Ligand Substitution in the Cyclopentadienyltricarbonyltungsten Radical

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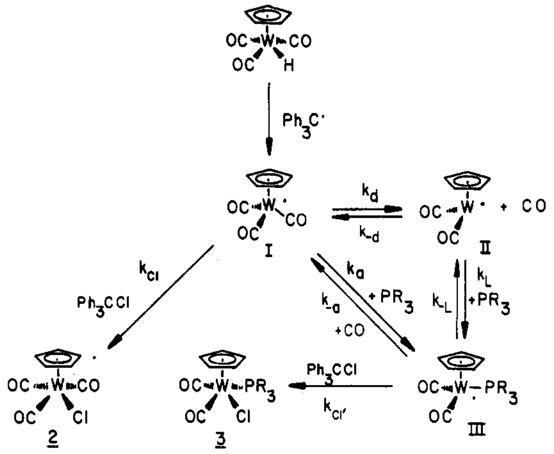
The substitution reactions of the CpW(CO)$_3$ radical with phosphines and phosphites have been studied by using a competition experiment. Reaction of CpW(CO)$_3$H with Ph$_3$C in the presence of Ph$_3$CCl and the ligand gave CpW(CO)$_3$Cl (**2**) and CpW(CO)$_2$(PR$_3$)Cl (**3**) as the only metal-containing products. Plots of **3**/**2** vs. [PR$_3$] were found to be linear with zero intercepts. The reactivity order PBu$_3$ > P(OPh)$_3$ > PPh$_3$ was observed, and substitution was significantly inhibited by CO. Furthermore plots of **3**/**2** vs. 1/[Ph$_3$CCl] at constant ligand concentration were found to be linear under nitrogen, but [Ph$_3$CCl] independent under CO. These results were interpreted in terms of an associative substitution pathway.

The mechanism of ligand substitution in transition-metal carbonyl complexes has received renewed attention in recent years with the realization that coordinatively unsaturated, 17-electron metal complexes are often more labile than their 18-electron analogues.[1-6] Indeed some 17-electron complexes exhibit substitution rates 10^{10} times faster than for isostructural 18-electron analogues.[4] A growing body of evidence indicates that a facile associative substitution pathway is responsible for the remarkable reactivity of these odd-electron species.[3-6]

Much of the earlier evidence for a possible dissociative pathway came from studies of metal–metal bonded dimers.[1,2] Under both thermal and photochemical conditions the dimers Cp$_2$M$_2$(CO)$_6$ (M = Cr, Mo, W) readily lose two molecules of CO to give the triply bonded dimers Cp$_2$M$_2$(CO)$_4$.[7] Metal–metal bond homolysis forming 17-electron CpM(CO$_3$) radicals is facile under these conditions, suggesting ligand dissociation in CpM(CO)$_3$ is involved. We recently reinvestigated this reaction and concluded that under thermal conditions metal–metal bond homolysis is not on the product-forming reaction pathway, but rather CO dissociation occurs from the intact dimer.[8] On the other hand, Hoffman and Brown have studied the substitution reactions of the CpM(CO)$_3$H hydrides (M = Mo, W) and found evidence for a chain mechanism involving substitution in the CpM(CO)$_3$ radical.[2a] Significantly, they observed the overall rate of substitution to vary with the nature of the entering ligand. This, now, suggests an associative substitution pathway but can also be rationalized by different rates of chain transfer and chain termination. Thus, the 17-electron CpM(CO)$_3$ radicals are not involved in the formation of the Cp$_2$M$_2$(CO)$_4$ dimers, but they do exhibit substitution lability. Herein we report our study of the substitution reactions of the CpW(CO)$_3$ radical in which we demonstrate a facile associative substitution pathway.[8b]

Scheme I



Results and Discussion

The Competition Experiments. We have employed the competition experiment outlined in Scheme I to study the substitution reactions of the CpW(CO)$_3$ radical. Stoichiometric generation of CpW(CO)$_3$ is achieved by hydrogen abstraction from CpW(CO)$_3$H (**1**) by the triphenylmethyl radical. The subsequent competition between chlorine abstraction from Ph$_3$CCl and substitution

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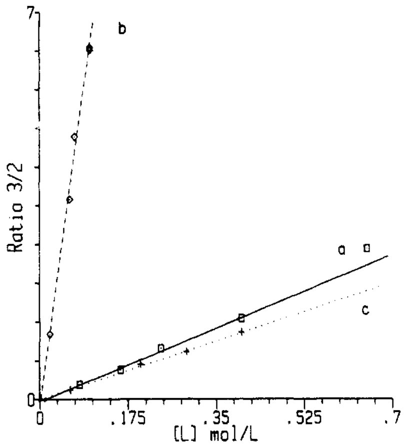

Figure 1. Observed ratio of $CpW(CO)_2(L)Cl$ to $CpW(CO)_3Cl$ (**3**/**2**) vs. ligand concentration: (a) L = PPh_3 (□) under N_2, slope = 4.27 (±0.09); (b) L = $P(OPh)_3$ (◇) under N_2, slope = 64.8 (±0.2); (c) L = $P(OPh)_3$ (+) under 1 atm of CO, slope = 3.07 (±0.03). All data are for reaction of **1** with $(Ph_3C)_2$ (0.156 M), Ph_3CCl (0.156 M), and the ligand in benzene at 24 °C with exclusion of light.

gives $CpW(CO)_3Cl$ (**2**) and $CpW(CO)_2(L)Cl$ (**3**) as the only metal-containing products. A similar competition experiment, only with photoinduced metal–metal bond cleavage to generate the 17-electron radicals, has been used by both Poë and Brown to study the substitution reactions of $Re(CO)_5$ and $Mn(CO)_5$.[3d,6a] We did not use this photochemical method because of problems associated with photoinduced CO dissociation in both the dimer and products.[9] An added advantage of our experiment is that the radical formed upon chlorine abstraction is the same radical used for the initial hydrogen abstraction, thus avoiding transient radical species of unknown reactivity.

A standard kinetic analysis of Scheme I employing the steady-state approximation and assuming all steps are irreversible gives the expression in eq 1 (see supplementary material for derivation of kinetic equations). Equation 1

$$\frac{3}{2} = \frac{k_a[L] + k_d}{k_{Cl}[RCl]} \qquad (1)$$

predicts a linear relationship between the ratio **3**/**2** and [L] under conditions of excess L and Ph_3CCl, which we find.[8] These data for reactions involving PPh_3 and $P(OPh)_3$ are presented in Figure 1. In both cases the plots are linear over a wide range of ligand concentrations and have zero intercepts. In addition, when PBu_3 is the entering ligand, almost complete substitution was observed at the lowest convenient concentration (**3**/**2** = 7.9, [PBu_3] = 6 × 10^{-3} M), preventing the range of data necessary to evaluate the ligand dependence.

In a typical reaction a benzene solution of $CpW(CO)_3H$ (0.06 mmol) was added slowly to 50 mL of benzene containing excess $[Ph_3C]_2$ (0.156 M), Ph_3CCl (0.156 M), and the ligand (0.08–0.65 M) in the dark. The solvent was removed and the residue redissolved in CH_2Cl_2 for infrared analysis of the product ratio. Both IR and NMR spectra of the crude reaction mixtures indicate that **2** and **3** are the only products of the reaction. None of the corresponding dimer or disubstitution products were observed in any of these reactions. If the entering ligand was $P(OPh)_3$ or PBu_3, then only the cis isomer of **3** and none of the corresponding trans isomer could be observed. However, when PPh_3 was used, both *cis*- and *trans*-$CpW(CO)_2(PPh_3)Cl$ were obtained in about a 9/1 ratio.[10]

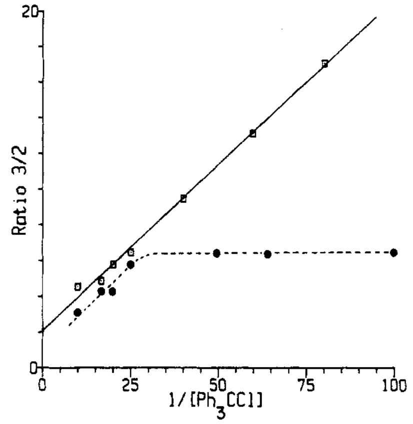

Figure 2. Observed ratio of $CpW(CO)_2(P(OPh)_3)Cl$ to $CpW(CO)_3Cl$ (**3a**/**2**) vs. $1/[Ph_3CCl]$: (a) under nitrogen (□); (b) under 1 atm of CO (●, (**3**/**2**) observed × 10). All data are for reaction of **1** with $P(OPh)_3$ (0.2 M), $(Ph_3C)_2$ (0.156 M), and Ph_3CCl in benzene at 24 °C with exclusion of light.

The positive slope, zero intercept, and entering ligand dependence are all indicative of a dominant associative substitution process. According to eq 1 the slope is given by $k_a/k_{Cl}[Ph_3CCl]$. An accurate value for the halogen abstraction rate constant k_{Cl} is not available. However, using the value of 1.3 × 10^4 M^{-1} s^{-1} found by Laine and Ford for the reaction of $CpW(CO)_3$ with CCl_4 as an approximation of k_{Cl},[11] we calculate values for k_a of 8.6 × 10^2 and 1.3 × 10^4 M^{-1} s^{-1} at 24 °C for L = PPh_3 and $P(OPh)_3$, respectively. These values compare well with those for associative substitution reactions of other 17-electron complexes. Substitution of CO by PPh_3 in $Mn(CO)_5$ is faster (1.7 × 10^7 M^{-1} s^{-1} at 0 °C)[3d] but slower in $V(CO)_6$ (2.5 × 10^{-1} M^{-1} s^{-1} at 25 °C).[3a]

The observed nucleophile reactivity order PBu_3 > $P(OPh)_3$ > PPh_3 is consistent with the associative nature of these reactions.[5a] The anomaly in this sequence is the greater reactivity of the less nucleophilic $P(OPh)_3$ over PPh_3, which points to the significance of steric effects in these reactions. Similar results were reported for radical chain substitution in $CpW(CO)_3H$, and in studies of $Mn(CO)_5$.[3a,4d] Kochi and co-workers have reported an extensive study of the associative substitution reactions of electrochemically generated radical $CpMn(CO)_2(py)^+$ with phosphines.[5a] Using two series of phosphines of constant steric and electronic properties, they were able to show that both factors influence the rate of reaction. Alternatively, the greater reactivity of phosphites over phosphines of comparable electron donor properties may reflect the importance of π-back-bonding in stabilizing the transition state for substitution in 17-electron systems and not just steric factors.

Inhibition by Carbon Monoxide. An assumption required for the derivation of eq 1 is that the reactions of the 17-electron intermediate $CpW(CO)_3$ (I) are all irreversible. Given the low concentration of CO and the high concentrations of both the ligand and Ph_3CCl, this seems reasonable. At higher concentrations of CO, however, reversibility might be expected. Indeed, we observe a significant [CO] dependent inhibition of substitution. In Figure 1c is a plot of **3**/**2** vs. [$P(OPh)_3$] under 1 atm of CO.

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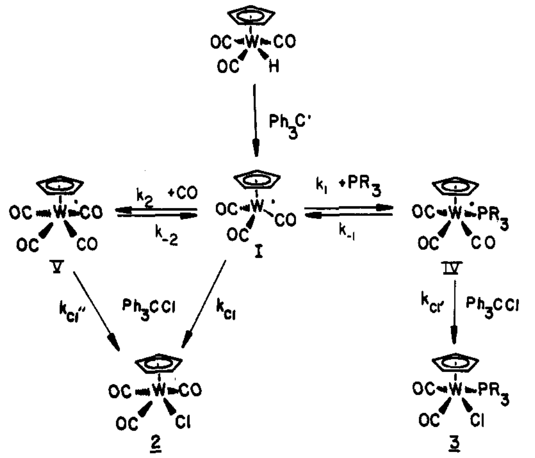
Scheme II



The [Ph$_3$CCl] Dependence. The observation of substitution inhibition by CO is consistent with either an associative or dissociative pathway as shown in Scheme I. The complete kinetic equations of both the associative and dissociative pathways under reversible conditions are given in eq 2 and 3 (see supplementary material). To

Associative Pathway

$$\frac{3}{2} = \frac{k_a k_{Cl'}[L]}{k_{Cl}(k_{-a}[CO] + k_{Cl'}[RCl])} \tag{2}$$

Dissociative Pathway

$$\frac{3}{2} = \frac{k_{Cl'} k_L K_d [L]}{k_{Cl}[CO](k_{-L} + k_{Cl'}[RCl])} \tag{3}$$

conclusively distinguish these mechanisms, we examined the relationship between the product ratio 3/2 and 1/[Ph$_3$CCl] under both a nitrogen and CO atmosphere. These data are presented in Figure 2. We observe a linear relationship under nitrogen but a significant region where the product ratio is [Ph$_3$CCl] independent under CO. Both pathways predict a [Ph$_3$CCl]-independent regime under the appropriate conditions, $k_{-a}[CO] >> k_{Cl'}[Ph_3CCl]$ for the associative pathway and $k_{-L} >> k_{Cl'}[Ph_3CCl]$ for the dissociative pathway. However, only the associative pathway predicts a change from [Ph$_3$CCl] independent to an inverse [Ph$_3$CCl] dependence upon reducing the CO concentration as observed. Note that even at high [Ph$_3$CCl] concentrations, we do not achieve the same limiting slope under CO as observed under nitrogen, suggesting that conditions where $k_{Cl'}[Ph_3CCl] >> k_{-a}[CO]$ are never obtained.

A 19-Electron Intermediate. There is a growing body of evidence that the 19-electron species can be stable to ligand dissociation and thus can be intermediates and not just transition states in the substitution reactions of 17-electron radicals (vide infra). We have also considered the possibility of stable 19-electron intermediates in our reactions (Scheme II) The kinetic expression for the product ratio 3/2 predicted by this mechanism is given in eq 4 (see supplementary material). Provided formation

$$\frac{3}{2} = \frac{k_{Cl'} k_1 [L]}{(k_{-1} + k_{Cl'}[RCl])\left(k_{Cl} + \dfrac{k_{Cl''} k_2 [CO]}{k_{-2} + k_{Cl''}[RCl]}\right)} \tag{4}$$

of the 19-electron species CpW(CO)$_3$(PR$_3$) (IV) and CpW(CO)$_4$ (V) is irreversible (k_{-1} and k_{-2} = 0), this expression simplifies to give eq 5 and is indistinguishable from eq 2.

$$\frac{3}{2} = \frac{k_1[L]}{k_{Cl}[RCl] + k_2[CO]} \tag{5}$$

The [Ph$_3$CCl] independent regime observed under a CO atmosphere can result when at low Ph$_3$CCl concentrations chlorine abstraction by CpW(CO)$_3$ (I) fails to compete with ligand addition. At higher Ph$_3$CCl concentrations reaction with I can compete and a [Ph$_3$CCl] dependence will be observed. Conversely, when k_2[CO] is small (nitrogen atmosphere), a linear 1/[Ph$_3$CCl] relationship is predicted.

Thus, these experiments are unable to distinguish a truly associative substitution pathway from one involving stable 19-electron intermediates. If indeed a reversible associative process is involved, then CO must be nucleophilic enough to compete with chlorine abstraction. While this may seem surprising, it is not unprecedented. Carbon monoxide can displace phosphine from Mn(CO)$_3$(PBu$_3$)$_2$ by an associative process.[3c] On the other hand, Poë and co-workeers did not observe CO inhibition in their study of the Re(CO)$_5$ radical.[6a]

Conclusions

Our results clearly rule out a dissociative substitution pathway for the transient CpW(CO)$_3$ radical and establish the associative nature of the substitution process. At present, however, we are unable to distinguish between a 19-electron transition state and a stable 19-electron intermediate in these reactions. This report and others have now established associative substitution mechanisms for a number of isolable and transient 17-electron complexes,[3-6] including those cases where evidence suggestive of a dissociative existed.[2,3,67] Thus the generality of low-energy associative substitution involving 19-electron intermediates or transition states seems firmly established.

It is less clear why 17–19-electron interconversions are so facile. We favor the view that interaction of the entering nucleophile with the singly occupied metal orbital can result in a stabilizing two-center–three-electron (2c–3e) interaction in the 19-electron transition state or intermediate.[4a,12] Others have recently suggested that the stability of 19-electron structures may be enhanced by delocalization of the odd electron onto a ligand.[4d] For example, Blaha and Wrighton have proposed formation of a η^4-Cp ligand centered radical to help explain addition of benzyl radical to the ring in (C$_5$H$_5$)Fe(CO)$_2$(L).[2h] Similarly, Narayanan and Kochi have observed hydrogen addition to CO ligands in electrochemically generated 19-electron metal carbonyls.[5f] It should be noted, however, that 19- and 20-electron metallocenes with metal-centered HOMO's have been observed to react at the ring carbons, not the metal.[13]

Even more subtle effects may be involved. Reaction of Cp$_2$Mn with phosphines forms the stable 19-electron complexes Cp$_2$Mn(PR$_3$) and even 21-electron complexes Cp$_2$Mn(dipos).[14] The EPR spectra indicate a ^{6}S high-spin configuration, and the crystal structures reveal significant "tilting" of the Cp ligands. Lauher and Hoffmann have explained the occurrence of tilted Cp ligands in the complexes Cp$_2$Mo(NO)R in terms of electron counts in excess of 18.[15] Indirect evidence also indicates that 19-electron

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complexes $CpMo(CO)_2(PR_3)_2$ are stable to ligand dissociation.[16] Thus, at least in complexes with η^5-Cp ligands, structural and bonding changes can help alleviate the energetic consequences of placing an electron in an orbital that is at least partially antibonding. The examples cited show that in Cp_2ML_n systems the 2c–3e interaction can be bonding, but firm evidence for a stable $CpW(CO)_3(PR_3)$ species in our reactions is lacking.

Experimental Section

All manipulations were carried out under an atmosphere of purified nitrogen either in a Vacuum Atmospheres Model HE-553 glovebox or with use of standard Schlenk techniques. Infrared spectra were obtained on a Perkin-Elmer Model 781 spectrophotomer. ^1H NMR spectra were obtained on a Varian EM-390 spectrometer. Analyses were performed by Robertson Laboratories, Inc., Florham Park, NJ. Benzene was distilled from a sodium benzophenone ketyl. Ph_3CCl (98%, Aldrich) was purified by recrystallization from toluene/hexane containing a small amount of acetyl chloride.[17a] $[Ph_3C]_2$ was prepared from Ph_3CCl and zinc dust by the literature method and recrystallized from toluene (−78 °C).[17b] PPh_3 was recrystallized from hexane/methanol, and PBu_3 and $P(OPh)_3$ were distilled before use. Compound **1** was prepared by the literature method,[18] purified by repeated sublimation, and stored cold in the dark. Authentic samples of the chloride **2** and the phosphine-substituted analogues **3a–d** were prepared by literature methods.[10] This gave cis-substituted products in all cases except where L = PPh_3. Pure *cis*-$CpW(CO)_2(PPh_3)Cl$ could be obtained from the method of Blumer, Barnett, and Brown,[10a] but other methods gave cis/trans mixtures. We were unable to obtain the trans isomer in pure form.

Preparation of (η^5-C_5H_5)$W(CO)_2(P(OPh)_3)Cl$ (3a). This previously unreported compound was prepared by the method of Blumer et al.[10a] A solution of 370 mg (1 mmol) of **2** and 620 mg (2 mmol) of $P(OPh)_3$ in 40 mL of CH_2Cl_2 was treated with 150 mg (2 mmol) of Me_3NO at room temperature. After 30 min the solvent was removed and the residue chromatographed on Florisil eluting one orange band with CH_2Cl_2–hexane (1:1). Two recrystallization from CH_2Cl_2–hexane yielded 260 mg of pure **3a** as orange plates (39% theory): mp 153–157 °C; IR (CH_2Cl_2) 1975 (s), 1895 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.17 (s, 5 H, Cp), 7.2–7.4 (m, 15 H, Ph's). Anal. Calcd for $C_{25}H_{20}ClO_5PW$: C, 46.14; H, 3.10; P, 4.75. Found: C, 46.11; H, 2.99; P, 4.67.

Competition Experiments. In a typical experiment a solution of $CpW(CO)_3H$ (0.06 mmol) in 5 mL of benzene was added slowly to 50 mL of benzene containing excess $[Ph_3C]/2$ (0.156 M), Ph_3CCl (0.156 M), and the ligand (0.08–0.65 M) at 24 °C in the dark. After 15 min the solvent was removed in vacuo (ca. 3 h) and the residue redissolved in 5 mL of CH_2Cl_2 for infrared analysis. It was necessary to use as reference a CH_2Cl_2 solution of the same concentration of $[Ph_3C]_2$, Ph_3CCl, and the ligand to remove weak aromatic overtones in the carbonyl region. In all cases the high-energy CO stretching band in **2** (2046 cm^{-1}) and the low-energy band in **3a–c** (1850–1895 cm^{-1}) were cleanly separated from the overlapping bands around 1960 cm^{-1} in both compounds. The product ratio **3**/**2** was determined from the observed ratio A ($\sim$1890)/A (2046), correcting for differences in molar absorptivities. Samples were also isolated by column chromatography, and their identity was confirmed by comparison with authentic samples. In reactions involving PPh_3 we obtained mixtures of *cis*- and *trans*-$CpW(CO)_2(PPh_3)Cl$ in about a 9/1 ratio. Cis/trans isomerization does not occur under the reaction conditions, and we were unable to obtain the trans isomer in pure form; thus the product ratio was calculated by assuming that both isomers have the same molar absorptivity at 1863 cm^{-1}. In all other cases only a single isomeric product was obtained.

Carbon monoxide inhibition studies were performed as above only with CO-saturated solutions.

Molar absorptivities were determined for the infrared CO stretching bands of compounds **2** and **3a–c** in CH_2Cl_2 by the Beer's law procedure. $CpW(CO)_3Cl$ (**2**):[17] 2046 (1820), 1960 cm^{-1} (3340 L/(mol cm)). $CpW(CO)_2(P(OPh)_3)Cl$ (**3a**): 1975 (2063), 1895 cm^{-1} (1290 L/(mol cm)). *cis*-$CpW(CO)_2(PPh_3)Cl$ (*cis*-**3b**):[10c,d] 1958 (2380), 1863 cm^{-1} (1390 L/(mol cm)). $CpW(CO)_2(PBu_3)Cl$ (**3c**):[10b] 1940 (2340), 1845 cm^{-1} (1700 L/(mol cm)).

Control Experiments. A number of control experiments were performed to check the general validity of the competition experiment in Scheme I. (a) In the absence of Ph_3CCl the reaction of $CpW(CO)_3H$ with $[Ph_3C]_2$ gave Ph_3CH and $[CpW(CO)_3]_2$. (b) There was only a slow reaction (hours) of $CpW(CO)_3H$ with Ph_3CCl. (c) Known mixtures of **2** and **3** are stable in the presence of Ph_3CCl, $[Ph_3C]_2$, and ligands under conditions for the reaction and analysis provided light is excluded. Rapid substitution in both **1** and **2** is observed even under normal fluorescent lighting. (d) The product ratio was found to be independent of the $[Ph_3C]_2$ concentration.

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Registry No. **1**, 12128-26-6; **2**, 12128-24-4; **3a**, 102616-32-0; *cis*-**3b**, 71425-48-4; **3c**, 102616-33-1.

Supplementary Material Available: Derivations of the kinetic equations (1)–(5) (5 pages). Ordering information is given on any current masthead page.

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