Title

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19-Electron Intermediates in the Ligand Substitution of $CpW(CO)_3^\bullet$ with a Lewis Base

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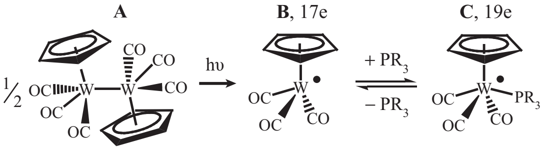
Odd-electron species are important intermediates in organometallic chemistry, participating in a variety of catalytic and electron-transfer reactions which produce stable even-electron products.[1-3] While electron deficient 17-electron (17e) radicals have been well characterized, the possible existence of short-lived 19-electron (19e) radicals has been a subject of continuing investigation. 19e radicals have been postulated as intermediates in the photochemical ligand substitution and disproportionation reactions of organometallic dimers containing a single metal-metal bond,[4-7] yet the reactions of these intermediates on diffusion-limited time scales (ns–μs) have never been directly observed. This study resolves the 19e dynamics in the ligand substitution of 17e radicals $CpW(CO)_3^\bullet$ (Cp = C_5H_5) with the Lewis base $P(OMe)_3$, providing the first complete description 19e reactivity.

We recently investigated the ultrafast dynamics of $CpW(CO)_3^\bullet$ (**B**) with three Lewis bases PR_3 (R = OMe, Bu, Ph) and directly monitored the formation of 19e radicals $CpW(CO)_3PR_3^\bullet$ (**C**) on a picosecond time scale.[8,9] As depicted below, irradiation of $[CpW(CO)_3]_2$ (**A**) at visible wavelengths results in metal-metal bond homolysis and formation of two 17e radicals **B**. Coordination of a strong Lewis base PR_3 with **B** generates 19e radicals **C** that are in an equilibrium with **B.**



(1)

Although some 17e and 19e radicals disproportionate by an in-cage mechanism on a picosecond time scale,[8,9] the majority of the 19e species **C** persist beyond 1 ns; the subsequent reactions are resolved in this study.

Figure 1 shows time-resolved transient difference spectra in the CO stretching region on nanosecond (Figure 1a) and microsecond (Figure 1b) time scales for 1.5 mM **A** and 85 mM $P(OMe)_3$ in CH_2Cl_2. Irradiation at 532 nm with a Nd:YAG laser generated the radical species in equation 1, and subsequent reactions were probed with step-scan FTIR spectroscopy. Details of the experimental setup have been described elsewhere.[10] Negative absorptions in Figure 1 originate from the bleaching of reactant species while positive absorptions correspond to products formed after photolysis. Peak assignments are based on literature data[8,9,11] and density functional theory (DFT) calculations[12] (see the Supporting Information (SI) for details).

On the nanosecond time scale, two strong parent bleaches appear at 1901 and 1955 cm^{-1} from the *anti*-isomer of **A**.[13] A weak product absorption from the *gauche*-isomer of **A** is also apparent at 2010 cm^{-1}, indicating that within 25 ns a small portion of the 17e $CpW(CO)_3^\bullet$ radicals **B** have dimerized to regenerate **A**.[15] Peaks from **B** appear at 1880 and 1994 cm^{-1} while a single peak from the 19e species **C** is visible at 1855 cm^{-1}. The 17e and 19e species (**B**, **C**) are in equilibrium ($K_{eff} \cong 3.4\ M^{-1}$) and decay concomitantly,[16] with monoexponential fits to **C** (see Figure 2) and **B** giving decay times of 277 ± 18 ns and 288 ± 10 ns, respectively.[17] Peaks from the disproportionated products $CpW(CO)_3^-$ (**G**) and $CpW(CO)_3P(OMe)_3^+$ (**F**) are observed at 1775 and 2065 cm^{-1} and grow in with rise times of 199 ± 36 and 265 ± 78 ns, respectively. The intensity of these peaks indicate that the disproportionation yield is low and the reaction is a minor pathway (< 20%) at this concentration of $P(OMe)_3$ (85 mM).[18]

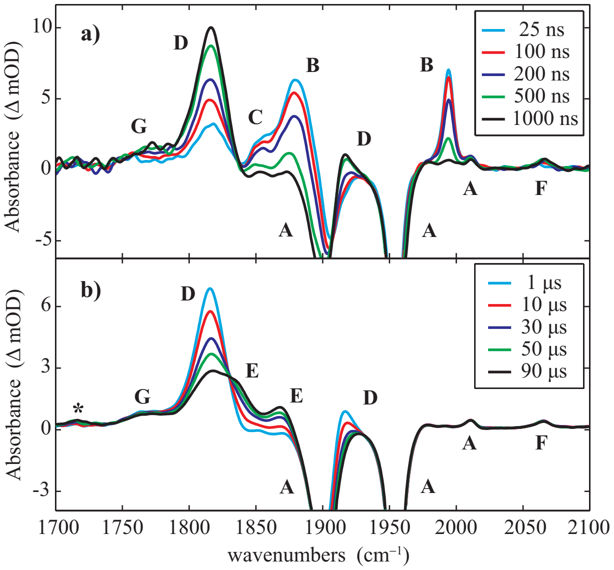


Figure 1. Time-resolved IR spectra in the CO stretching region on a) nanosecond and b) microsecond time scales[14] for 1.5 mM $[CpW(CO)_3]_2$ and 85 mM $P(OMe)_3$ in CH_2Cl_2.

Surprisingly, in addition to the products from disproportionation, two new peaks labeled **D** grow in at 1815 and 1916 cm^{-1}. Kinetic fits to the data yield rise times of 280 ± 9 ns (Figure 2) and 274 ± 18 ns, respectively. The correlation of these time constants with the decay of 17e and 19e species in addition to an isosbestic point at 1838 cm^{-1} indicate that species **D** is formed from the 19e species **C**. Based on the kinetics and peak positions, **D** is assigned to the 17e radical $CpW(CO)_2P(OMe)_3^\bullet$. DFT calculations predict a shift in CO stretching frequency from **B** to

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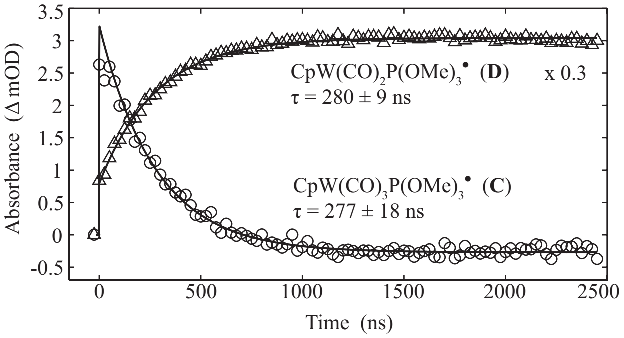


Figure 2. Kinetic data and monoexponential fits (solid lines) for $CpW(CO)_3P(OMe)_3^\bullet$ (**C**) and $CpW(CO)_2P(OMe)_3^\bullet$ (**D**) on the nanosecond time scale. Kinetics for **D** are scaled by 0.3 for clarity.

D of 60 and 77 cm^{-1} for the lower and higher frequency modes, respectively, which are in excellent agreement with the experimentally observed shifts of 65 and 78 cm^{-1} (see SI for details). The major reaction pathway of 19e species $CpW(CO)_3P(OMe)_3^\bullet$ (**C**) on the nanosecond time scale is thus found to be spontaneous loss of a carbonyl group to form the 17e species **D**.[19]

Assuming **B** and **C** are in equilibrium[16] and the only reaction pathway of these radicals is formation of **D**, the dynamics of **C** (or **B**) should exhibit a monoexponential decay, as shown in Figure 2, according to the following kinetic equation:

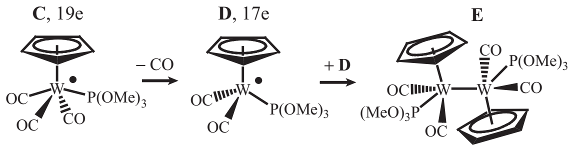
$$[\mathbf{C}] = [\mathbf{C}]_0 e^{\frac{-k_{\mathrm{diss}}}{1+(K_{\mathrm{eff}}[P(OMe)_3])^{-1}}t} \tag{2}$$

where $[\mathbf{C}]_0$ is the initial concentration of **C**, K_{eff} is the effective **B**/**C** equilibrium constant,[16] and k_{diss} is the rate constant for CO dissociation from **C**. A time constant of 280 ± 9 ns implies a value of $k_{diss} = (1.6 \pm 0.3) \times 10^7\ s^{-1}$. Using simple transition state theory, the rate constant suggests a barrier of 7.6 ± 0.3 kcal/mol for spontaneous loss of CO from the 19e species **C**.[20]

This result is surprising since dissociation of a carbonyl typically requires ca. 40 kcal/mol of energy in even-electron transition metal complexes,[21] yet the process appears to be thermodynamically favorable in the case of this 19e species. The lability of the metal-CO bond in **C** most likely arises from the population of a metal-to-ligand anti-bonding orbital by the “19th” electron, which weakens the metal-CO bond.[3] Numerous studies have shown that the ligand substitution reactions of 17e radicals such as $CpM(CO)_3^\bullet$ (M = Cr, W), $CpFe(CO)_2^\bullet$, $M(CO)_5^\bullet$ (M = Mn, Re), or $V(CO)_6^\bullet$ proceed by an associative mechanism,[1,5,6,22] but this study is the first evidence that a 19e species is an intermediate rather than transition-state in the ligand substitution reaction.[23] In contrast to this observation, nanosecond time resolved studies on the similar dimer $[CpFe(CO)_2]_2$ monitored the ligand substitution of $CpFe(CO)_2^\bullet$ with $P(OMe)_3$ but found no evidence for a 19e intermediate;[22] the intermediates were likely present but too low in concentration to be detected.

On the microsecond time scale (see Figure 1b), the 17e radical **D** decays while new absorptions appear at 1835 and 1868 cm^{-1} which are assigned to the ligand substitution dimer $[CpW(CO)_2P(OMe)_3]_2$ (**E**) based on DFT calculations and literature values for the Mo containing analog of **E**.[24] The decay of **D** and the rise of **E** are correlated, as evident by the isosbestic point at 1831 cm^{-1} in Figure 1b; thus, the only reaction on the microsecond time scale is the dimerization of **D** to form **E**.[14]

In summary, the primary reaction of 19e intermediates (**C**) on diffusion-limited time scales is the spontaneous loss of CO to form ligand substitution products:



(3)

This type of reactivity is likely to be typical for 17e/19e radicals in Lewis bases, and experiments are currently in progress to examine the reaction with a variety of transition metal complexes.[25]

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Supporting Information Available: Complete reference 12, table with observed and calculated DFT frequencies for relevant species, time-resolved spectra in neat CH_2Cl_2, a description of the kinetic analysis, and a discussion of the peak labeled * in Figure 1b.

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(12) DFT calculations have been carried out with Gaussian 03, revision B.04 (Frisch, et al. Gaussian, Inc., Pittsburgh, PA, 2003) applying the B3LYP functional and generic basis sets (LANL2DZ effective core potential for W and 6-31g(d) or 6-31+g(d) basis sets for all other atoms).
(13) Note that the bleaches for **A** are not entirely displayed in Figure 1 and that the dynamics of **A** are due to spectral overlap of **B** and **F** with the bleach at 1901 cm^{-1} and overlap of a second peak from **C** with the bleach at 1955 cm^{-1}.
(14) See the SI for a discussion of the peak labeled *, which likely arises from $CpW(CO)_2P(OMe)_3^-$ and is formed by electron transfer from **C** to **D**.
(15) In the presence of organic halides such as CCl_4, Cl atom abstraction by **B** may occur; however, spectral data in neat CH_2Cl_2 (see SI) indicate that Cl atom abstraction does not occur on the time scale of this experiment.
(16) Since the concentrations of radical species **B** and **C** are not constant, the two species cannot be in dynamic equilibrium. The reaction quotient Q, however, maintains a constant value over the lifetimes of these radical species so that they appear in quasi-equilibrium. Assuming the same oscillator strength for the peaks at 1885 cm^{-1} (**C**) and 1994 cm^{-1} (**B**), an "effective" equilibrium constant can be defined and is found to have a value of $K_{eff} = 3.4 \pm 0.4\ M^{-1}$.
(17) Errors correspond to 95% confidence intervals.
(18) See the SI for a further discussion of disproportionation. The mechanism is a subject of continuing investigation in our laboratory.
(19) Results on the ultrafast time scale (refs. 8 and 9) rule out the possibility that **D** is formed directly from **B** since coordination of $P(OMe)_3$ with **B** was directly observed in these studies and no evidence for species **D** was found.
(20) Assuming simple transition state theory, $k_{diss} = (k_BT/h)\exp(-\Delta G^\ddagger/k_BT)$, where k_B is the Boltzmann constant, h Planck's constant, T ambient temperature, and $\Delta G^\ddagger$ the free energy of activation.
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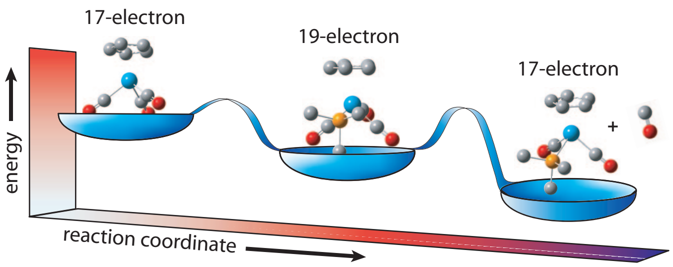

The photochemical reactions of $[CpW(CO)_3]_2$ with the Lewis base $P(OMe)_3$ are examined on the nanosecond and microsecond time scales using step-scan FTIR spectroscopy. Photolysis at 532 nm produces the 17-electron (17e) radicals $CpW(CO)_3^{\bullet}$, which are in equilibrium with the 19-electron (19e) radicals $CpW(CO)_3P(OMe)_3^{\bullet}$ on the nanosecond time scale. The reactions of the 19e radical are directly observed for the first time; the major reaction pathway is spontaneous loss of a carbonyl to form the 17e species $CpW(CO)_2P(OMe)_3^{\bullet}$, with a barrier of 7.6 ± 0.3 kcal/mol for this process. The minor reaction pathway (<20%) at this concentration of $P(OMe)_3$ (85 mM) is disproportionation to form the products $CpW(CO)_3P(OMe)_3^+$ and $CpW(CO)_3^-$. On the microsecond time scale, the 17e radicals $CpW(CO)_2P(OMe)_3^{\bullet}$ dimerize to form the ligand substitution product $[CpW(CO)_2P(OMe)_3]_2$. These results indicate that the 19e species is a stable intermediate rather than transition-state in the ligand substitution reaction, and this type of reactivity is likely to be typical of 17e organometallic radicals which undergo associative substitution mechanisms.

Supporting Information

19-Electron Intermediates in the Ligand Substitution of $CpW(CO)_3^\bullet$ with a Lewis Base

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I. Calculated and observed vibrational frequencies

Table S1 contains density functional theory (DFT) calculated vibrational frequencies and observed frequencies for relevant species in the photochemistry of $[CpW(CO)_3]_2$. All calculations were carried out using the program package Gaussian03 with the B3LYP hybrid method.[1] It is composed of Becke's three-parameter exchange-functional[2] and the Lee-Yang-Parr non-local correlation functional.[3] Generic basis sets consist of the double-zeta LANL2DZ in conjunction with the relativistic effective core potential (ECP) of Hay and Wadt[4] for tungsten and 6-31g(d) or 6-31+g(d) basis sets for all other atoms. The Hessian matrices were calculated at the stationary points in order to ensure that true minima on the potential energy hypersurfaces had been found and the harmonic vibrational frequencies for CO groups, appropriately scaled, are contained in Table S1.

Table S1. Observed and DFT calculated frequencies of relevant species in the photochemistry of $[CpW(CO)_3]_2$ with the Lewis base $P(OMe)_3$

	calculated*	observed
anti-$[CpW(CO)_3]_2$ (**A**)	1892 (0.0), 1915 (0.2), 1924 (0.8), 1932 (0.0), 1968 (1.0), 2000 (0.0)[a]	1901 (s), 1955(s)
gauche-$[CpW(CO)_3]_2$ (**A**)	1902 (0.2), 1909 (0.3), 1937 (0.4), 1944 (0.0), 1970 (0.6), 2014 (0.4)[a]	2010 (w)
$CpW(CO)_3^\bullet$ (17e, **B**)	1906 (0.6), 1907 (0.4), 1987 (0.3)[b]	1880 (s), 1994 (s)
$CpW(CO)_3P(OMe)_3^\bullet$ (19e, **C**)	1867 (0.5), 1878 (0.4), 1961 (0.4)[b]	1855 (m)
$CpW(CO)_2P(OMe)_3^\bullet$ (17e, **D**)	1847 (0.6), 1910 (0.3)[b]	1815 (s), 1916 (m)
anti-$[CpW(CO)_2P(OMe)_3]_2$ (**E**)	1839 (0.0), 1871 (0.7), 1882 (0.2), 1920 (0.0)[a]	1835 (m), 1868 (m)
gauche-$[CpW(CO)_2P(OMe)_3]_2$ (**E**)	1847 (0.2), 1862 (0.6), 1875 (0.0), 1929 (0.2)[a]	
$CpW(CO)_3P(OMe)_3^+$ (18e, **F**)	1977 (0.5), 2000 (0.2), 2057 (0.3)[b]	2065 (w)
$CpW(CO)_3^-$ (18e, **G**)	1785 (0.6), 1786 (0.7), 1880 (0.4)[b]	1775 (w)
$CpW(CO)_2P(OMe)_3^-$ (18e)	1753 (0.6), 1815 (0.4)[b]	1715 (w)
$CpW(CO)_3Cl$ (18e)	1966 (0.3), 1985 (0.5), 2046 (0.2)[a]	not observed
anti-$[CpW(CO)_3]_2^-$	1839 (0.1), 1842 (0.0), 1862 (0.0), 1869 (0.8), 1881 (1.9), 1940 (0.0)[a]	not observed

*calculated frequencies are scaled by the factor 0.9614[5]; [a] basis set 6-31g(d), [b] basis set 6-31+g(d); relative intensities are given in parentheses (w = weak, m = medium, s = strong; calculated intensities are normalized with respect to the 1968 cm^{-1} mode of *anti*-$[CpW(CO)_3]_2$).

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II. Spectral data in neat CH_2Cl_2

Figure S1 contains time-resolved transient difference spectra for 1.5 mM $[CpW(CO)_3]_2$ (**A**) in neat CH_2Cl_2 on the microsecond time scale. The only reaction is observed to be dimerization of the 17-electron (17e) radicals $CpW(CO)_3^\bullet$ (**B**) to regenerate $[CpW(CO)_3]_2$ (**A**), as evident by the isosbestic points at 1901, 1976, and 2004 cm^{-1}. Dimerization of the radicals **B** causes recovery of the bleaches for *anti* – **A** at 1907 and 1955 cm^{-1}. The radicals also dimerize to form *gauche* – **A** in a nonequilibrium concentration, causing the rise of the product peak at 2010 cm^{-1}. On a longer time scale, *gauche* – **A** should isomerize to reform *anti* – **A**. Note that no peaks attributable to $CpW(CO)_3Cl$, the product from Cl atom abstraction of CH_2Cl_2 by **B**, are observed on the time scale of this experiment.[6]

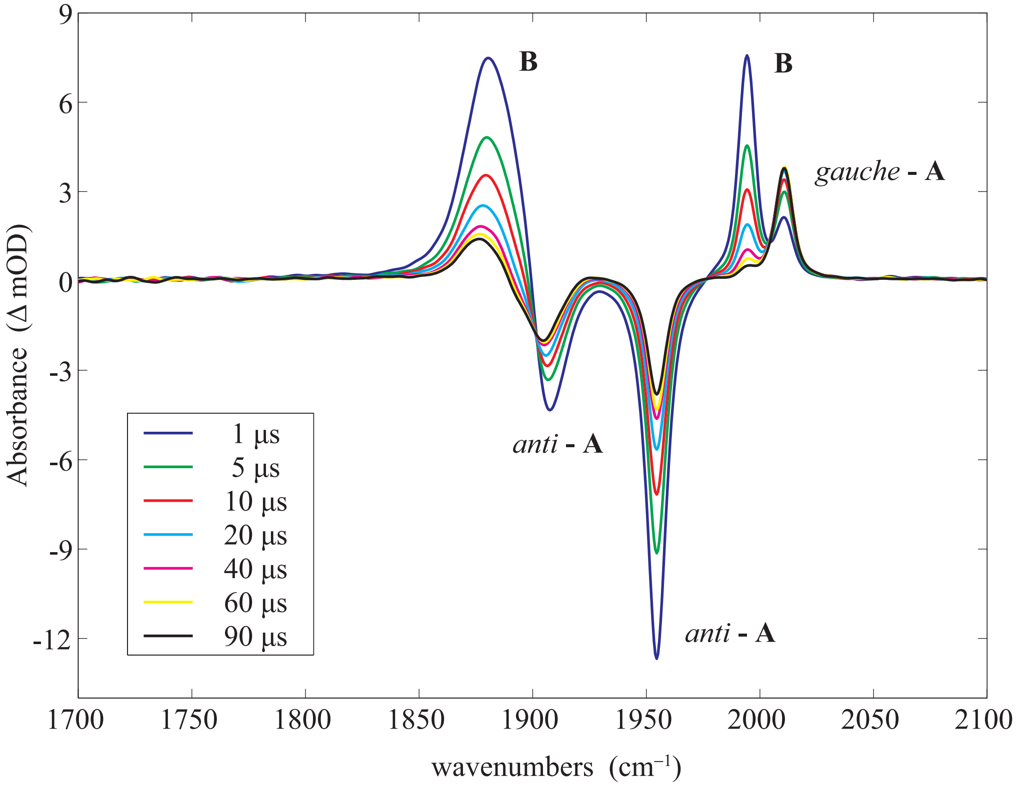
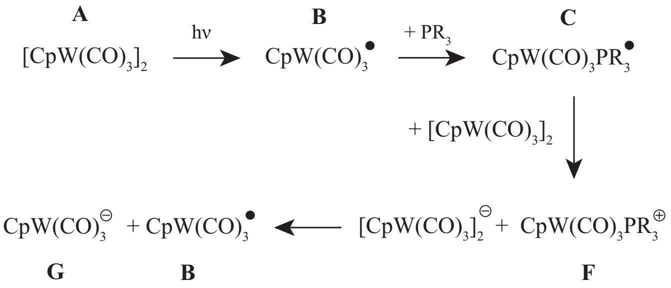


Figure S1. Time-resolved IR spectra in the CO stretching region on the microsecond time scale for 1.5 mM $[CpW(CO)_3]_2$ (**A**) in neat CH_2Cl_2.

III. Disproportionation dynamics

Disproportionation of $[CpW(CO)_3]_2$ (**A**) in the presence of Lewis bases PR_3 forms the products $CpW(CO)_3PR_3^+$ (**F**) and $CpW(CO)_3^-$ (**G**). In our previous investigations on the ultrafast time scale, we observed the formation of disproportionated products by in-cage electron transfer from the 19-electron (19e) species **C** to the 17e species **B**.[7,8] On diffusion-limited time scales (ns-µs), however, disproportionation may occur by the same mechanism we observed on the ultrafast time scale or by a more complex mechanism as proposed by Tyler et al.

Scheme S1. Mechanism of disproportionation as proposed by Tyler[9]



and shown in Scheme S1.[9] In Tyler's mechanism, disproportionation is still initiated by the 19e species **C**: electron transfer from **C** to **A** leads to formation of the cationic disproportionated product **F** and a negatively charged parent dimer $[CpW(CO)_3]_2^-$; successive metal-metal bond rupture of the negatively charged dimer yields a 17e radical **B** and the anionic disproportionated product **G**.

As shown in Figure 1 of the communication, we observe the formation of disproportionated products on the nanosecond time scale, yet no absorption attributable to the negatively charge dimer $[CpW(CO)_3]_2^-$ (see Table S1 for calculated vibrational frequencies) is observed in the experiment. These results do not discredit the mechanism proposed by Tyler et al. since the intermediate $[CpW(CO)_3]_2^-$ may be too short-lived to build up a population which we can detect with the experimental apparatus. Further experiments are in progress to examine the disproportionation mechanism in detail as well as the competition between ligand substitution and disproportionation with various Lewis bases.[10]

IV. Kinetic analysis

Kinetic data were derived from the spectral data at different time steps. The absorbance values within distinct spectral ranges[11] for the various chemical species were averaged at each individual time delay. The kinetics for each species were then fit to an exponential convoluted with a Gaussian to account for limited time resolution and accurately reflect the instrument response function.

V. Formation of $CpW(CO)_2P(OMe)_3^-$

The weak peak at 1715 cm^{-1} labeled * in Figure 1b of the communication is tentatively assigned to $CpW(CO)_2P(OMe)_3^-$. DFT calculations (see Table S1) predict a shift in CO stretching frequency from $CpW(CO)_2P(OMe)_3^\bullet$ (**D**) to $CpW(CO)_2P(OMe)_3^-$ of 94 cm^{-1}, which is in excellent agreement with the experimentally observed shift of 100 cm^{-1}. Electron transfer from the 19e species $CpW(CO)_3P(OMe)_3^\bullet$ (**C**) to **D** would form this new species as well as the cationic disproportionated product $CpW(CO)_3P(OMe)_3^+$ (**F**). Although no change in the peak for **F** is observable on the microsecond time scale, DFT calculations indicate that this peak possesses half the oscillator strength of the peak from $CpW(CO)_2P(OMe)_3^-$, so no change in intensity would likely be observable within experimental noise.

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Complete reference 12:

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(11) Spectral ranges are as follows: $CpW(CO)_3$ 1865-1875 cm^{-1}; $CpW(CO)_3P(OMe)_3$ 1850-1860 cm^{-1}, $CpW(CO)_2P(OMe)_3$ 1815 cm^{-1}; $CpW(CO)_3^-$ 1750-1780 cm^{-1}; $CpW(CO)_3P(OMe)_3^+$ 2045-2085 cm^{-1}.