

2080 cm<sup>-1</sup> in the IR spectrum (KBr disk).

Compounds **4** and **5** contrast with the other monotransition metal-gold hydrides (**1-3** and those listed in the Introduction<sup>3-7</sup>) in that they clearly do not have gold-hydride interactions. In all of the other compounds gold-hydride interactions have either been demonstrated<sup>3,4</sup> or are considered very likely.<sup>5-7</sup> The factors which influence the stability of gold-hydride interactions are not well understood, and it is clear that more studies of the type reported in this paper are needed.

**Summary.** Two new transition metal-gold hydrides [Au<sub>2</sub>Ru(H)<sub>2</sub>(dppm)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (**1**) and [AuIr(H)<sub>2</sub>(bipy)(PPh<sub>3</sub>)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub> (**2**) have been synthesized. In **1** the hydride positions were located and refined by single-crystal X-ray crystallography and were found to be dibridging the Ru to Au bonds. In **2** the hydride positions were deduced from X-ray crystallography and NMR spectroscopy and are dibridging the IR to Au bond. <sup>31</sup>P and <sup>1</sup>H NMR results indicate significant gold-hydride interaction as determined by large spin-spin coupling between the hydride ligands and the gold phosphine phosphorus atoms. These results are important not only because gold-hydride interactions are rare but because they strongly imply that gold-hydride interactions are likely in a variety of gold-alloy hydride clusters. The trans M-Au-PPh<sub>3</sub> stereochemistry which has been found in **1** and **2** is also present in [Au<sub>5</sub>Re(H)<sub>4</sub>(PPh<sub>3</sub>)<sub>7</sub>](PF<sub>6</sub>)<sub>2</sub>,<sup>5</sup> [Au<sub>3</sub>RhH(CO)(PPh<sub>3</sub>)<sub>5</sub>]PF<sub>6</sub>,<sup>5</sup> [Au<sub>4</sub>Ir(H)<sub>2</sub>(PPh<sub>3</sub>)<sub>6</sub>]BF<sub>4</sub>,<sup>6</sup> and [Au<sub>2</sub>IrH(PPh<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>.<sup>7</sup> In addition all of these compounds lack a terminal metal-hydride stretch in the IR spectrum although such an absorption was easily observed in [AuIrH(CO)(PPh<sub>3</sub>)<sub>4</sub>]<sup>+</sup>

(**4**) and [AuIrH(PPh<sub>3</sub>)<sub>4</sub>]<sup>+</sup> (**5**). Compounds **4** and **5** have terminally bound iridium hydride ligands. The conclusions from this study are as follows: (i) a hydride ligand which bridges to gold does not require a trans μ-H-Au-PPh<sub>3</sub> stereochemistry as previously thought,<sup>3-7</sup> and (ii) gold-hydride interactions are probably much more prevalent in gold-alloy cluster hydrides than thought previously.<sup>3-7</sup>

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**Registry No.** **1**, 102538-84-1; **2**, 102575-52-0; **4**, 102538-86-3; **5** (X = BF<sub>4</sub>), 102538-88-5; **5** (X = NO<sub>3</sub>), 102628-79-5; AuPPh<sub>3</sub>NO<sub>3</sub>, 14897-32-6; Ru(H)<sub>2</sub>(dppm)<sub>2</sub>, 89613-08-1; [Ir(H)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(acetone)<sub>2</sub>]BF<sub>4</sub>, 72414-17-6; [Ir(H)<sub>2</sub>(bpy)(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>, 102538-90-9; IrH(CO)(PPh<sub>3</sub>)<sub>3</sub>, 17250-25-8; [Au<sub>2</sub>IrH(NO<sub>3</sub>)(PPh<sub>3</sub>)<sub>4</sub>]BF<sub>4</sub>, 93895-71-7; Ru, 7440-57-5; Au, 7440-57-5; Ir, 7439-88-5.

**Supplementary Material Available:** ORTEP drawings of **1** and **2** and the <sup>1</sup>H NMR spectrum of the dppm methylene resonances of **1** with selective <sup>31</sup>P decoupling (Figures S1-S3) and listings of general temperature factor expressions, calculated hydrogen atom positional parameters, distances and angles, least-squares planes, and observed and calculated structure factor amplitudes for **1** and **2** (Tables S1-S12) (96 pages). Ordering information is given on any current masthead page.

## Kinetics and Mechanisms of Carbonyl Substitution Reactions of Bis(η<sup>5</sup>-cyclopentadienyl) Dicarboxyl Compounds of the Titanium Triad Metals

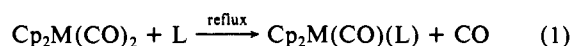
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**Abstract:** Kinetic studies were performed for CO substitution reactions of (η<sup>5</sup>-ring)<sub>2</sub>M(CO)<sub>2</sub>, where (η<sup>5</sup>-ring) = Cp, Cp\*, or Ind<sup>1</sup> and M = Ti, Zr, or Hf. Nucleophiles used for these reactions include PMe<sub>2</sub>Ph, PMePh<sub>2</sub>, PPh<sub>3</sub>, P(OEt)<sub>3</sub>, P(*n*-Bu)<sub>3</sub>, and CO. The reaction rates of the titanium compounds were first order in substrate and zero order in entering nucleophile at nucleophile concentrations which gave the limiting reaction rate. The results indicate a dissociative mechanism. Activation parameters for these reactions are also in agreement with a dissociative process. In contrast, reaction rates of the zirconium and hafnium compounds are first order in both substrate and entering nucleophile, indicating an associative mechanism. This mechanistic difference may be attributed to steric considerations caused by the smaller size of titanium. Equilibrium constants and rate constants indicate a strong preference of the Ti, Zr, and Hf metallocene compounds for CO over PR<sub>3</sub>.

Studies on cyclopentadienyltitanium triad metal carbonyl compounds have increased,<sup>2,3</sup> since the first example, bis(η<sup>5</sup>-cyclopentadienyl)titanium dicarbonyl, was reported by Murray<sup>4</sup> in 1959. The primary method of synthesis for these compounds is through reduction of the bis(η<sup>5</sup>-cyclopentadienyl)metal dichloride in the presence of CO. Numerous reducing agents such as sodium,<sup>5</sup> electric current,<sup>6</sup> aluminum,<sup>7</sup> and magnesium<sup>8</sup> have been used.

Work on the titanium triad of metallocene has included substituting a carbonyl ligand by a phosphine or phosphite group. One of the reactions<sup>9</sup> for Cp<sub>2</sub>M(CO)(PR<sub>3</sub>) formation is shown in eq 1, where M = Ti, Zr, or Hf and L = PR<sub>3</sub>. Refluxing the



reaction solutions is essential in order to remove generated CO from the solution. A method of synthesis for Cp<sub>2</sub>Ti(CO)(PR<sub>3</sub>)

(1) Cp = η<sup>5</sup>-cyclopentadienyl, Cp\* = η<sup>5</sup>-pentamethylcyclopentadienyl, and Ind = η<sup>5</sup>-indenyl.

(2) Sikora, D. J.; Macomber, D. W.; Rausch, M. D. *Adv. Organomet. Chem.*, in press.

(3) Bottrill, M.; Gavens, P. D.; McMeeking, J. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1981; Vol. 3, pp 285-291.

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developed<sup>10</sup> later involves photolysis of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  in the presence of  $\text{PR}_3$  ( $\text{R} = \text{Et}, \text{Ph}$ ). For this reaction it is very important to purge the solution with an inert gas, again to remove the liberated CO. If the reaction solutions were not purged, no detectable reaction took place.

Compounds which are disubstituted with alkylphosphines or -phosphites,  $\text{Cp}_2\text{Ti}(\text{PR}_3)_2$ , have been reported<sup>11</sup> only for  $\text{R} = \text{OMe}$  and  $\text{Me}$ . The disubstituted compounds  $\text{Cp}_2\text{Ti}(\text{P}(\text{OMe})_3)_2$ <sup>11a</sup> and  $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$ <sup>11b</sup> were synthesized by reduction of  $\text{Cp}_2\text{TiCl}_2$  in the presence of the phosphorus ligand. Attempts to substitute both carbonyl ligands on  $\text{Cp}_2\text{M}(\text{CO})_2$  have been unsuccessful.<sup>10</sup>

The physical properties of the metallocene dicarbonyls are well-known.<sup>2</sup> Yet despite thorough characterization of these compounds and syntheses of numerous substitution products, there appears to be no report of mechanistic studies performed on CO substitution reactions of these metallocenes. Qualitative results<sup>10</sup> from the synthesis of  $\text{Cp}_2\text{Ti}(\text{CO})(\text{PR}_3)$ , where  $\text{R} = \text{Et}$  or  $\text{Ph}$ , suggest that the phosphine substitution reactions are associative. The presence of cyclopentadienyl rings certainly allows for the possibility of an associative reaction path through  $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ -ring slippage.<sup>12</sup> However, kinetic studies are required to adequately address this question.

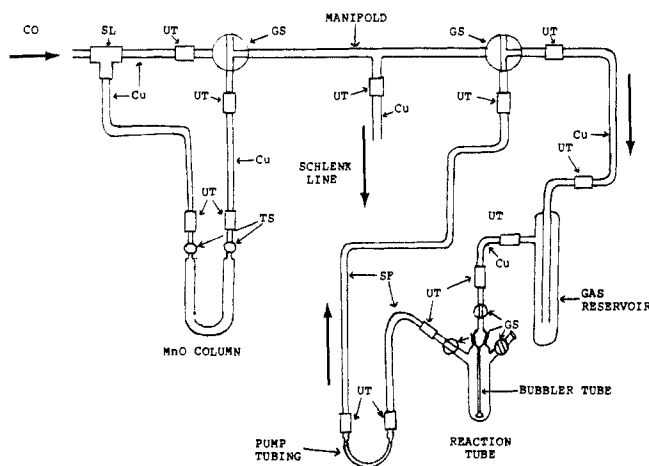
The goal of the present study has been to elucidate the mechanism for reactions of the type shown in eq 1. To this end reaction rates and activation parameters have been determined for these reactions, which we believe represents the first kinetic study of ligand substitution reactions of early transition-metal organometallic compounds. Also, in order to quantify the greater preference of these metallocenes for CO over phosphines and phosphites, the equilibrium constants of some reactions have been determined.

### Experimental Section

**Compounds and Solvents.** All manipulations, except kinetic reactions, involving metallocene dicarbonyl compounds of titanium, zirconium, or hafnium were performed under an atmosphere of He by using standard Schlenk techniques or in a  $\text{N}_2$ -filled glovebox. Decalin, cyclohexane, hexane, and THF were distilled over Na under either a He or a  $\text{N}_2$  atmosphere. The hexane was stored over  $\text{H}_2\text{SO}_4$  and washed with a  $\text{NaHCO}_3$  solution before distillation. The He used was passed through a 1-m  $\times$  13-cm column which was packed with Ridox and maintained at 110 °C.

Bis( $\eta^5$ -cyclopentadienyl)hafnium dichloride was obtained from Aldrich Chemical Co. The  $^{13}\text{CO}$  was obtained from Monsanto Research Corp., and 80–200-mesh Alumina was purchased from Alcoa Chemicals. Ridox was obtained from Fisher Scientific Products. The compounds  $\text{Cp}_2\text{Ti}(\text{CO})_2$ ,<sup>8b</sup>  $\text{Cp}^*\text{Ti}(\text{CO})_2$ ,<sup>8b</sup>  $\text{Ind}_2\text{Ti}(\text{CO})_2$ ,<sup>13</sup>  $\text{Cp}_2\text{Zr}(\text{CO})_2$ ,<sup>8b, 14</sup> and  $\text{Cp}_2\text{Hf}(\text{CO})_2$ ,<sup>8b, 14</sup> were prepared by literature methods.

**Instrumentation.** Infrared spectra were obtained on either a Nicolet 7199 FT-IR or a Perkin-Elmer 337 spectrophotometer with 0.2-mm KBr-windowed cells. Nuclear magnetic resonance spectra were obtained on either a JEOL FX-90Q or a JEOL FX-270 spectrometer. Kinetic reactions were performed in either a Haake temperature bath or a Neslab RTE-8 refrigeration circulating bath, with temperatures regulated to



**Figure 1.** Gas manifold and reaction tube configuration for the reaction of  $\text{Cp}_2\text{M}(\text{CO})_2$  with  $^{12}\text{CO}$ , where  $\text{M} = \text{Ti}, \text{Zr},$  or  $\text{Hf}$ ; Cu, copper tubing; GS, ground glass stopcock; SF, stainless steel flex tubing; SL, Swagelok fitting; TS, Teflon stopcock; UT, Ultra-Torr fitting; unmarked tubing is glass.

$\pm 0.2$  °C. The mass spectral measurements were obtained by Dr. D. Hung of Northwestern University Analytical Services Laboratory on a HP5985A spectrometer using a 70-eV ionization. The  $^{13}\text{C}$  NMR spectrum of  $^{13}\text{CO}$  was recorded by Ray C. Wieboldt of Northwestern University Analytical Services Laboratory on a JEOL FX-270 spectrometer.

**Kinetic Apparatus.** Special gas manifold and reaction tube configurations were required to perform the substitution reactions in the total exclusion of oxygen. A standard Schlenk line was used to supply He and vacuum to the reaction apparatus. All connections between pieces of glassware were effected with Cajon Ultra-Torr fittings and stainless steel flex tubing or copper tubing, except that the manifold was joined to the Schlenk line by a 40-cm length of 2-cm-diameter rubber vacuum tubing. The reaction tube was 3 cm in diameter by 15 cm in length and fitted with a 14/20 ground glass joint and two No. 2 Kontes stopcocks as side arms. A 14/20 Schlenk flask adapter was fitted with a bubbling tube which ended in a 8-mm-diameter, very coarse porosity frit. A highly porous frit is required in order to minimize restriction to gas flow. The bubbling tube was of such a length that when the reaction tube was assembled, the frit was positioned 4 mm from the bottom of the reaction tube.

The same manifold and reaction tube were used for the  $^{13}\text{CO}$ -exchange reactions, but the configuration of the apparatus was changed, Figure 1. In this configuration, instead of continually sweeping the reaction solution with fresh gas, the reaction vessel was nearly a closed system. The system was open to the extent that aliquots of the solution were withdrawn and CO was bled in to maintain a constant pressure during the course of the reaction. The atmosphere in the reaction tube was continually recirculated by a Cole Parmer-Masterflex variable-speed pump. A 15-cm length of 5-mm butyl rubber tubing was required by the pump head, which was the only nonglass or nonmetal section of the closed reaction system. Special glassware was made by Mike Souza of William A. Sales Ltd.

**Kinetic Measurements.** For CO substitution reactions, approximately  $3 \times 10^{-3}$  M solutions of the appropriate dicarbonyl metallocene compound in decalin were used. Prepared samples of 2.0 mL were placed in a constant-temperature bath. The reactions were monitored over 3–4 half-lives with IR spectroscopy by abstracting 6–10 0.2-mL aliquots periodically and injecting these samples into an IR cell which had been purged with  $\text{N}_2$ .

Rate constants were determined by measuring the decrease of one of the carbonyl bands of the starting carbonyl compound (typically the highest frequency band). Plots of  $\ln A$  vs. time were linear for at least three half-lives, and  $k_{\text{obsd}}$  was the slope of this line as determined by the least-squares method. Where the reactions proceeded only by a dissociative mechanism, the first-order rate constants were equal to the  $k_{\text{obsd}}$  values for the reactions. Where the reactions proceeded by an associative mechanism,  $k_{\text{obsd}}$  values were measured under pseudo-first-order conditions. Pseudo-first-order conditions were achieved by performing the kinetic reactions with at least a 15-fold excess of entering nucleophile. Second-order rate constants were obtained as the slopes calculated by plotting  $k_{\text{obsd}}$  vs. ligand concentration for a series of reactions at the same temperature. Correlations of these least-squares lines were very good ( $r^2 > 0.996$ ). Activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were the slope times  $R$

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**Table I.** Infrared Carbonyl Stretching Frequencies for  $(\eta^5\text{-ring})_2\text{M}(\text{CO})_2$  in Decalin

$(\eta^5\text{-ring})_2\text{M}(\text{CO})_2$	CO stretches, $\text{cm}^{-1}$
$\text{Cp}_2\text{Ti}(\text{CO})_2^a$	1973 m, 1895 s <sup>b</sup>
$\text{Cp}_2\text{Ti}(\text{C}^{13}\text{CO})_2$	1928 m, 1850 s
$\text{Cp}_2\text{Ti}(\text{CO})(\text{PMe}_3)^c$	1861 s
$\text{Cp}_2\text{Ti}(\text{CO})(\text{PMe}_2\text{Ph})$	1860 s <sup>d</sup>
$\text{Cp}_2\text{Ti}(\text{CO})(\text{PMePh}_2)$	1860 s <sup>e</sup>
$\text{Cp}_2\text{Ti}(\text{CO})(\text{PPh}_3)^f$	1858 s
$\text{Cp}_2\text{Ti}(\text{CO})(\text{P}(n\text{-Bu})_3)$	1868 s
$\text{Cp}_2\text{Ti}(\text{CO})(\text{P}(\text{OEt})_3)$	1874 s <sup>g</sup>
$\text{Cp}_2\text{Ti}(\text{CO})(\text{P}(\text{O}-i\text{-Pr})_3)$	1869 s
$\text{Cp}^*_2\text{Ti}(\text{CO})_2^h$	1939 s, 1856 s
$\text{Cp}^*_2\text{Ti}(\text{C}^{13}\text{CO})_2$	1890 s, 1801 s
$\text{Ind}_2\text{Ti}(\text{CO})_2^c$	1980 s, 1911 sh, 1902 m
$\text{Ind}_2\text{Ti}(\text{C}^{13}\text{CO})_2$	1936 s, 1868 sh, 1860 m
$\text{Cp}_2\text{Zr}(\text{CO})_2^j$	1973 s, 1883 s <sup>j</sup>
$\text{Cp}_2\text{Zr}(\text{C}^{13}\text{CO})_2$	1927 m, 1840 s
$\text{Cp}_2\text{Zr}(\text{CO})(\text{PMe}_2\text{Ph})$	1851 s
$\text{Cp}_2\text{Zr}(\text{CO})(\text{PMePh}_2)^k$	1853 s
$\text{Cp}_2\text{Zr}(\text{CO})(\text{PPh}_3)^l$	1857 s
$\text{Cp}_2\text{Zr}(\text{CO})(\text{P}(n\text{-Bu})_3)$	1848 s
$\text{Cp}_2\text{Zr}(\text{CO})(\text{POEt}_3)$	1867 s <sup>m</sup>
$\text{Cp}_2\text{Zr}(\text{CO})(\text{P}(\text{O}-i\text{-Pr})_3)$	19861 s
$\text{Cp}_2\text{Hf}(\text{CO})_2^j$	1967 s, 1874 s
$\text{Cp}_2\text{Hf}(\text{C}^{13}\text{CO})_2$	1921 s, 1832 s
$\text{Cp}_2\text{Hf}(\text{CO})(\text{PMe}_2\text{Ph})$	1834 s

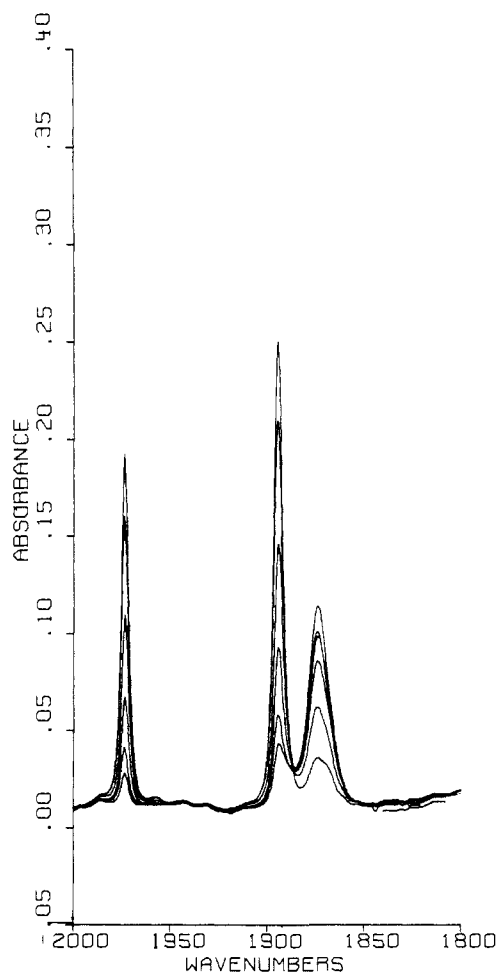
<sup>a</sup>Previously reported, ref 4. <sup>b</sup> $\epsilon = 8.8 \times 10^3$ . <sup>c</sup>Previously reported, ref 9. <sup>d</sup> $\epsilon = 5.5 \times 10^3$ . <sup>e</sup> $\epsilon = 5.7 \times 10^3$ . <sup>f</sup>Previously reported, ref 10. <sup>g</sup> $\epsilon = 5.8 \times 10^3$ . <sup>h</sup>Previously reported, ref 8a. <sup>i</sup>Previously reported, ref 14. <sup>j</sup> $\epsilon = 9.7 \times 10^3$ . <sup>k</sup>Previously reported: Gell, K. I.; Schwartz, J. J. *Am. Chem. Soc.* **1981**, *103*, 2687–2695. <sup>l</sup>Previously reported, ref 14. <sup>m</sup> $\epsilon = 6.7 \times 10^3$ .

and the intercept times  $10^3R$ , respectively, calculated by the least-squares method for the plot of  $\ln(k/T)$  vs.  $1/T$ , where  $T$  = temperature and  $k$  = either a first- or second-order rate constant. Correlations of the activation parameter least-squares lines were also very good ( $r^2 > 0.998$ ).

**Equilibrium Constants.** Measurements of equilibrium constants were performed in storage tubes of known volume fitted with Kontes Teflon stopcocks. A carefully measured amount of the phosphorus ligand was added to a decalin solution of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  or  $\text{Cp}_2\text{Zr}(\text{CO})_2$ . The concentration of the solution in metal compound was in the range of  $6\text{--}9 \times 10^{-3}$  M. Three reaction mixtures were used for each equilibrium constant, with the phosphorus ligand concentration varied over at least a 7-fold range. Absolute ligand concentrations were within the range of  $0.005\text{--}1.0$  M. Final concentrations of the metal compounds were determined from IR spectra. An extinction coefficient of  $5.6 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$  was used for the  $\text{Cp}_2\text{Ti}(\text{CO})(\text{PR}_3)$  compounds, since  $\text{Cp}_2\text{Ti}(\text{CO})(\text{PEt}_3)$ ,  $\text{Cp}_2\text{Ti}(\text{CO})(\text{PMe}_2\text{Ph})$ ,  $\text{Cp}_2\text{Ti}(\text{CO})(\text{PMePh}_2)$ , and  $\text{Cp}_2\text{Ti}(\text{CO})(\text{P}(\text{OEt})_3)$  have coefficients within  $250 \text{ cm}^{-1} \text{ M}^{-1}$  of this value. Values of the other extinction coefficients are as follows:  $\text{Cp}_2\text{Ti}(\text{CO})_2 - \epsilon_{1895} = 8.8 \times 10^3$ ,  $\text{Cp}_2\text{Zr}(\text{CO})_2 - \epsilon_{1883} = 9.7 \times 10^3$ ,  $\text{Cp}_2\text{Zr}(\text{CO})(\text{P}(\text{OEt})_3) - \epsilon_{1867} = 6.7 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$ . Final concentrations of the other compounds were calculated from the differences of the starting and final concentrations of the metal compounds. The CO concentration was estimated by assuming that all of the released CO entered the gas phase above the solution and then using that partial pressure of CO to calculate<sup>15</sup> the amount of CO dissolved in the decalin.

**$\text{Cp}_2\text{M}(\text{C}^{13}\text{CO})_2$ : M = Ti, Zr, and Hf.** Solutions of the metallocene dicarbonyl compounds were prepared in thoroughly degassed solvents to give concentrations of  $3 \times 10^{-3}$  to  $1 \times 10^{-4}$  M in metal compound. A volume of 20 mL of each solution was stirred under an atmosphere of  $^{13}\text{CO}$  at 1 atm of pressure, for at least 15 h. The atmosphere of  $^{13}\text{CO}$  was changed twice. After the third atmosphere the solvent was removed under vacuum and the resulting crystalline solid was transferred to a drybox. As shown from IR spectra the  $(^{13}\text{CO})_2$  compounds composed at least 98% of the isolated products.

**$\text{Cp}_2\text{Ti}(\text{CO})\text{L}$ : L =  $\text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{PMePh}_2$ ,  $\text{PPh}_3$ ,  $\text{P}(n\text{-Bu})_3$ ,  $\text{P}(\text{OEt})_3$ , and  $\text{P}(\text{O}-i\text{-Pr})_3$ .**  **$\text{Cp}_2\text{Zr}(\text{CO})\text{L}$ : L =  $\text{PMe}_2\text{Ph}$ ,  $\text{PMePh}_2$ ,  $\text{PPh}_3$ ,  $\text{P}(n\text{-Bu})_3$ ,  $\text{P}(\text{OEt})_3$ , and  $\text{P}(\text{O}-i\text{-Pr})_3$ .**  **$\text{Cp}_2\text{Hf}(\text{CO})\text{L}$ : L =  $\text{PMe}_2\text{Ph}$ .** These compounds were prepared only during kinetic reactions or while measuring equilibrium constants. The conditions used were analogous to those of the thermal synthetic method in the literature.<sup>10</sup> The IR carbonyl bands are listed in Table I.

**Figure 2.** Overlaid spectra for reaction of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  with 0.13 M  $\text{P}(\text{OEt})_3$  in decalin at 46.6 °C.**Table II.** Kinetic Parameters for Substitution Reactions (Equations 1–3) of  $(\eta^5\text{-ring})_2\text{M}(\text{CO})_2$  with CO or  $\text{PR}_3$  in Decalin

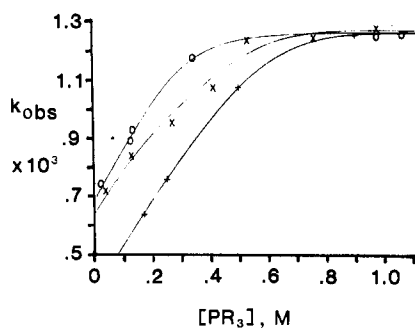
$(\eta^5\text{-ring})_2\text{M}(\text{CO})_2$	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu	$k$ ( $\text{s}^{-1}$ ) <sup>a</sup> at 45 °C	$k_{\text{rel}}^b$ at 45 °C
$\text{Cp}_2\text{Ti}(\text{C}^{13}\text{CO})_2^c$	$26.9 \pm 0.4$	$11.7 \pm 1.1$	$8.14 \times 10^{-4f}$	1.0
$\text{Cp}_2\text{Ti}(\text{CO})_2^d$	$27.9 \pm 1.8$	$15.0 \pm 5.6$	$8.78 \times 10^{-4f}$	1.08
$\text{Cp}^*_2\text{Ti}(\text{C}^{13}\text{CO})_2^e$	$28.5 \pm 0.5$	$14.1 \pm 1.5$	$2.15 \times 10^{-4f}$	0.26
$\text{Ind}_2\text{Ti}(\text{C}^{13}\text{CO})_2^e$	$24.1 \pm 1.6$	$7.9 \pm 5.4$	$9.11 \times 10^{-3f}$	11.2
$\text{Cp}_2\text{Zr}(\text{CO})_2^g$	$12.0 \pm 0.4$	$-31.2 \pm 1.4$	$6.22 \times 10^{-3g}$	7.64
$\text{Cp}_2\text{Hf}(\text{CO})_2^g$	$12.6 \pm 0.8$	$-31.0 \pm 2.6$	$4.22 \times 10^{-1h}$	3.01
$\text{Cp}_2\text{Hf}(\text{CO})_2^d$	$15.2 \pm 0.6$	$-31.0 \pm 1.2$	$3.91 \times 10^{-5g}$	0.048

<sup>a</sup>Error in  $k$ ,  $\pm 5\%$  max;  $k$  represents a first- or second-order rate constant as marked. <sup>b</sup>Relative reaction rates for  $[\text{Pr}_3] = 1$  M or for CO pressure of 1 atm ( $5.8 \times 10^{-3}$  M at 45 °C), determined by comparison of  $k_{\text{obs}}$  values. <sup>c</sup>Reactions with CO, at 1 atm. <sup>d</sup>Reactions with  $\text{PMe}_2\text{Ph}$ . <sup>e</sup>Reactions with  $\text{P}(\text{OEt})_3$ . <sup>f</sup>First-order rate constant. <sup>g</sup>Second-order rate constant ( $\text{s}^{-1} \text{ M}^{-1}$ ), calculated from one rate constant.

## Results

Kinetic reactions of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  with phosphines can be divided into two groups. The first group consists of those phosphines ( $\text{PMe}_2\text{Ph}$ ,  $\text{PMePh}_2$ , and  $\text{P}(\text{OEt})_3$ ) which gave a quantitative yield of  $\text{Cp}_2\text{Ti}(\text{CO})(\text{PR}_3)$  as  $\text{Cp}_2\text{Ti}(\text{CO})_2$  reacts with  $\text{PR}_3$ . Quantitative appearances of the monophosphine products were measured by monitoring the carbonyl bands of the product's IR spectra for eq 1. A representative example of the IR spectra recorded during kinetic reactions is shown in Figure 2. All of these reactions were first order in substrate and zero order in nucleophile for high concentrations of phosphine ( $>0.5$  M). At the high phosphine concentrations, these three nucleophiles yielded the same value for the observed rate constants. Activation parameters for the reactions using  $\text{P}(\text{OEt})_3$  as the nucleophile are given in Table II. For phosphine concentrations lower than about 0.5 M, the rate

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**Figure 3.** Plot of  $k_{\text{obsd}}$  vs.  $\text{PR}_3$  concentration for the reaction of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  with  $\text{P}(\text{OEt})_3$ ,  $\text{PMe}_2\text{Ph}$ , and  $\text{PMePh}_2$  in decalin; (O)  $\text{P}(\text{OEt})_3$ ; (x)  $\text{PMe}_2\text{Ph}$ ; (+)  $\text{PMePh}_2$ .

**Table III.** Second-Order Rate Constants for the Reactions (Equation 1) of  $\text{Cp}_2\text{M}(\text{CO})_2$  with  $\text{PR}_3$  in Decalin

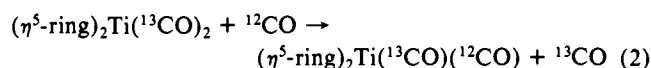
$\text{Cp}_2\text{M}(\text{CO})_2$	nucleophile	$T, ^\circ\text{C}$	$k, \text{s}^{-1} \text{M}^{-1}$
$\text{Cp}_2\text{Zr}(\text{CO})_2$	$\text{PMe}_2\text{Ph}$	25.9	$3.27 \times 10^{-3}$
$\text{Cp}_2\text{Zr}(\text{CO})_2$	$\text{PMePh}_2$	25.9	$1.62 \times 10^{-3}$
$\text{Cp}_2\text{Zr}(\text{CO})_2$	$\text{PPh}_3$	50.4	$4.8 \times 10^{-5b}$
$\text{Cp}_2\text{Zr}(\text{CO})_2$	$\text{P}(n\text{-Bu})_3$	25.9	$4.63 \times 10^{-5}$
$\text{Cp}_2\text{Zr}(\text{CO})_2$	$\text{P}(\text{OEt})_3$	25.9	$1.64 \times 10^{-3}$
$\text{Cp}_2\text{Zr}(\text{CO})_2$	$\text{P}(\text{OEt})_3$	35.9	$3.39 \times 10^{-3}$
$\text{Cp}_2\text{Zr}(\text{CO})_2$	$\text{P}(\text{OEt})_3$	46.0	$6.22 \times 10^{-3}$
$\text{Cp}_2\text{Zr}(\text{CO})_2$	$\text{P}(\text{O-}i\text{-Pr})_3$	25.9	$4.6 \times 10^{-5b}$
$\text{Cp}_2\text{Hf}(\text{CO})_2$	$\text{PMe}_2\text{Ph}$	50.1	$5.77 \times 10^{-5}$
$\text{Cp}_2\text{Hf}(\text{CO})_2$	$\text{PMe}_2\text{Ph}$	60.2	$1.24 \times 10^{-4}$
$\text{Cp}_2\text{Hf}(\text{CO})_2$	$\text{PMe}_2\text{Ph}$	70.3	$2.47 \times 10^{-4}$

<sup>a</sup> Error in  $k_2$ ,  $\pm 5\%$  max. <sup>b</sup> Estimated from one rate constant.

constants decrease as the concentrations decrease. The dependence of  $k_{\text{obsd}}$  on  $[\text{PR}_3]$  is shown in Figure 3.

The second group consists of those phosphines which yield a less than quantitative amount of the monophosphine product. Among this group are  $\text{P}(n\text{-Bu})_3$ ,  $\text{PPh}_3$ ,  $\text{PCy}_3$ , and  $\text{P}(\text{O-}i\text{-Pr})_3$ . Typically the product band slowly increased for the first one-fourth to one-half of the reaction and then began to decrease. The phosphorus ligands can be ordered by the amount of product that was present in the reaction solution when the product had reached a maximum concentration. The ligand ordering from greater to lesser maximum concentration of product is as follows:  $\text{P}(n\text{-Bu})_3 \sim \text{P}(\text{O-}i\text{-Pr})_3 > \text{PPh}_3 > \text{PCy}_3$ . For reactions with  $\text{PCy}_3$ , no product was detected. If the reactions were allowed to proceed beyond the time when all of the  $\text{Cp}_2\text{Ti}(\text{CO})_2$  had reacted, then the CO bands of monophosphine products would also disappear. At this point if the reaction tubes were closed and left for about 12 h, the final product would be  $\text{Cp}_6\text{Ti}_6\text{O}_8$ .<sup>16</sup> The time required for the formation of  $\text{Cp}_6\text{Ti}_6\text{O}_8$  was shorter when the poorer nucleophiles were used. The hexameric titanium cluster was characterized by its deep blue color and by mass spectral data.

Kinetic data were collected for the CO-exchange reactions of  $\text{Cp}_2\text{Ti}(\text{CO})_2$ ,  $\text{Cp}^*\text{Ti}(\text{CO})_2$ , and  $\text{Ind}_2\text{Ti}(\text{CO})_2$ . These reactions, shown in eq 2 where  $(\eta^5\text{-ring}) = \text{Cp}$ ,  $\text{Cp}^*$ , or  $\text{Ind}$ , were first order in Ti complex and zero order in CO. The activation



parameters for the reactions are listed in Table II. The exchange rate for the reaction of  $\text{Ind}_2\text{Ti}(\text{CO})_2$  was about 11 times faster than that of  $\text{Cp}_2\text{Ti}(\text{CO})_2$ , whereas the exchange rate for the  $\text{Cp}^*\text{Ti}(\text{CO})_2$  reactions was about one-fourth the rate for  $\text{Cp}_2\text{Ti}(\text{CO})_2$ .

The reactions of  $\text{Cp}_2\text{M}(\text{CO})_2$ , where  $\text{M} = \text{Zr}$  or  $\text{Hf}$ , with phosphorus ligands, eq 1, were first order in both substrate and entering nucleophile. Dependence of the observed rate constants on nucleophile concentration was measured for  $\text{PMe}_2\text{Ph}$  with both the Zr and Hf compounds and for  $\text{PMePh}_2$ ,  $\text{P}(n\text{-Bu})_3$ , and  $\text{P}(\text{OEt})_3$

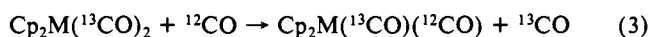
**Table IV.** Equilibrium Constants for the Reactions (Equation 1) of  $\text{Cp}_2\text{M}(\text{CO})_2$  with  $\text{PR}_3$  in Decalin at  $30.0^\circ\text{C}^a$

$\text{Cp}_2\text{M}(\text{CO})_2$	nucleophile	cone angle <sup>b</sup>	$\Delta\text{HNP}^c$	$K_{\text{eq}}$
$\text{Cp}_2\text{Ti}(\text{CO})_2$	$\text{PMe}_3$	118	114	$1.9 \pm 0.2 \times 10^{-3}$
$\text{Cp}_2\text{Ti}(\text{CO})_2$	$\text{PMe}_2\text{Ph}$	122	281	$2.7 \pm 0.3 \times 10^{-4}$
$\text{Cp}_2\text{Ti}(\text{CO})_2$	$\text{PMePh}_2$	136	424	$6.7 \times 0.2 \times 10^{-5}$
$\text{Cp}_2\text{Ti}(\text{CO})_2$	$\text{PPh}_3$	145	573	$7 \pm 2 \times 10^{-7}$
$\text{Cp}_2\text{Ti}(\text{CO})_2$	$\text{P}(n\text{-Bu})_3$	132	131	$1.7 \pm 0.2 \times 10^{-6}$
$\text{Cp}_2\text{Ti}(\text{CO})_2$	$\text{P}(\text{OEt})_3$	109	520	$2.9 \pm 0.3 \times 10^{-4}$
$\text{Cp}_2\text{Ti}(\text{CO})_2$	$\text{P}(\text{O-}i\text{-Pr})_3$	130	500	$2.8 \pm 0.4 \times 10^{-6}$
$\text{Cp}_2\text{Zr}(\text{CO})_2$	$\text{P}(\text{OEt})_3$	109	520	$3.3 \pm 0.1 \times 10^{-3}$

<sup>a</sup>  $\pm 0.1^\circ\text{C}$ . <sup>b</sup> Cone angle of phosphorus ligand. Tolman, C. A. *Chem. Rev.* 1977, 77, 313-348. <sup>c</sup> Basicity of phosphorus ligand. Streuli, C. A. *Anal. Chem.* 1960, 32, 985-987.  $\Delta\text{HNP}$  = half-neutralization potential as compared with that of  $N,N'$ -diphenylguanidine in nitromethane. Greater basicity is indicated by smaller  $\Delta\text{HNP}$  values.

with the Zr compound. The resulting second-order rate constants are summarized in Table III. Activation parameters for these reactions are listed in Table II. A zero intercept, within experimental error, for the plots of  $k_{\text{obsd}}$  vs.  $[\text{PR}_3]$  indicates that there is no first-order rate constant for the reactions. Kinetic reactions for  $\text{Cp}_2\text{Zr}(\text{CO})_2$  were performed at a single nucleophile concentration with  $\text{PPh}_3$  and  $\text{P}(\text{O-}i\text{-Pr})_3$ . There appeared to be no tendency for any of the Zr and Hf monophosphine reaction products to decompose, as did the reaction products of Ti.

Kinetic parameters for the reactions of  $\text{Cp}_2\text{M}(\text{CO})_2$  with  ${}^{12}\text{CO}$ , where  $\text{M} = \text{Zr}$  or  $\text{Hf}$ , eq 3, were also obtained. Carbon monoxide exchange rates for the zirconocene compounds were



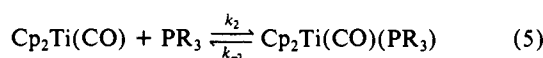
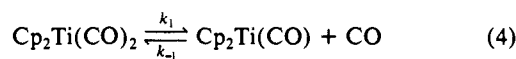
too fast to measure by the techniques available. Only a lower limit for the rate constant could be determined,  $k_{\text{obsd}} < 2 \times 10^{-2}$ . The activation parameters calculated for the reactions of the hafnium compound are listed in Table II.

Equilibrium constants were measured for reactions of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  with  $\text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{PMePh}_2$ ,  $\text{PPh}_3$ ,  $\text{P}(n\text{-Bu})_3$ ,  $\text{P}(\text{OEt})_3$ , and  $\text{P}(\text{O-}i\text{-Pr})_3$  and for reactions of  $\text{Cp}_2\text{Zr}(\text{CO})_2$  with  $\text{P}(\text{OEt})_3$  at  $30^\circ\text{C}$ , eq 1. These values are listed in Table IV. An equilibrium constant was not measured for the reaction of  $\text{Cp}_2\text{Hf}(\text{CO})_2$  with a phosphine at this temperature, due to the slowness of the reaction ( $k_{\text{PMe}_2\text{Ph}} = 7 \times 10^{-6}$  at  $30^\circ\text{C}$ ).

## Discussion

**Substitution Mechanism for Titanium Compounds.** Our initial investigations on the reactions of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  with a wide range of phosphines and phosphites supported the earlier qualitative observation<sup>10</sup> that the reaction was dependent on nucleophile concentration. The better nucleophiles (i.e., the phosphorus ligands with smaller cone angles and/or greater basicities, Table IV) reacted more rapidly than the poorer nucleophiles. A ligand concentration dependence was also observed for the reaction rates.

Further work involving higher concentrations of  $\text{PMe}_2\text{Ph}$ ,  $\text{PMePh}_2$ , and  $\text{P}(\text{OEt})_3$  shows that the observed rate constants level off for ligand concentrations above 0.5 M, Figure 3. More importantly, the rate constants for all three of these nucleophiles level off at the same  $k_{\text{obsd}}$  value. The rate constant obtained from the  ${}^{13}\text{CO}$ -exchange reactions of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  also matched the first-order rate constant values from the high  $[\text{PR}_3]$  reactions. These results indicate the reactions proceed by a dissociation ( $\text{S}_{\text{N}}1$ ) pathway. The most probable mechanism would be loss of a CO ligand, as the rate-determining step, with subsequent addition of a phosphorus ligand to the vacant coordination site, eq 4 and 5.



The activation parameters (Table II) calculated by using the rate constants at high nucleophile concentrations and those calculated from the  ${}^{13}\text{CO}$ -exchange reactions are consistent with those

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of other reactions<sup>17,18</sup> that proceed by a CO dissociation mechanism.

The decrease in  $k_{\text{obsd}}$  for reactions which were less than 0.5 M in  $\text{PR}_3$  suggests that the  $k_{-1}$  term is significant. When the steady-state approximation is used and  $k_{-2}$  is considered to be insignificant,  $k_{\text{obsd}}$  can be approximated in terms of  $k_1$ ,  $k_{-1}$ , and  $k_2$ , eq 6. This equation approximates the behavior of  $k_{\text{obsd}}$  as a

$$k_{\text{obsd}} = (k_1 k_2 [\text{PR}_3]) / (k_{-1} [\text{CO}] + k_2 [\text{PR}_3]) \quad (6)$$

function of  $[\text{PR}_3]$ , Figure 3, with the exception that it predicts a zero intercept where a non-zero intercept is observed. An exact solution for the expression of  $k_{\text{obsd}}$  is rather complex without making a number of assumptions which would be invalid for the reactions of eq 4 and 5. However, a solution including  $k_{-2}$  predicts roughly the same  $\text{PR}_3$  concentration dependence of  $k_{\text{obsd}}$  as does eq 6, except that the intercept is a function of  $k_{-2}$ .

It is suggested that the titanocene compounds prefer to coordinate to CO compared to  $\text{PR}_3$  by the fact that it is necessary to remove liberated CO from reaction solutions in order for the reactions to proceed to completion. This preference for CO coupled with the evidence of a significant  $k_{-1}[\text{CO}]$  term in eq 6 suggested that the equilibrium constant for eq 1 might be so small that even trace amounts of CO left in the solvent cage of  $\text{Cp}_2\text{Ti}(\text{CO})$  could back react to a great enough extent to effectively compete with  $\text{PR}_3$ . The measured equilibrium constants were found to be very small, ranging between  $10^{-3}$  and  $10^{-6}$  (Table IV).

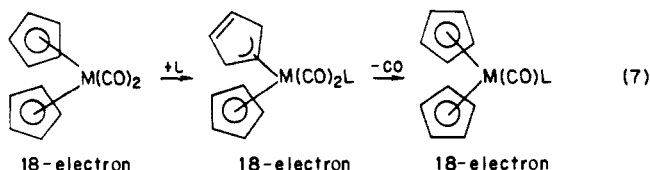
Arranging the phosphorus ligands according to equilibrium constants gives the following ordering:  $\text{PMe}_3 > \text{P}(\text{OEt})_3 \approx \text{PMe}_2\text{Ph} > \text{PMePh}_2 > \text{P}(\text{O}-i\text{-Pr})_3 > \text{P}(n\text{-Bu})_3 > \text{PPh}_3$ . If the phosphorus ligands are ordered according to reaction rate constants for eq 1 at ligand concentrations of approximately 0.13 M, the same arrangement as for the equilibrium constants is obtained. The similarity of these two orderings supports the supposition that CO is effectively competing with  $\text{PR}_3$  for capture of the reaction intermediate which is probably  $\text{Cp}_2\text{Ti}(\text{CO})$ . In summary, all the data collected on reactions of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  with  $\text{PR}_3$  and CO support a CO dissociation ( $\text{S}_{\text{N}}1$ ) mechanism.

For reactions of  $\text{Cp}^*\text{Ti}(\text{CO})_2$  and  $\text{Ind}_2\text{Ti}(\text{CO})_2$ , a CO dissociation pathway is again indicated. The activation parameters are indicative of CO dissociation, and the CO-exchange reactions are independent of CO concentration. As expected<sup>19</sup> for a CO dissociation mechanism, changing the cyclopentadienyl groups to indenyl groups has a small rate-enhancing effect. The indenyl ligand is more electron withdrawing than the cyclopentadienyl ligand, as can be seen in the IR spectra of the compounds, Table I. By withdrawing more electron density from the metal,  $\pi$  back bonding from the metal to the CO ligand is decreased, resulting in a weaker M-CO bond. The opposite effect is observed for  $\text{Cp}^*\text{Ti}(\text{CO})_2$ , where the pentamethylcyclopentadienyl ligand donates more electron density to the metal than does cyclopentadienyl ligand strengthening the M-CO bond. What may be surprising is that the indenyl ligand effect<sup>12e</sup> does not promote an associative pathway.

**Substitution Mechanism for Zirconium and Hafnium Compounds.** Kinetic reactions for the dicarbonyl metallocene compounds of zirconium and hafnium with phosphorus ligands and with CO indicated a different mechanism than that for the titanium compounds. The reaction rates are first order in metal compound and in entering nucleophile, suggesting the reaction mechanism is associative ( $\text{S}_{\text{N}}2$ ). This conclusion was further supported by the activation parameters, Table II. A large negative  $\Delta\text{S}^\ddagger$  is indicative of a decrease in the number of degrees of freedom in the formation of the transition state, and a  $\Delta\text{H}^\ddagger$  between about 10–15 kcal/mol is characteristic<sup>20</sup> of a bond-forming process in

the rate-determining step. Plots of  $k_{\text{obsd}}$  vs.  $[\text{PR}_3]$  were linear and gave a zero intercept, indicating that there is not also a dissociative mechanism involved in the substitution reactions.

Previous studies<sup>12</sup> have indicated that the cyclopentadienyl ring can slip from  $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$  during the associative reactions of some such compounds with phosphorus ligands. Reducing the coordination number of the ring allows the complex to maintain a stable 18-electron<sup>21</sup> system, as the entering nucleophile forms a bond to the metal (eq 7). Other alternatives could be envisioned, such as formation of a 20-electron metal center, but that would be energetically less favorable.



A large rate difference was observed between the CO-exchange reactions and the substitution reactions using phosphorus ligands. This result is expected in view of the known<sup>8,9</sup> high CO preference over phosphorus ligands of the corresponding titanium compounds. The equilibrium constant for eq 1 with  $\text{Cp}_2\text{Zr}(\text{CO})_2$  and  $\text{P}(\text{OEt})_3$  is very low,  $3.3 \times 10^{-3}$  (Table IV) showing a preference for CO over  $\text{P}(\text{OEt})_3$  which is expected to be displayed in the metal's preference for entering ligands.

It was not the purpose of this study to try to quantify the various factors that contribute to the nucleophilic strength of phosphorus atom ligands toward the substrate  $\text{Cp}_2\text{Zr}(\text{CO})_2$ . This would require a much more detailed study which we are not prepared to make, because even such a study may well fall short of quantifying all the different parameters that contribute to the nucleophilic strengths of particular nucleophiles toward particular organometallic complexes. The large amount of experimental data already available and the complexity of the problem was discussed recently.<sup>22</sup> All we can say with the limited data at hand is that these early transition low valent metal (Zr(II)) systems prefer  $\pi$  acids to  $\sigma$  bonding ligands. The most striking example of this is that CO exchange with  $\text{Cp}_2\text{Zr}(\text{CO})_2$  was too fast for us to measure, whereas substitution reactions with phosphines and phosphites proceed at much slower rates. Why is this? We do not know, but it may have to do with the electropositive nature of the early transition metals, which means when in low oxidation states these metals have a propensity to give up electron density. One other point is that CO is small in size, and steric factors do contribute to nucleophilic strength in these systems.

Unfortunately, the CO-exchange reactions of  $\text{Cp}_2\text{Zr}(\text{CO})_2$  were too fast to monitor at or above 20 °C by taking IR spectra of withdrawn aliquots. Monitoring the carbonyl exchange by <sup>13</sup>C NMR seemed like a possible method of determining the exchange rate. It was estimated from the peak separation of the resonances for <sup>13</sup>CO, 184.4 ppm, and  $\text{Cp}_2\text{Zr}(\text{CO})_2$ , 264.5 ppm, that a  $3 \times 10^4$  exchange rate would be required to observe peak coalescence. Estimating the temperature of that exchange rate from a  $\Delta\text{H}^\ddagger$  value of 10 kcal/mol and a  $k_{\text{obsd}}$  value of  $5 \times 10^{-2}$  at 28 °C gave an approximate value of 200 °C. At 170 °C  $\text{Cp}_2\text{Zr}(\text{CO})_2$  irreversibly decomposed, eliminating the possibility of obtaining activation parameters by <sup>13</sup>C NMR.

**Comparison of  $\text{Cp}_2\text{M}(\text{CO})_2$ , where M = Ti, Zr, or Hf.** Similarity in the three metallocene dicarbonyl compounds of titanium, zirconium, and hafnium can be seen in their preference for carbon monoxide over phosphines or phosphites. This favoring of CO is shown in the equilibrium constants for the Ti and Zr compounds, Table IV, and in the associative rate constants of the Zr and Hf compounds, Table III. The relatively high electron density on the electropositive metals in these metallocene compounds can be inferred from their relatively low IR carbonyl stretching fre-

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quencies, Table I. The electropositive nature of the metals improves  $\pi$  back bonding from the metal to the CO ligand and is probably responsible for the greater stability of the CO product as compared with the  $\text{PR}_3$  product. Carbonyl ligands have the ability to withdraw electron density from the metal through  $\pi$  back bonding. Conversely, phosphorus ligands bond mainly by  $\sigma$  electron donation with the effect of increasing the electron density on the metal. As can be inferred from the electronegativity values (Ti, 1.32; Zr, 1.22; Hf, 1.23 on the Allred-rochow scale)<sup>23</sup> and from ionization potentials (Ti(II), 2.65; Zr(II), 2.22; Hf(II), 2.25 MH/mol)<sup>24</sup> of these metals, they prefer lower rather than higher electron densities. This is the effect that is observed in the preference for the  $\pi$  acid CO over  $\text{PR}_3$ .

Substitution reactions of the zirconium compounds are faster than corresponding reactions of either titanium or hafnium compounds (Table II). This was perhaps to be expected, for it has long been known that low valent transition-metal complexes undergo ligand substitution with relative rates of first row < second row > third row (e.g., Cr < Mo > W,<sup>25</sup> Co < Rh > Ir,<sup>2a</sup> Ni < Pd > Pt<sup>26</sup>). It is also of interest to note that some of the best homogeneous catalysts are found<sup>27</sup> among the second-row organometallic systems of Mo, Ru, Rh, and Pd. An explanation for the greater reactivity of the second row transition-metal complexes has been given based on  $\sigma$  and  $\pi$  bonding<sup>26</sup> and in terms of the low electronegativity of first-row metals as one factor and a good matching of the orbital energies of the third-row metals with CO as the second factor.<sup>28</sup>

The unique feature observed for the first time in this study is that the mechanism of ligand substitution changes in a given triad of transition metals. It is not known why reactions of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  proceed by dissociation ( $\text{S}_{\text{N}}1$ ), whereas analogous substitution reactions of corresponding zirconium and hafnium compounds proceed by association ( $\text{S}_{\text{N}}2$ ). The implication may be that there is a delicate balance of factors which can alter the substitution reaction pathway. One such factor is steric and a partial explanation for the lack of an associative pathway for the reactions of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  may involve the smaller size of the titanium metal relative to zirconium and hafnium. The M-centroid, i.e., the metal to ring center, distance for  $\text{Cp}_2\text{Ti}(\text{CO})_2$ <sup>29</sup> is 0.15 Å shorter than for the zirconium<sup>30</sup> and hafnium<sup>31</sup> analogues. The LUMO for  $\text{Cp}_2\text{M}(\text{CO})_2$  involves<sup>32</sup> the XZ orbitals of the metal center. Therefore, entering nucleophiles would attack in the area between

the plane of the carbonyl ligands and the rings, with attack centered between the CO's. With the shorter M-centroid distance for the titanium compounds, such attack would be more hindered than for the zirconium and hafnium compounds. Additionally, the d orbitals of Ti do not extend out as far as those of Zr and Hf, thus making it harder for nucleophiles to successfully attack the LUMO of the Ti compounds.

The steric restrictions of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  can be seen from the ordering of the phosphorus ligands according to equilibrium constants (Table IV) for eq 1. The primary influence is the cone angle of the phosphorus ligand, with smaller ligands having a larger equilibrium constant. A 10-fold increase in the equilibrium constant for  $\text{PR}_3 = \text{P}(\text{OEt})_3$  is seen for reactions with  $\text{PR}_3$  of  $\text{Cp}_2\text{Zr}(\text{CO})_2$  over  $\text{Cp}_2\text{Ti}(\text{CO})_2$ , further indicating the more sterically constrained nature of the titanium compound.

## Conclusion

Carbonyl substitution reactions of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  appear to take place by a CO dissociation ( $\text{S}_{\text{N}}1$ ) mechanism. In marked contrast, the substitution reactions of  $\text{Cp}_2\text{Zr}(\text{CO})_2$  and  $\text{Cp}_2\text{Hf}(\text{CO})_2$  proceed by an associative ( $\text{S}_{\text{N}}2$ ) mechanism. The associative pathway probably involves  $\eta^2 \rightarrow \eta^3 \rightarrow \eta^2$ -ring slippage in order to maintain an 18-electron count around the metal centers. The distinct difference between the substitution mechanisms for  $\text{Cp}_2\text{Ti}(\text{CO})_2$  vs.  $\text{Cp}_2\text{Zr}(\text{CO})_2$  and  $\text{Cp}_2\text{Hf}(\text{CO})_2$  may be at least partially explained by the smaller size of the titanium atom. The titanium compound may be too sterically constrained to accept an entering nucleophile. That  $\text{Cp}_2\text{Zr}(\text{CO})_2$  reacts the fastest is in accord with the known<sup>26</sup> behavior of low-valent transition-metal complexes where ligand substitution varies in the order first row < second row > third row.

Equilibrium constants and rate constants for the metallocene dicarbonyl compounds of titanium, zirconium, and hafnium indicate that these compounds have a strong preference for CO over phosphorus ligands. A preference for the  $\pi$  acid CO by these metallocene compounds is consistent with the electropositive nature of these metals, which are prone to give up electrons.

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**Registry No.**  $\text{Cp}_2\text{Ti}(\text{CO})_2$ , 102588-60-3;  $\text{Cp}_2\text{Ti}(\text{CO})_2$ , 12129-51-0;  $\text{Cp}^*\text{Ti}(\text{CO})_2$ , 102588-61-4;  $\text{Ind}_2\text{Ti}(\text{CO})_2$ , 102588-62-5;  $\text{Cp}_2\text{Zr}(\text{CO})_2$ , 59487-85-3;  $\text{Cp}_2\text{Hf}(\text{CO})_2$ , 59487-86-4;  $\text{PMe}_2\text{Ph}$ , 672-66-2;  $\text{PMePh}_2$ , 1486-28-8;  $\text{PPh}_3$ , 603-35-0;  $\text{P}(n\text{-Bu})_3$ , 998-40-3;  $\text{P}(\text{OEt})_3$ , 122-52-1;  $\text{P}(O\text{-}i\text{-Pr})_3$ , 116-17-6;  $\text{PMe}_3$ , 594-09-2;  $\text{Cp}_2\text{Ti}(\text{CO})(\text{PMe}_2\text{Ph})$ , 102576-12-5;  $\text{Cp}_2\text{Ti}(\text{CO})(\text{PMePh}_2)$ , 102576-13-6;  $\text{Cp}_2\text{Ti}(\text{CO})(\text{P}(n\text{-Bu})_3)$ , 102576-14-7;  $\text{Cp}_2\text{Ti}(\text{CO})(\text{P}(\text{OEt})_3)$ , 102576-15-8;  $\text{Cp}_2\text{Ti}(\text{CO})(\text{P}(O\text{-}i\text{-Pr})_3)$ , 102576-16-9;  $\text{Cp}_2\text{Zr}(\text{CO})_2$ , 91203-07-5;  $\text{Cp}_2\text{Zr}(\text{CO})(\text{PMe}_2\text{Ph})$ , 102576-17-0;  $\text{Cp}_2\text{Zr}(\text{CO})(\text{P}(n\text{-Bu})_3)$ , 102576-18-1;  $\text{Cp}_2\text{Zr}(\text{CO})(\text{P}(\text{OEt})_3)$ , 102576-19-2;  $\text{Cp}_2\text{Zr}(\text{CO})(\text{P}(O\text{-}i\text{-Pr})_3)$ , 102576-20-5;  $\text{Cp}_2\text{Hf}(\text{CO})_2$ , 102576-21-6;  $\text{Cp}_2\text{Hf}(\text{CO})(\text{PMe}_2\text{Ph})$ , 102576-22-7.

**Supplementary Material Available:** Listing of the observed rate constants for the reactions of the Ti, Zr, and Hf compounds with  $\text{PR}_3$  and CO (5 pages). Ordering information is given on any current masthead page.

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