

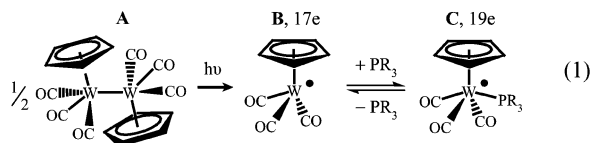
19-Electron Intermediates in the Ligand Substitution of  $\text{CpW}(\text{CO})_3^*$  with a Lewis BaseJames F. Cahoon,<sup>†</sup> Matthias F. Kling,<sup>†,‡</sup> Karma R. Sawyer,<sup>†</sup> Heinz Frei,<sup>§</sup> and Charles B. Harris<sup>\*,†</sup>

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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.<sup>1–3</sup> 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,<sup>4–7</sup> 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  $\text{CpW}(\text{CO})_3^*$  (Cp =  $\text{C}_5\text{H}_5$ ) with the Lewis base  $\text{P}(\text{OMe})_3$ , providing the first complete description of 19e reactivity.

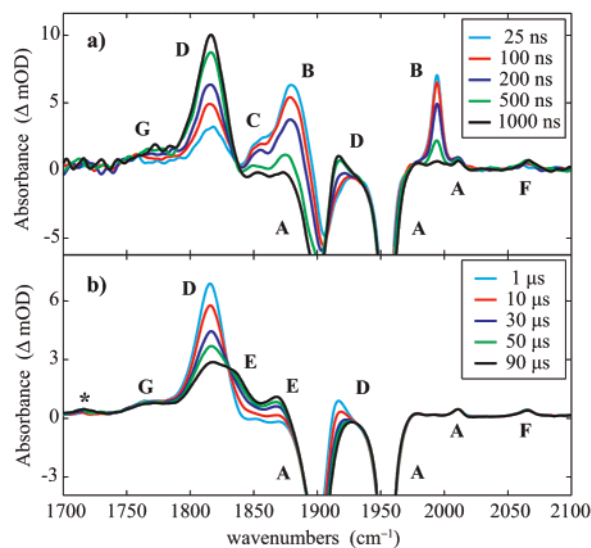
We recently investigated the ultrafast dynamics of  $\text{CpW}(\text{CO})_3^*$  (B) with three Lewis bases  $\text{PR}_3$  (R = OMe, Bu, Ph) and directly monitored the formation of 19e radicals  $\text{CpW}(\text{CO})_3\text{PR}_3^*$  (C) on a picosecond time scale.<sup>8,9</sup> As depicted below,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



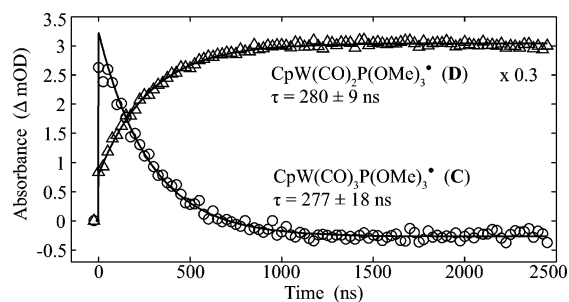
Although some 17e and 19e radicals disproportionate by an in-cage mechanism on a picosecond time scale,<sup>8,9</sup> the majority of the 19e species C persist beyond 1 ns; the subsequent reactions are resolved in this study.

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  $\text{P}(\text{OMe})_3$  in  $\text{CH}_2\text{Cl}_2$ . 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.<sup>10</sup> 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<sup>8,9,11</sup> and density functional theory (DFT) calculations<sup>12</sup> (see the Supporting Information (SI) for details).

On the nanosecond time scale, two strong parent bleaches appear at 1901 and 1955  $\text{cm}^{-1}$  from the *anti*-isomer of A.<sup>13</sup> A weak product



**Figure 1.** Time-resolved IR spectra in the CO stretching region on (a) nanosecond and (b) microsecond time scales<sup>14</sup> for 1.5 mM  $[\text{CpW}(\text{CO})_3]_2$  and 85 mM  $\text{P}(\text{OMe})_3$  in  $\text{CH}_2\text{Cl}_2$ .



**Figure 2.** Kinetic data and monoexponential fits (solid lines) for  $\text{CpW}(\text{CO})_3\text{P}(\text{OMe})_3^*$  (C) and  $\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3^*$  (D) on the nanosecond time scale. Kinetics for D are scaled by 0.3 for clarity.

absorption from the *gauche*-isomer of A is also apparent at 2010  $\text{cm}^{-1}$ , indicating that within 25 ns a small portion of the 17e  $\text{CpW}(\text{CO})_3^*$  radicals B have dimerized to regenerate A.<sup>15</sup> Peaks from B appear at 1880 and 1994  $\text{cm}^{-1}$ , while a single peak from the 19e species C is visible at 1855  $\text{cm}^{-1}$ . The 17e and 19e species (B, C) are in equilibrium ( $K_{\text{eff}} \approx 3.4 \text{ M}^{-1}$ ) and decay concomitantly,<sup>16</sup> with monoexponential fits to C (see Figure 2) and B giving decay times of  $277 \pm 18$  and  $288 \pm 10$  ns, respectively.<sup>17</sup> Peaks from the disproportionated products  $\text{CpW}(\text{CO})_3^-$  (G) and  $\text{CpW}(\text{CO})_3\text{P}(\text{OMe})_3^+$  (F) are observed at 1775 and 2065  $\text{cm}^{-1}$  and grow in with rise times of  $199 \pm 36$  and  $265 \pm 78$  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  $\text{P}(\text{OMe})_3$  (85 mM).<sup>18</sup>

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Surprisingly, in addition to the products from disproportionation, two new peaks labeled **D** grow in at 1815 and 1916  $\text{cm}^{-1}$ . Kinetic fits to the data yield rise times of  $280 \pm 9$  (Figure 2) and  $274 \pm 18$  ns, respectively. The correlation of these time constants with the decay of 17e and 19e species in addition to an isosbestic point at 1838  $\text{cm}^{-1}$  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  $\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3^{\bullet}$ . DFT calculations predict a shift in CO stretching frequency from **B** to **D** of 60 and 77  $\text{cm}^{-1}$  for the lower and higher frequency modes, respectively, which are in excellent agreement with the experimentally observed shifts of 65 and 78  $\text{cm}^{-1}$  (see SI for details). The major reaction of 19e species  $\text{CpW}(\text{CO})_3\text{P}(\text{OMe})_3^{\bullet}$  (**C**) on the nanosecond time scale is thus found to be spontaneous loss of a carbonyl group to form the 17e species **D**.<sup>19</sup>

Assuming **B** and **C** are in equilibrium<sup>16</sup> 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:

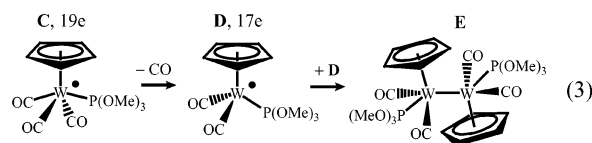
$$[\text{C}] = [\text{C}]_0 \exp\{-k_{\text{diss}}t/[1 + (K_{\text{eff}}[\text{P}(\text{OMe})_3])^{-1}]\} \quad (2)$$

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

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,<sup>21</sup> 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.<sup>3</sup> Numerous studies have shown that the ligand substitution reactions of 17e radicals, such as  $\text{CpM}(\text{CO})_3^{\bullet}$  ( $\text{M} = \text{Cr}, \text{W}$ ),  $\text{CpFe}(\text{CO})_2^{\bullet}$ ,  $\text{M}(\text{CO})_5^{\bullet}$  ( $\text{M} = \text{Mn}, \text{Re}$ ), or  $\text{V}(\text{CO})_6^{\bullet}$ , proceed by an associative mechanism,<sup>1,5,6,22</sup> but this study is the first evidence that a 19e species is an intermediate rather than a transition state in the ligand substitution reaction.<sup>23</sup> In contrast to this observation, nanosecond time-resolved studies on the similar dimer  $[\text{CpFe}(\text{CO})_2]_2$  monitored the ligand substitution of  $\text{CpFe}(\text{CO})_2^{\bullet}$  with  $\text{P}(\text{OMe})_3$  but found no evidence for a 19e intermediate.<sup>22</sup> 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  $\text{cm}^{-1}$  which are assigned to the ligand substitution dimer  $[\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3]_2$  (**E**) based on DFT calculations and literature values for the Mo containing analogue of **E**.<sup>24</sup> The decay of **D** and the rise of **E** are correlated, as evident by the isosbestic point at 1831  $\text{cm}^{-1}$  in Figure 1b; thus, the only reaction on the microsecond time scale is the dimerization of **D** to form **E**.<sup>14</sup>

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:



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  $\text{CH}_2\text{Cl}_2$ , 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>.

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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  $\text{cm}^{-1}$  and overlap of a second peak from **C** with the bleach at 1955  $\text{cm}^{-1}$ .
- (14) See the SI for a discussion of the peak labeled \*, which likely arises from  $\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3^{\bullet}$  and is formed by electron transfer from **C** to **D**.
- (15) In the presence of organic halides, such as  $\text{CCl}_4$ , Cl atom abstraction by **B** may occur; however, spectral data in neat  $\text{CH}_2\text{Cl}_2$  (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  $\text{cm}^{-1}$  (**C**) and 1994  $\text{cm}^{-1}$  (**B**), an “effective” equilibrium constant can be defined and is found to have a value of  $K_{\text{eff}} = 3.4 \pm 0.4 \text{ M}^{-1}$ . Further assuming  $K_{\text{eff}} \approx K_{\text{eq}}$  and using the thermodynamic relation  $\Delta G^\circ = -RT \ln(K_{\text{eq}})$ , where  $\Delta G^\circ$  is the change in standard Gibbs energy,  $K_{\text{eq}}$  the equilibrium constant,  $R$  the ideal gas constant, and  $T$  the absolute temperature, the value for  $K_{\text{eff}}$  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  $\text{P}(\text{OMe})_3$  with **B** was directly observed in these studies and no evidence for species **D** was found.
- (20) Assuming simple transition state theory,  $k_{\text{diss}} = (k_B T/h) \exp(-\Delta G^\ddagger/k_B T)$ , 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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- (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.
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