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

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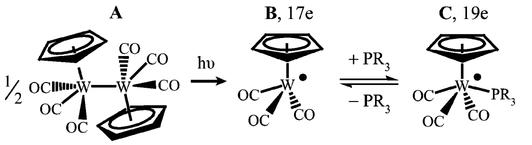
Odd-electron species are important intermediates in organometallic chemistry, participating in a variety of catalytic and electron-transfer reactions which produce stable even-electron products.[1−3] While electron-deficient 17-electron (17e) radicals have been well characterized, the possible existence 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 (nanosecond to microsecond) 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 of 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 eq 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).

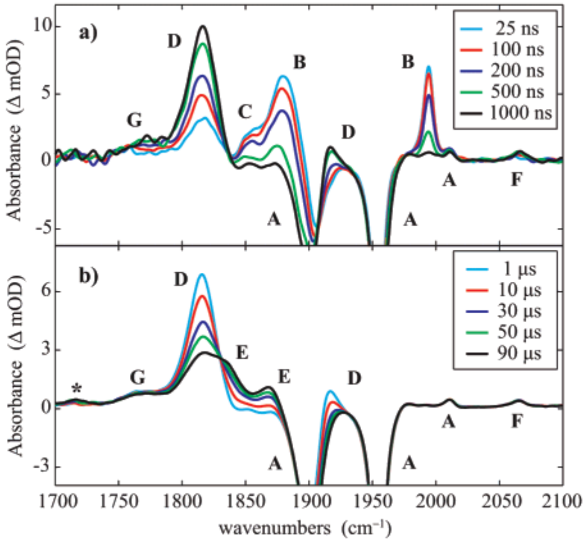


Figure 1. Time-resolved IR spectra in the CO stretching region on (a) nanosecond and (b) microsecond time scales[14] for 1.5 mM $[CpW(CO)_3]_2$ and 85 mM $P(OMe)_3$ in CH_2Cl_2.

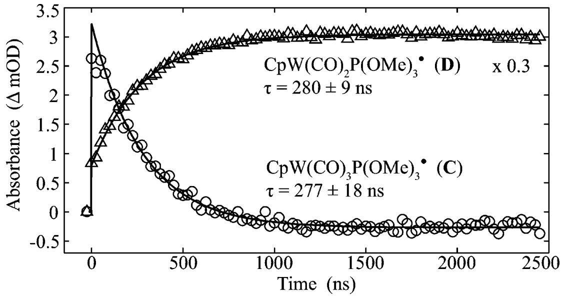


Figure 2. Kinetic data and monoexponential fits (solid lines) for $CpW(CO)_3P(OMe)_3^\bullet$ (**C**) and $CpW(CO)_2P(OMe)_3^\bullet$ (**D**) on the nanosecond time scale. Kinetics for **D** are scaled by 0.3 for clarity.

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 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 indicates that the disproportionation yield is low and the reaction is a minor pathway (<20%) at this concentration of $P(OMe)_3$ (85 mM).[18]

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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 (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} indicates that species **D** is formed from the 19e species **C**. On the basis of 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 **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 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 subsequent reaction of these radicals involves 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:

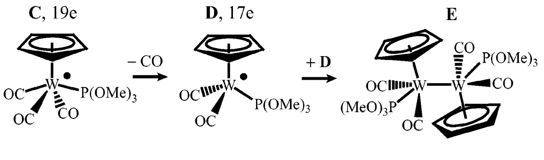
$$[\mathbf{C}] = [\mathbf{C}]_0 \exp\{-k_{\mathrm{diss}}t/[1 + (K_{\mathrm{eff}}[P(OMe)_3])^{-1}]\} \qquad (2)$$

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 $k_{\mathrm{diss}} = (1.6 \pm 0.3) \times 10^7\ s^{-1}$. 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 emphasizes the difference between even- and odd-electron species; dissociation of a carbonyl from even-electron transition metal complexes typically requires ca. 40 kcal/mol of energy,[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 antibonding orbital by the "19th" electron, which weakens the metal−CO bonds.[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 a 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 analogue 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.

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Supporting Information Available: Complete ref 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. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217−1227 and references therein.
(2) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189−1216.
(3) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325−331.
(4) Philbin, C. E.; Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 4434−4436.
(5) Turaki, N. N.; Huggins, J. M. *Organometallics* **1986**, *5*, 1703−1706.
(6) Trogler, W. C. *Int. J. Chem. Kinet.* **1987**, *19*, 1025−1047.
(7) Bitterwolf, T. E. *Coord. Chem. Rev.* **2001**, *211*, 235−254.
(8) Kling, M. F.; Cahoon, J. F.; Glascoe, E. A.; Shanoski, J. E.; Harris, C. B. *J. Am. Chem. Soc.* **2004**, *126*, 11414−11415.
(9) Cahoon, J. F.; Kling, M. F.; Schmatz, S.; Harris, C. B. *J. Am. Chem. Soc.* **2005**, *127*, 12555−12565.
(10) Sun, H.; Frei, H. *J. Phys. Chem. B* **1997**, *101*, 205−209.
(11) Virrels, I. G.; George, M. W.; Johnson, F. P. A.; Turner, J. J.; Westwell, J. R. *Organometallics* **1995**, *14*, 5203−5208.
(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 $K_{\mathrm{eff}} = 3.4 \pm 0.4\ M^{-1}$. Further assuming $K_{\mathrm{eff}} \cong K_{\mathrm{eq}}$ and using the thermodynamic relation $\Delta G^\circ = -RT\ln(K_{\mathrm{eq}})$, where ΔG° is the change in standard Gibbs energy, K_{eq} the equilibrium constant, R the ideal gas constant, and T the absolute temperature, the value for K_{eff} gives $\Delta G^\circ = -2.4 \pm 0.3$ kcal/mol. Thus, the 19e species **C** is estimated to be 2−3 kcal/mol lower in energy than the 17e species **B**, likely due to an increase in bond order of 0.5 between the two species (see ref 3).
(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, $k_{\mathrm{diss}} = (k_BT/h)\exp(-\Delta G^\ddagger/k_BT)$, where k_B is the Boltzmann constant, h Planck's constant, T ambient temperature, and $\Delta G^\ddagger$ the free energy of activation.
(21) Rosa, A.; Baerends, E. J.; van Gisbergen, S. J. A.; van Lenthe, E.; Groeneveld, J. A.; Snijders, J. G. *J. Am. Chem. Soc.* **1999**, *121*, 10356−10365.
(22) Dixon, A. J.; Gravelle, S. J.; Vandeburgt, L. J.; Poliakoff, M.; Turner, J. J.; Weitz, E. *J. Chem. Soc., Chem. Commun.* **1987**, 1023−1025.
(23) Note that concentration-dependent studies would not reveal whether the 19e species is an intermediate or transition state since the same kinetic behavior would be expected in both cases.
(24) Haines, R. J.; Nolte, C. R. *J. Organomet. Chem.* **1970**, *24*, 725−736.

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