2$ ≅ (depe)$_2$ < (dppe)$_2$ < {P(OMe)$_3$}$_4$ ≪ (tmeda)(CO)$_2$ ≅ (py)$_2$(CO)$_2$ < (dppe)(CO)$_2$ ≅ (CNBu^t)$_2$(CO)$_2$ ≪ (CO)$_4$.

The strong influence of the symmetry relationship between ligands and redox orbital on the oxidation potentials of these compounds is further highlighted by the observation that even replacing the triply bonded carbon atom of the alkylidyne ligand with germanium has little effect on the oxidation potential, as evidenced by data for the recently reported compound W(GeAr)(PMe$_3$)$_4$Cl (Ar = C_6H_3-2,6-(mesityl)$_2$).[56] This compound possesses a similar molecular structure and identical (d_{xy})^2 electron configuration as those of the tungsten−alkylidyne compounds reported here; it is reversibly oxidized at −0.91 V vs FeCp$_2^{0/+}$ (in C_6H_5F), which is remarkably close to that observed for its closest analogue W(CPh)(PMe$_3$)$_4$Cl (**17**, −0.85 V in THF; see Table 1). The fact that the potentials of these compounds are nearly identical, despite the electronic differences between carbon and germanium, is a consequence of the fact that their common redox-active d_{xy} HOMO is orthogonal to orbitals of the axial CR and GeR ligands. The near independence of the oxidation potential on the nature of the W≡E bond and on the extent of unsaturation in the alkylidyne R group also indicates that, for these compounds, the π-acceptor characteristics of the alkylidyne ligand play essentially no role in determining the oxidation potential. This finding is in contrast to the conclusion from analyses of metal−alkylidyne oxidation potentials using Pickett's model (vide supra),[51] and suggests a difficulty in developing physical interpretations of empirical ligand electrochemical parameters derived within models that do not take account of symmetry.[57]

To gain insight into the trends in first oxidation potential of the W(CR)L$_n$L′$_{4-n}$X compounds, their correspondence to calculated properties of the d_{xy}-derived redox orbital was examined. Interestingly, there is not an obvious relationship between the oxidation potential and the calculated atomic contributions to the HOMO. For example, the oxidation potentials of the W(CH)(dmpe)$_2$X compounds (X = F, Cl, Br, I, OTf, CN, Bu^n, OSiMe$_3$; **1**−**8**) span a range of 0.30 V, but the calculated contribution of the X ligand to the d_{xy} HOMO to the nearest whole percent is zero (Table 1). Similarly, the potentials of the trimethylphosphine and trimethylphosphite derivatives of type W(CPh)L$_4$Cl (L = PMe$_3$ (**17**), P(OMe)$_3$ (**26**)) differ by 0.57 V, yet possess relative W and PR$_3$ contributions to the HOMO that are within 1% of each other. Thus, there are inductive influences by the ligands on the oxidation potential that are not manifested in the atomic parentage of the d_{xy}-derived redox orbital.

The influence of the ligands on oxidation potential is better captured by the calculated energy of the d_{xy}-derived HOMO, which is found to exhibit a strong linear correlation with the first oxidation potential of W(CR)L$_n$L′$_{4-n}$X compounds **1**−**21** and **23**−**31**. The linear fit to these data, shown in Figure 3, possesses a slope of near unity: $E_{1/2}$ = −0.97(E(d_{xy})) − 5.44 (R^2 = 0.97). The root-mean-square (RMS) error of $E_{1/2}^{0/+}$, as a function of d_{xy} energy, is only 0.096 V. The compound W(CPh)(CO)$_4$Cl (**32**) is not included in the fit because the d_{xy} orbital is the HOMO-2 and lies well below the π(W≡CR) HOMO in energy (ΔE(HOMO/HOMO-2) = 0.67 eV); the data point for this compound lies >0.5 V off the linear fit (see Figure S2 in the Supporting Information), which is consistent with the oxidation involving a different redox orbital than those of the other compounds. The observation of a linear relationship between the oxidation potential and redox-orbital energy for a series of compounds is not generally expected, because the oxidation potential is a property that relates the reduced and oxidized compounds whereas the orbital energy is a property only of the reduced compound. A rigorous theoretical calculation of the solution-phase redox potential typically involves summing the gas-phase adiabatic ionization energy of the reactant with the difference between the reactant and product free energies of solvation, along the lines of a Born−Haber thermochemical cycle.[58,59] The Koopmans-

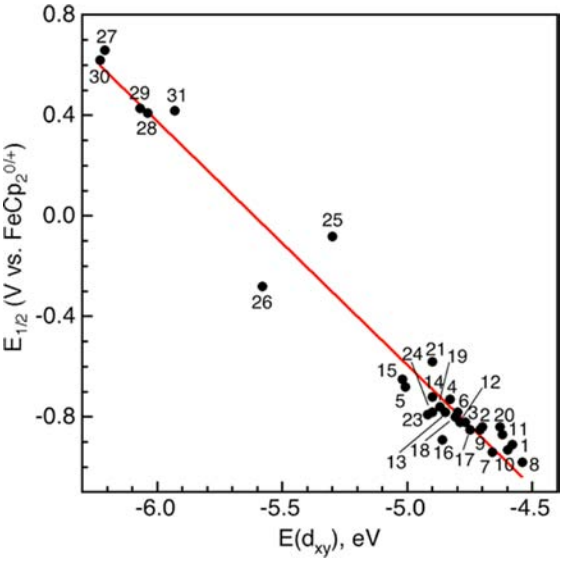


Figure 3. Relationship between the first oxidation potential and calculated d_{xy} orbital energy for W(CR)L$_n$L′$_{4-n}$X complexes. The line is a linear regression fit ($E_{1/2}$ = −0.97(E(d_{xy})) − 5.44 (R^2 = 0.97)) to complexes **1**−**21** and **23**−**31** (Table 1; excludes [W(CPh)(dppe)$_2$(NCCH$_3$)]$^+$ and W(CPh)(CO)$_4$Cl).

Theorem-like relationship between the oxidation potential and calculated gas-phase HOMO energy observed here (Figure 3) provides a considerably less-expensive computational descriptor.[60] The fact that it does not take account of differences in free energies of solvation of the oxidized and reduced species, electronic relaxation effects, and inner-sphere reorganization energies of the oxidized compounds, among other factors, suggests that each factor is either constant across the series of compounds or varies linearly with redox potential.[61]

Linear relationships between redox potentials and calculated redox-orbital energies[48,50,59,62] (and, similarly, calculated vertical ionization energies)[63] have been noted for several classes of inorganic compounds, and these form the basis for Bursten's ligand-additivity model for redox potentials.[50] However, an unusual property of the linear correlation for $W(CR)L_nL'_{4-n}X$ compounds is that the slope is approximately unity. Although this represents the idealized case, it contrasts with the more common observation that the slope differs from 1 by ±0.5 or more. While the possibility that the unity slope may reflect a fortuitous cancellation of errors cannot be excluded, the at-face-value implication of the slope that inner-sphere reorganization energies are constant or negligible across the series is chemically reasonable. Evidence for this is provided by experimental studies of the molecular structures of $(d_{xy})^2$ and $(d_{xy})^1$ $[W(CR)L_4X]^{0/+}$ redox congeners (L = phosphine).[10,14,41] Because of the axial nonbonding nature of the d_{xy} orbital, these pairs of compounds possess identical formal W≡CR and W−X bond orders and their bonding differs principally in that the extent of W→L π backbonding is weaker for the d^1 than for the d^2 configuration. The molecular structures of pairs of $[W(CPh)L_4X]^{0/+}$ complexes exhibit correspondingly small differences between the lengths of these metal−ligand bonds (Δd(W≡C) ≅ 0 Å, Δd(W−P) = 0.05−0.08 Å, Δd(W−X) = 0.02−0.05 Å), from which it may be inferred that the oxidation is characterized by a small inner-sphere reorganization energy. It is also intuitively plausible that differential solvation energies should be constant across this series of compounds, because of the similarities among their peripheral substituents.

Given the simplicity of the physical underpinnings of the linear correlation and the inclusion of both reversible and irreversible potentials, it is unsurprising that some compounds lie off the line, the most notable of which are $W(CPh)\{P(OMe)_3\}_4Cl$ (**26**) and $W\{CCH{=}C(c\text{-}C_4H_8)\}\{PPh(CH_2CH_2PPh_2)_2\}(CO)Cl$ (**25**) (Figure 3). Because this central portion of the correlation contains relatively few data points, it is difficult to pinpoint the factors that result in these differences in the absence of a full theoretical treatment of their oxidation potentials. In this context, the extensive data set reported here may be useful for benchmarking and improving these theoretical methods. Despite this caveat, the observed linear correlation provides a convenient, low-computational-cost descriptor for assigning the nature of the redox-active orbital for this class of compounds and for predicting the first oxidation potentials of other $W(CR)L_nL'_{4-n}X$ compounds.

CONCLUSIONS

In this study, we have explored the relationship between the electrochemical properties and electronic structures of complexes of the type $W(CR)L_nL'_{4-n}X$. The first oxidation potentials of these complexes can be tuned over a range of ~2 V through ligand variation. According to density functional theory calculations, the HOMO for nearly all of these compounds is derived from the d_{xy} orbital; this serves as the redox orbital for the oxidation. The HOMO is metal centered; it possesses sizable contributions from L and negligible contributions from the CR and X ligands due to its equatorial π symmetry and axial δ symmetry. Consistent with this, the oxidation potential is more sensitive to variation of the L ligands ($\Delta E_{1/2}$ = 0.5 V/L across the series) than to the CR (0.15 V) and X ligands (0.30 V). The importance of these symmetry relationships is further illustrated by the fact that the compounds $W(CPh)(PMe)_4Cl$ and $W(GeAr)(PMe_3)_4Cl$[56] are oxidized at potentials within 0.06 V of each other, despite their different W≡E ligating atoms. The oxidation potentials of $W(CR)L_nL'_{4-n}X$ complexes are linearly related to the energies of their d_{xy} HOMOs (slope ≈ 1). One implication of the unity slope is that that inner-sphere reorganization energies associated with one-electron oxidation are negligible across this series. This conclusion substantiates inferences from previous structural studies of d^2/d^1 pairs of $[W(CR)L_4X]^{0/+}$ complexes, which found that distortions of the inner coordination sphere upon oxidation are small.[10,14,41]

The linear relationship between oxidation potential and HOMO energy provides a convenient computational descriptor for predicting the redox potentials of new or unstudied $W(CR)L_nL'_{4-n}X$ compounds. In this context, efforts are underway to extend the range of redox tuning beyond 2 V, with the aim of designing photoredox chromophores with highly reducing excited states suitable for activating inert substrates such as CO_2.

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under a nitrogen atmosphere using standard glovebox and Schlenk techniques. Solvents for the synthesis of tungsten−methylidyne complexes were purified as follows: THF, toluene, diethyl ether, and 1,2-dimethoxyethane (DME) were stirred over sodium wire, distilled, and stirred over Na/K alloy, from which they were transferred under vacuum immediately prior to use; pentane was stirred sequentially over a mixture of 5% nitric acid in concentrated sulfuric acid, potassium carbonate, and calcium hydride, from which it was distilled; *N,N*-dimethylformamide (DMF) was stirred over barium oxide and then vacuum distilled; and dichloromethane and acetonitrile were stirred over CaH_2 and distilled immediately prior to use. For other purposes, solvents (HPLC grade, stored under nitrogen) were purified by passing them under nitrogen pressure through an anaerobic, stainless-steel system consisting of either two 4.5 in. × 24 in. (1 gal) columns of activated A2 alumina (acetonitrile, Et_2O, CH_2Cl_2, and THF) or one column of activated A2 alumina and one column of activated BASF R3-11 catalyst (toluene, pentane).[64] Dichloromethane-d_2 was stirred over calcium hydride and benzene-d_6 and THF-d_8 were stirred over Na/K alloy, from which they were transferred under vacuum prior to use. NMR spectra were recorded at room temperature with Bruker AF300, DRX 400, and AF500 spectrometers. Chemical shifts were measured relative to solvent resonances (^1H, ^{13}C) or external standards of 85% H_3PO_4 in D_2O (^{31}P) or $CFCl_3$ (^{19}F).

The compounds $W(CH)(dmpe)_2X$ (X = Cl,[65] Br,[66,67] Bu^n[67,68]), $W(CH)(PMe_3)_4Cl$,[65] $W(CBu^t)(PMe_3)_4Cl$,[65] $W(CPh)(dmpe)_2Br$,[14] $W(CPh)(PMe_3)_4Br$,[69] $W(CPh)(dppe)_2Cl$,[70] $[W(CPh)(dppe)_2(NCCH_3)][PF_6]$,[41] $W(CC_6H_4\text{-}4\text{-}CCR)(dmpe)_2Cl$ (R = H, $SiPr^i_3$),[7] $W(CPh)(dppe)(CO)_2Cl$,[67,71] $W(CPh)(tmeda)(CO)_2Cl$,[71] $W(CPh)(tmeda)(CO)_2Br$,[71] $W(CPh)(CNBu^t)_2(CO)_2Br$,[67,72] and $W(CPh)(py)_2(CO)_2Br$[67,71,73] were prepared according to standard procedures or simple modifications thereof. The complexes $W(CBu^t)(dmpe)_2Cl$[65] and $W(CPh)\{P(OMe)_3\}_4Cl$[74] were prepared via the two-electron reduction of $W(CR)Cl_3(dme)$[70,75] with Na/Hg amalgam in the presence of a slight excess of the phosphorus ligand, following the procedure for $W(CPh)(dppe)_2Cl$;[70] the NMR spectra of the products matched those reported for samples prepared by the original synthetic procedures. The compounds W(CH)(dmpe)$_2$F, W(CH)(dmpe)$_2$I, W(CH)(dmpe)$_2$(OTf), W(CH)(dmpe)$_2$(CN), W(CH)(dmpe)$_2$(OSiMe$_3$), W(CPh)(dmpe)$_2$Cl, W(CPh)(dmpe)$_2$(OTf), W(CPh)(dmpe)$_2$(OPh), and W(CPh)(depe)$_2$Cl were prepared by standard reductive or ligand-substitution reactions similar to those reported for the analogous compounds above; full details of their synthesis and characterization are provided in the Supporting Information. Tetrabutylammonium hexafluorophosphate was prepared by the standard procedure,[76] recrystallized three times from 95% ethanol, and dried under vacuum at 80−110 °C for a minimum of 24 h. Ferrocene was recrystallized three times from 95% ethanol and then sublimed under vacuum.[77] All other chemicals were reagent grade or comparable quality and were used as-received. Elemental analyses were performed by Onieda Research Services (Whitesboro, NY) or Midwest Microlab, LLC (Indianapolis, IN).

Electrochemical Measurements. Electrochemical experiments were performed at room temperature under a nitrogen atmosphere in a glovebox using a Bioanalytical Systems 100 B/W Electrochemical Workstation and C3 cell stand. A three-electrode configuration was used, consisting of a working electrode (platinum disk, area = 0.2 cm^2; gold disk, area = 0.02 cm^2; or glassy carbon, area = 0.07 cm^2), Pt-wire auxiliary electrode, and Ag-wire quasi-reference electrode. The electrodes were polished prior to each experiment. Samples consisted of (0.3−5.0) × 10^{-3} M analyte in solution containing 0.1−0.3 M [NBu$_4$][PF$_6$]. Cyclic voltammetric experiments were conducted over a range of scan rates (0.010−10 V s^{-1}) to establish electrochemical reversibility, where observed. Ferrocene was used as an internal electrode-potential standard;[78] under the experimental conditions, the FeCp$_2^{0/+}$ couple exhibited $i_{pc}/i_{pa} \cong 1$ and ΔE_p = 0.09−0.27 V. For selected experiments in CH$_2$Cl$_2$ or MeCN solution, the reference electrode employed the Ag/AgCl$^+$ couple, with a saturated solution of AgNO$_3$ filling the reference electrode chamber. Peak currents were determined from scans that extended at least 0.30 V beyond the peak potentials before reaching the switching potential.

Computational Studies. Density functional theory calculations were performed using Gaussian 09.[79] Calculations employed the hybrid density functional B3P86,[80] which according to benchmarks ranks among the best functionals for predicting the molecular structures of third-row transition-metal complexes.[81] Geometries were optimized without symmetry constraints. No imaginary frequencies were obtained in subsequent vibrational calculations, confirming that the optimized structures (see Table S5 in the Supporting Information) reside at potential-surface minima. For atoms H through Cl, Dunning/Huzinaga full double-ζ basis sets with *p*-type polarizations on H and *d*-type polarizations on all other atoms were used.[82] The LANL2DZ double-ζ basis sets and effective-core-potentials (ECP)[83] were used for W, Br, and I. To establish the validity of these basis sets, calculations using triple-ζ quality basis sets were performed on six compounds;[67] the double-ζ and triple-ζ quality basis sets gave molecular structures that are in satisfactory agreement with each other (see Table S3 in the Supporting Information). Atomic parentages of orbitals based on Mulliken population analysis were calculated using the program AOMix;[84] similar results were obtained with the NBO program[85] for a test set of four compounds (see Table S4 in the Supporting Information).[67]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures and characterization data for W(CR)L$_n$L′$_{4-n}$X complexes; electrode potentials for reductions and second oxidations; calculated orbital energies and atomic contributions for frontier orbitals; comparisons of calculated energies and bond distances using double-ζ and triple-ζ-quality basis sets; comparisons of orbital atomic contributions using AOMix and NBO procedures; and Cartesian coordinates of DFT-optimized geometries of W(CR)L$_n$L′$_{4-n}$X complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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