Homogeneous Catalytic Carbonylation of Nitroaromatics. 7. Transesterification and an Intramolecular Ligand-Hopping Mechanism for Isomerization in the Bis(methoxycarbonyl) Complex $Ru(Ph_2PCH_2CH_2PPh_2)(CO)_2[C(O)OCH_3]_2$

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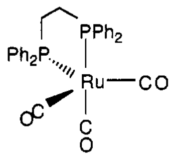
The bis(methoxycarbonyl) complex (*OC*-6-32)-dicarbonylbis(methoxycarbonyl)[1,2-bis(diphenylphosphino)ethane]ruthenium(II) (**3**) isomerizes to (*OC*-6-2′2)-dicarbonylbis(methoxycarbonyl)[1,2-bis(diphenylphosphino)ethane]ruthenium(II) (**3′**) via an intramolecular methoxide migration to an adjacent metal carbonyl. Isolation of pure **3**, followed by dissolution in benzene-d_6 at ambient temperature, results in the formation of an equilibrium mixture of the two species within 3 h. The assignment of methoxide migration as the mechanism of isomerization is based on kinetic analysis of the isomerization via NMR spectroscopic methods, ^{13}CO ligand exchange with **3**, and attempted isotopic crossover experiments. Reacting **3** with $Ru(dppe)(CO)_2[C(O)OCD_3]_2$ in a 1.15:1 ratio under ambient conditions over 2 days did not result in observable scrambling of the isotopic labels. Transesterification of the two methoxycarbonyl groups occurs rapidly in the presence of excess alcohol. The rates of exchange with CD_3OD for the two methoxycarbonyl ligands on **3** were found to be independent of each other and were quantified by NMR spectroscopic methods.

Introduction

Methoxycarbonyl and related hydroxycarbonyl and carbamoyl complexes have been proposed as intermediates in numerous catalytic and stoichiometric reactions.[1–3] The chemistry of the few known examples of bis(methoxycarbonyl) complexes is summarized below. The mechanism of formation of $Pt(dppe)[C(O)OCH_3]_2$ from $Pt(dppe)(OCH_3)_2$ was found to occur by migratory insertion of a coordinated CO into the $Pt–OCH_3$ bond.[4] The complex $Cs\{Co(CO)_3[C(O)OCH_3]_2\}$ was the first crystallographically characterized bis(methoxycarbonyl) metal species and was found to undergo reductive elimination of dimethyl carbonate leaving $Cs[Co(CO)_4]$.[5] In comparison, thermal decomposition of $Pd(bipy)[C(O)OCH_3]_2$ yielded bipy, CH_3OH, and Pd metal.[6] The importance of the ancillary ligands on the reactivity of a bis(methoxycarbonyl) complex was established in an Fe(II) system[7] that was isoelectronic to the ruthenium complex described here. Exchange with alcohols (transesterification) occurred readily on $Fe(CO)_4[C(O)OCH_3]_2$ but not on the more electron rich and sterically crowded complex $Fe(PPh_3)(CO)_3[C(O)OCH_3]_2$.[7] For the unsubstituted compound, it was found that methoxide dissociation from the metal complex occurred, followed by the reaction of $\{Fe(CO)_5[C(O)OCH_3]\}^+$ with ethanol.

$$ArNO_2 + 3CO + CH_3OH \rightarrow ArNHC(O)OCH_3 + 2CO_2 \quad (1)$$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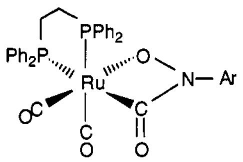
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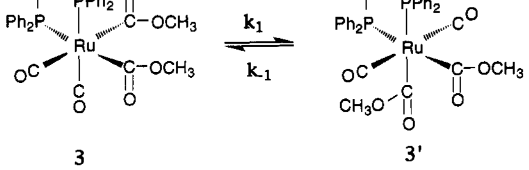
During the course of studying the homogeneous catalytic carbonylation of nitroaromatics (eq 1) using $Ru(dppe)(CO)_3$ (**1**), the four-member metallocyclic intermediate $Ru(dppe)(CO)_2[C(O)N(Ar)O]$ (**2**) formed rapidly following the interaction of $ArNO_2$ with **1** under CO.[8] This species reacted quantitatively with CH_3OH under CO, as shown in eq 2, to generate the isomeric, bis(methoxycarbonyl)

$$Ru(dppe)(CO)_2[C(O)N(Ar)O] + 2CH_3OH + 2CO \rightarrow ArNH_2 + CO_2 + Ru(dppe)(CO)_2[C(O)OCH_3]_2 \quad (2)$$

complexes (*OC*-6-32)-dicarbonylbis(methoxycarbonyl)-[1,2-bis(diphenylphosphino)ethane]ruthenium(II) (**3**) and (*OC*-6-2′2)-dicarbonylbis(methoxycarbonyl)[1,2-bis(diphenylphosphino)ethane]ruthenium(II) (**3′**) in approximately a 4 to 1 ratio. *In-situ*, high-pressure infrared spectroscopy established that **3** and **3′** are the predominant species under catalytic conditions.[8] This paper describes results that



3
3′
(3)

[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1994.

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establish the mechanism of the isomerization shown in eq 3 along with the reactivity of 3 and 3′ with alcohols and ^{13}CO.

Experimental Section

General Methods. Standard Schlenk techniques were implemented when working with all organometallic compounds. A nitrogen-filled Vacuum Atmospheres drybox equipped with a Dri-Train Model 40-1 inert-gas purifier was employed for manipulations carried out under glovebox conditions. Nuclear magnetic resonance spectroscopy was performed on a Varian-Unity 300 instrument, and infrared spectra were collected on a Mattson Polaris spectrometer. A triple quadrupole mass spectrometer (API III LC-MS-MS system, Sciex, Thornhill, Ontario, Canada) was used for the ionspray mass spectrometric experiments.

All chemicals were purchased from Aldrich Chemical Co., except $Ru_3(CO)_{12}$ and dppe [1,2-bis(diphenylphosphino)ethane], which were purchased from Strem Chemical. Toluene, diethyl ether, and hexane were freshly distilled from benzophenone ketyl under nitrogen. Methylene chloride was distilled from calcium hydride. Anhydrous CH_3OH packed under nitrogen was purchased from Aldrich Chemical Co. Benzene-d_6 and toluene-d_8 were either purchased from Cambridge Isotope Laboratories, dried with 4-Å activated molecular sieves, and degassed with several freeze–pump–thaw cycles before use or purchased from Aldrich Chemical Co. packed in an ampule under vacuum and used without further purification. Ru(dppe)$(CO)_3$ was prepared from the literature procedure.[9] Carbon-^{13}C monoxide in glass vessels and lecture bottles was purchased from Isotech Inc.

Preparation of Pure 3. This is a modified preparation of a mixture of 3 and 3′ along with the complete description of the recrystallization that leads to pure 3. A 50-mL stainless steel autoclave containing Ru(dppe)$(CO)_3$ (461 mg, 0.791 mmol) was purged three times with CO (15 atm) and maintained at 1 atm during reactant injection. *p*-Nitrotoluene (407 mg, 2.97 mmol) was dissolved in 15 mL of deoxygenated toluene and injected into the autoclave via an exhaust valve. After 5 min, 3 mL of CH_3OH was injected in the same manner and the autoclave was sealed, pressurized to 14 atm, and placed in the aluminum block heated to 85 °C. After 25 min the autoclave was removed from the block and cooled to ambient temperature in an ice bath. The pressure was released, and the solution was transferred immediately to a 100-mL round-bottom flask and concentrated under vacuum to a volume of approximately 8 mL. At this point the yield observed by ^{31}P NMR integration of the mixture of 3 and 3′ was 90%. To this light brown oil was added 10 mL of dry diethyl ether, causing a separation of a small amount of a red-brown viscous tar. After 5 min the supernatant solution was transferred to a 50-mL flask, 5 mL of hexanes was added, and the flask was capped with a stopper and placed in a freezer at −14 °C. Spherical shaped clusters of crystals of 3 grew overnight in 20–60% isolated yield.

Kinetics of the Isomerization of 3 to 3′. Crystalline nodules of isomerically pure 3 were weighed in the glovebox (10 mg, 1.5×10^{-2} mmol), placed in a 5-mm NMR tube, and capped with a septum. This was removed from the box, and dried C_6D_6 (0.5 mL) was added via syringe. As soon as a homogeneous solution was achieved with the aid of a vortex mixer, the tube was placed in the NMR spectrometer, and a ^1H NMR spectrum was collected every 10 min at 21 °C until the reaction was complete.

Exchange of Methoxide on 3 and 3′ with CD_3OD and Other Alcohols. Several experiments were run at various concentrations of CD_3OD using the following method: In a glovebox, 3 (11.6 mg, 1.7×10^{-2} mmol) was weighed, was placed in a 5-mm NMR tube, and was capped with a septum. The tube was removed from the box, and dried C_6D_6 (0.5 mL) was added via syringe. Upon addition of 50 μL of CD_3OD (2.2 M final concentration) the sample was immediately placed in the NMR spectrometer, and a ^1H NMR spectrum was obtained every 10 min. Monitoring the disappearance of the methoxy resonances vs an internal standard of triphenylmethane was used to determine the reaction rate.

Other alcohols, such as phenol, were observed by NMR spectroscopy to exchange with 3, but we have not yet attempted to isolate and fully characterize the products.

Preparation of Ru(dppe)$(CO)_2[C(O)OCD_3]_2$ (3-d_6, 3′-d_6). Dissolving 3 (100 mg, 0.15 mmol) in 1.0 mL of neat CD_3OD, and allowing the resulting solution to stand for 3 h at ambient temperature followed by removal of CD_3OD and CH_3OD under vacuum, generated 3-d_6 and 3′-d_6 in a 99% yield. Monitoring the reaction progress with ^{31}P NMR spectroscopy showed separate signals for 3 verses the singly (3-d_3) and doubly (3-d_6) exchanged compounds. The latter two gave identical ^{31}P NMR signals at 45.13 (d, J_{PP} = 12.5 Hz) and 51.47 (d, J_{PP} = 12.5 Hz) ppm.

Crossover Experiment with 3, 3′ and 3-d_6, 3′-d_6. Two 0.5-mL C_6D_6 solutions were prepared for the crossover experiment; the first contained 3 and 3′ (80.2 mM), and the second 3-d_6 and 3′-d_6 (69.2 mM). The two solutions were combined and placed into a septum-sealed, nitrogen-purged NMR tube giving final concentrations of 40.1 mM in 3 and 3′ and 34.6 mM in 3 and 3′-d_6. The tube was immediately placed in the NMR spectrometer, and a ^{31}P NMR spectrum was collected. The reaction was monitored over 3 days with no detectable change in the ratio of 3 to 3-d_6. At this time the solution was placed in a 25-mL Schlenk flask, and the solvent was removed under vacuum. The solid, pure 3 and 3′, and pure 3-d_6 and 3′-d_6 were analyzed using ionspray mass spectroscopy. For this technique, 1 mg of the solid was dissolved in 1 mL of a 2/5 ratio of acetonitrile/methylene chloride. The samples were pumped at 5–10 mL/min with a Harvard Apparatus syringe pump into the ionspray interface of an API III triple quadrapole mass spectrometer (Sciex). The spectra were acquired in the positive-ion mode over the range *m/z* 600–730 with a 0.1-A step and 20-ms dwell time. The molecular masses were determined from the Sciex Masspec program. The mass axis was calibrated in the positive ion mode using a mixture of polypropylene glycols.

Carbon ^{13}C Monoxide Isotopic Labeling Studies of 3 and 3′. Either glass break-seal flasks or lecture bottles of ^{13}CO were employed for this work. An example of the use of each follows. The first example makes use of a high-pressure NMR tube designed by Roe.[10] In the glovebox the sapphire tube was loaded with crystalline 3 and 3′ (0.4 mL of a 30 mM solution of 3 and 3′ in C_6D_6). The valve was fastened to the top flange of the tube and closed, and the tube was removed from the glovebox. After placement of the apparatus in the safety shield, the tube was connected via a Swagelok fitting to a line designed to be evacuated and filled with ^{13}CO from a lecture bottle. The line was evacuated for 5 min, and the valve of the NMR tube was opened briefly to allow the removal of nitrogen from the head space and closed before the solution in the tube bumped. Three cycles were carried out in which the tube was pressurized with 3 atm of ^{13}CO, the valve was closed, the tube was agitated, and the gas was removed. After the third cycle the pressure of ^{13}CO was maintained at 3 atm. The solution was monitored via ^1H, ^{31}P, and ^{13}C NMR spectroscopy.

Alternatively, a standard NMR tube was attached to a 14/20 ground glass joint and a sample of pure 3 (10 mg, 0.015 mol) was loaded into the NMR tube in the glovebox. The tube was capped with a Teflon valve and attached to a small, glass manifold constructed for distilling solvent and carbon monoxide into the NMR tube. The ^{13}CO was provided via a break-seal flask attached to the manifold. The sample itself was left under full vacuum for 2.5 h to remove residual solvent. C_6D_6 (0.6 mL) and ^{13}CO (≈2 atm final pressure) were then distilled into the NMR tube by cooling the tube in liquid N_2, which was then sealed with a torch.

Formation of ^{13}CO-Labeled 3. The procedure used was similar to the above method employing the sealed glass NMR

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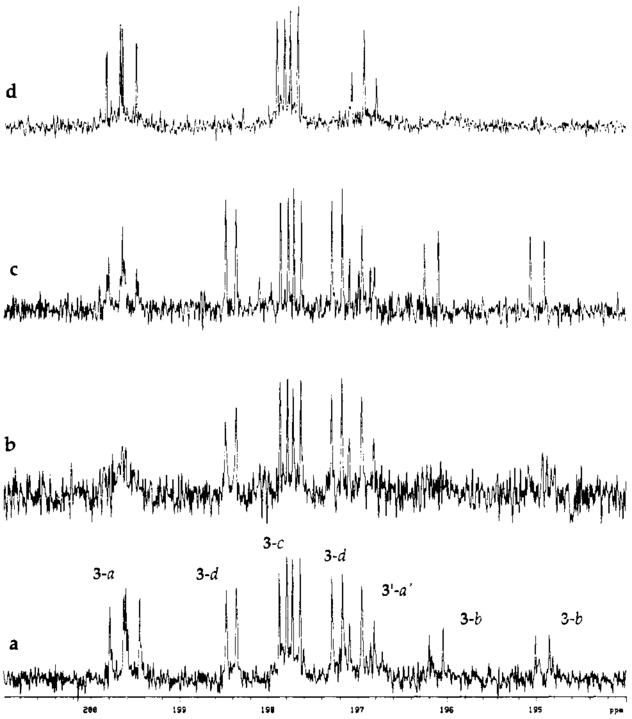


Figure 1. ^{13}C NMR spectra of **3** and **3′** under the following conditions: (a) ^{1}H decoupled; (b) ^{1}H coupled; (c) ^{1}H signal of methoxide *b* decoupled; (d) sample placed under 1.5 atm of ^{13}CO for 21 days.

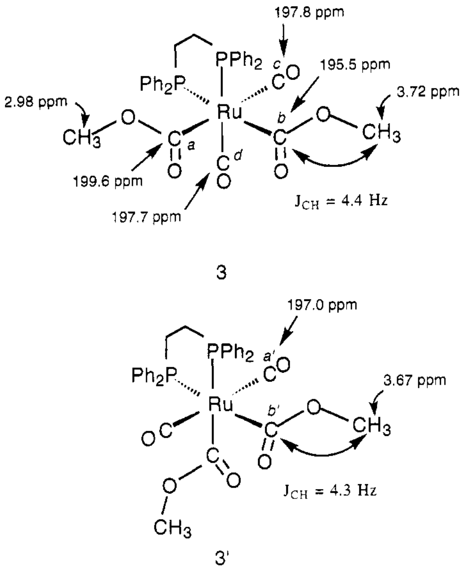
tube. To an NMR tube containing **2** (10 mg, 0.015 mmol) was added 10 μL of CH_3OH under nitrogen. The tube was evacuated, and C_6D_6 (0.5 mL) and ^{13}CO were distilled into the tube under vacuum. The tube was sealed while cooled in liquid nitrogen, and the ^{1}H, ^{31}P, and ^{13}C NMR spectra were collected at random time intervals over 2 weeks.

The amount of ^{13}CO contained in the NMR tube was determined from the volume (1.2 L) and pressure of the manifold system and the volume of the NMR tube (and valve assembly) when closed (3.2 mL).

Results

^{13}C NMR Spectroscopy of 3 and 3′. Since the original publication of the ^{13}C NMR spectrum of **3**,[8] we have been able to assign the resonances to specific carbons by a series of selective proton-decoupling experiments. The $^{13}C\{^1H\}$ NMR spectrum of $Ru(dppe)(CO)_2[C(O)OCH_3]_2$, Figure 1a, shows four intense resonances and one less intense resonance in the carbonyl region (190–200 ppm). Note that this region includes resonances due to both the CO and $C(O)OCH_3$ ligands. On the basis of the magnitude of the P–C coupling, these resonances consist of two carbon signals cis to both phosphorus atoms, designated as *a* and *c* in Scheme 1 [*c* = 197.8 ppm (J_{CP1} = 10.58 Hz, J_{CP2} = 11.2 Hz); *a* = 199.64 ppm ($J_{CP1,CP2}$ = 12.5 Hz)], and two carbon atoms located cis to one phosphorus atom and trans to the other phosphorus atom, designated as *b* and *d* [*b* = 195.5 ppm (dd, J_{CP1} = 12.11 Hz, J_{CP2} = 89.5 Hz); *d* = 197.7 ppm (dd, J_{CP1} = 9.1 Hz, J_{CP2} = 89.3 Hz)]. Also observed is a less intense resonance of **3′**, designated as *a′* in Scheme 1, seen as a triplet at 197.0 ppm with J_{CP} = 10.3 Hz. The resonances due to the $C(O)OCH_3$ ligands on **3′**, designated as *b′*, are too weak to be observed in this spectrum.

Scheme 1



When the proton-coupled ^{13}C NMR spectrum was collected on the same sample, two of the resonances of **3** displayed coupling (199.6, 195.5 ppm), while the remaining two were unchanged (197.8, 197.7 ppm) (Figure 1b). Also unchanged was the signal for the terminal carbonyl of **3′**. The observed $^1H–^{13}C$ coupling occurs between the methoxide protons and the carbonyl carbon (Scheme 1) of the $C(O)OCH_3$ ligand. This identifies the two resonances split by this coupling as *a* and *b* of **3**. This coupling was also observed in the ^{1}H NMR spectrum of $Ru(dppe)(^{13}CO)_2[^{13}C(O)OCH_3]_2$, and the couplings constants shown in Scheme 1 are based on these spectra.

Assigning the resonances of the $C(O)OCH_3$ ligands in the ^{1}H NMR spectrum was achieved through selective decoupling experiments. When the methoxide proton resonance at 2.98 ppm was irradiated, the carbon resonance centered at 199.6 ppm (carbonyl *a*) was unchanged relative to the fully decoupled spectrum. Conversely when the resonance at 3.72 ppm and the resonance for the symmetric species at 3.67 ppm were simultaneously decoupled (Figure 1c), the resonance for *b* at 195.4 ppm returns to the intensity seen in the fully decoupled spectrum. The assignment of resonance for CO *a′* is based on its consistent relative intensity in all coupled and decoupled spectra. Also seen in spectrum c is a weak resonance at 197.5 ppm (dd, J_{CP1} = 10.8 Hz, J_{CP2} = 86.2 Hz) which could be attributed to carbonyl *b′*.

Isomerization of 3 to 3′. Starting with pure **3**, one can monitor the change in concentration of **3** and **3′** with ^{1}H or ^{31}P NMR spectroscopy. At 21 °C in C_6D_6 **3** and **3′** exist in equilibrium, with a K_{eq} of 0.24 (eq 3). Only a small amount (3%) of **3** and **3′** decomposed in the solution to **1** and CH_3OH over 3 days. Graphing $-\ln([\mathbf{3}]_t - [\mathbf{3}]_{eq})$ vs time gives a slope equal to $(k_1 + k_{-1})$ = 0.019(2) (Figure 2). From this slope and the value for K_{eq} of 0.24 the following constants were derived: k_1 = 0.0040(4) min^{-1} and k_{-1} = 0.015(2) min^{-1}. In a separate study of the kinetics for the reaction of **3** and **3′** with aromatic amines we obtained values of k_1 and k_{-1} at 22, 32, 42, and 52 °C.[11] Figure 3 shows an Eyring plot of these data, listed in Table 1. $\Delta H^{\ddagger}$ for k_1 and k_{-1} were calculated to be 21.7(7) and 20.7(8) kcal/mol, and $\Delta S^{\ddagger}$ was found to be -4(2) and -4(3) eu, respectively. Plotting $\ln(K_{eq})$ vs $1/T$ gave ΔH = 0.9(3) kcal/mol and ΔS = 0.5(9) eu.

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(11) Gargulak, J. D.; Gladfelter, W. L. *J. Am. Chem. Soc.*, submitted for publication.

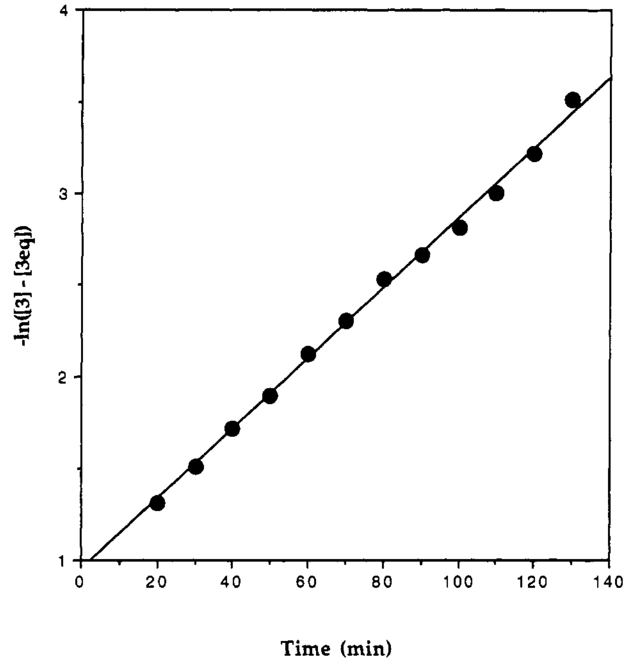


Figure 2. Kinetics for a solution of 3 approaching equilibrium with 3′ at 21 °C.

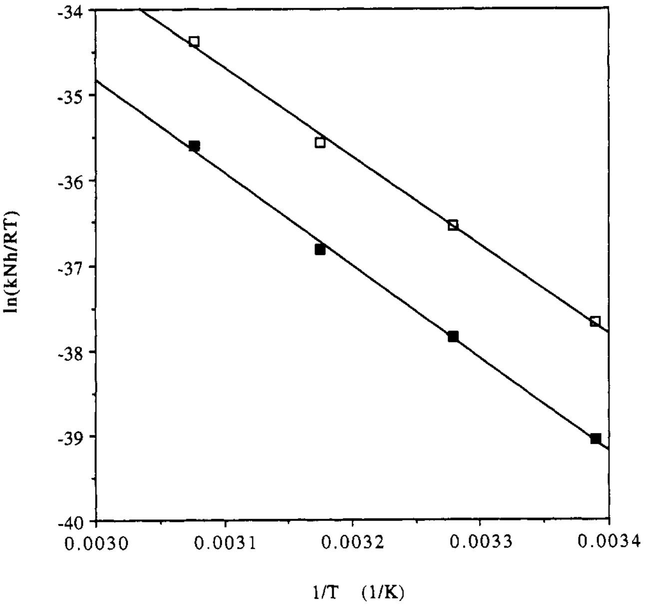


Figure 3. Eyring plot for the forward [k_1 (■)] and reverse [k_{-1} (□)] reactions in the isomerization between 3 and 3′ from 21 to 52 °C.

Table 1. Rates and Equilibrium Constant of 3 ⇌ 3′

temp (°C)	k_1 (min^{-1})	k_{-1} (min^{-1})	K_{eq}	ref
21	0.0040	0.015	0.27	this work
22	0.0040	0.016	0.25	11
32	0.014	0.051	0.27	11
42	0.040	0.14	0.29	11
52	0.14	0.48	0.29	11

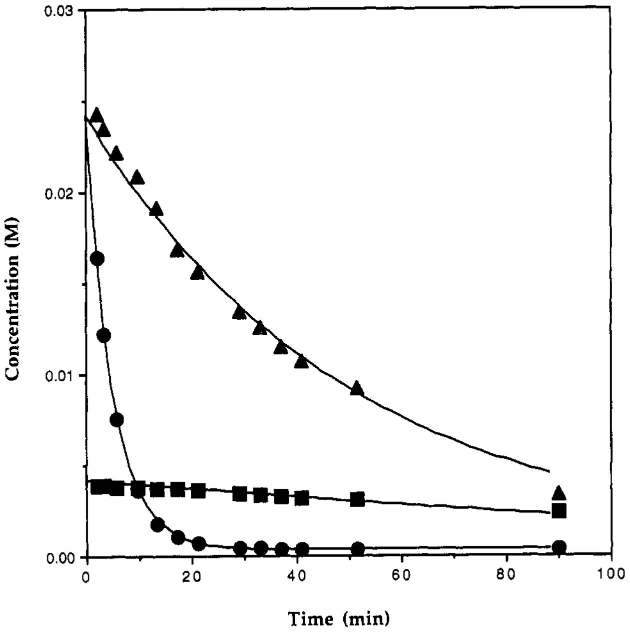


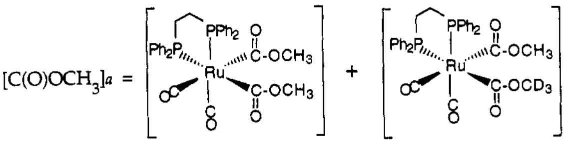
Figure 4. Kinetics of exchange at 21 °C of sites *a* (▲) and *b* (●) on 3 and *b*′ (■) on 3′ with CD_3OD calculated from the disappearance of the ^1H resonances. Initial conditions: $[3 + 3']_i = 0.031$ M; $[CD_3OD] = 2.2$ M.

Table 2. Effect of Concentration of CH_3OH and 3 on Rate Constants at 21 °C

$[CD_3OD]^a$	$[3 + 3']^a$	k_2^b	k_3^b
0.65	0.0688	0.45	0.036
2.20	0.0313	0.48	0.048
4.10	0.0285	0.48	0.048

[a] Concentration in M. [b] Units M^{-1} min^{-1}.

Exchange of Methoxide of 3 and 3′ with CD_3OD. After a solution of 3 and 3′ in C_6D_6 reached equilibrium (3 h) in an NMR tube under nitrogen, CD_3OD was added rapidly (final $[CD_3OD]$ ranged from 0.65 to 4.1 M), and the progress of the reaction was observed every 3.9 min using ^1H NMR spectroscopy. At 21 °C a typical exchange experiment has a concentration profile shown in Figure 4. The signal for 3′ was divided by 2 because its integral area represents two methoxides. Because the mixed species (3-d_3, both isomers) had the same chemical shift as 3, eqs 4 and 5 related the concentration of each methoxycarbonyl site to the concentrations used in the kinetic analysis. The signal at 3.72 ppm, which corresponds to the methoxide in position *b* (trans to the phosphine), disappeared rapidly as OCD_3 replaced OCH_3. The equilibrium concentrations of isotopomers at this coordination site was reached after 25 min under these conditions. The signal at 2.98 ppm, corresponding to the methoxide cis to the bidentate phosphine (position *a*), exchanged more slowly and reached equilibrium after 300 min. Changing the CD_3OD concentration from 0.65 to 4.1 M causes a proportional increase in the observed rate of transesterification for both methoxycarbonyl ligands indicating that the reaction was first order in CD_3OH. The data in Table 2 shows that the rate of exchange on the two methoxy sites of 3 are also first order with respect to the



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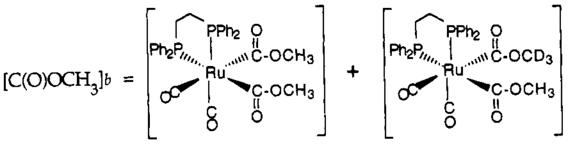

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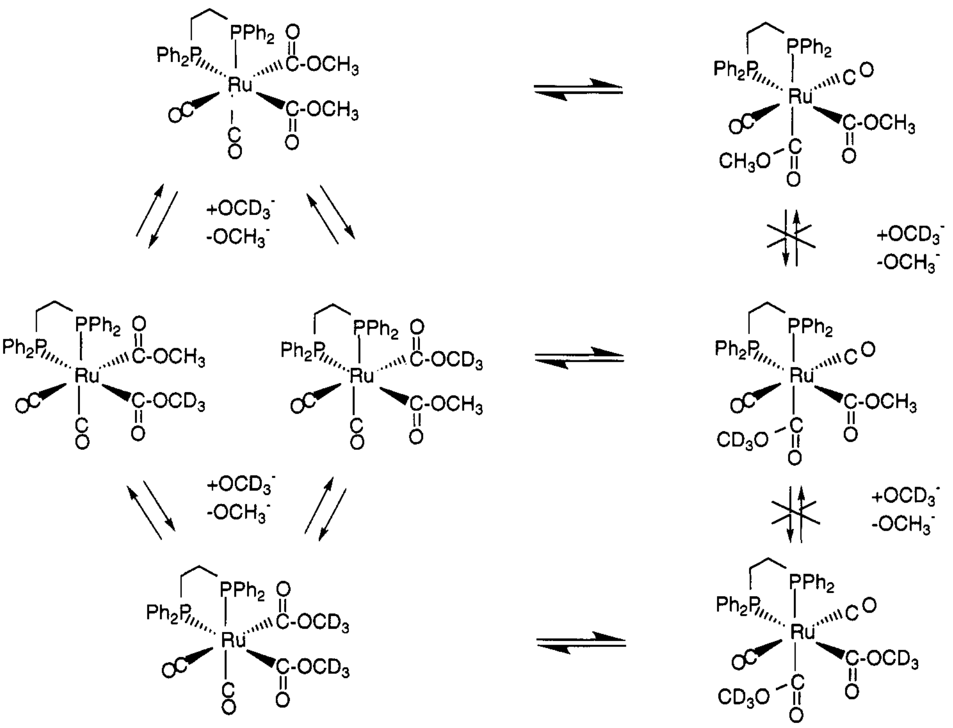

Figure 5. Equilibrium of species of 3 present in solution during exchange with CD_3OD.

concentration of the complex. The theoretical curves plotted in Figure 4 were obtained using a standard second-order isotopic exchange (eqs 6 and 7) rate law shown in eq 8.[12] In this treatment the two methoxide sites on 3

$$[C(O)OCH_3]_a + CD_3OD \underset{k_2}{\overset{k_2}{\rightleftharpoons}} [C(O)OCD_3]_a + CH_3OD \qquad (6)$$

$$[C(O)OCH_3]_b + CD_3OD \underset{k_3}{\overset{k_3}{\rightleftharpoons}} [C(O)OCD_3]_b + CH_3OD \qquad (7)$$

$$d[C(O)OCH_3]/dt = -k_{2(3)}[C(O)OCH_3][CD_3OD] + k_{2(3)}[C(O)OCD_3][CH_3OD] \qquad (8)$$

$$\ln\left(1 - \frac{[C(O)OCD_3]_t}{[C(O)OCD_3]_\infty}\right) = -k_{2(3)}(C_A + C_X)t \qquad (9)$$

were assumed to be completely independent in their reactivity. The concentration of OCD_3 (and consequently OCH_3) was calculated for sites *a* and *b* using the integrated form of the rate equation, eq 9. Because 3′ is of low concentration, and because the change in concentration 3′-h_6 with respect to the change in concentration of 3-h_6 was small, formation of 3-h_6 from isomerization of 3′-h_6 was assumed to be small and was neglected. In eq 9, C_A = $[C(O)OCD_3] + [C(O)OCH_3]$ and $C_x = [CD_3OD] + [CH_3OD]$. The values of the rates were calculated from the best fit to the experimental data, and k_2 was found to be 0.48 M^{-1} min^{-1} and k_3 was 0.048 M^{-1} min^{-1}.

The analysis of the disappearance of the signal for *b*′ was more involved and was based on several approximations. The calculated curve in Figure 4 representing the disappearance of the methoxy signal for the symmetric species 3′-h_6 was based on incorporation of CD_3O into 3′ through isomerization only. The signal for *b*′ was depleted by isomerization of 3′ to 3, rate = $2k_{-1}[3'\text{-}h_6] + k_{-1}[3'\text{-}h_3]$. The first term was multiplied times 2 because the isomerization of 3′-h_6 results in loss of 2 equiv of methoxide signal. The contribution of the forward rate constant, k_1, to the signal for *b*′ can be calculated in terms of the relative concentrations of each methoxycarbonyl on 3, defined in eqs 4 and 5. Equation 10 represents the rate used to

$$d[C(O)OCH_3]_{b'}/dt = -2k_{(-1)}[3'\text{-}h_6] + k_{(-1)}[3'\text{-}h_3] + k_1[C(O)OCH_3]_a + k_1[C(O)OCH_3]_b \qquad (10)$$

calculate the disappearance of signal for position *b*′. The solution was approximated by setting eq 10 equal to $\Delta[C(O)OCH_3]_{b'}/\Delta t$. The concentrations of $[C(O)OCH_3]_a$ and $[C(O)OCH_3]_b$ were calculated from the method described above at various time intervals. The amount of time between each point was 50 s. Given these parameters, the rate of change in concentration of $[C(O)OCH_3]_{b'}$ is shown in Figure 4. Figure 5 summarizes the processes occurring in this solution.

In the ^{31}P NMR spectroscopic studies of these solutions, a separate signal was observed for 3 [45.17 ppm (J_{P-P} = 12.7 Hz)] and the mixture of 3-d_3 and 3-d_6 [45.13 ppm (J_{P-P} = 12.7 Hz)].

Attempted Crossover Experiment of 3 and 3′ with 3-d_6 and 3′-d_6. A C_6D_6 solution of 3 and 3′ ([3 + 3′] = 40.1 mM) and 3-d_6 and 3′-d_6 ([3-d_6 + 3′-d_6] = 34.6 mM) was allowed to stand for 2 days at room temperature. During this time no change in the ratio of the ^{31}P NMR spectral signals for 3-h_6 and 3-d_6 was observed (1.15:1.0), Figure 6. If exchange were rapid during the crossover experiment, one would observe the statistical distribution of 0.58:1.75:0.50 for 3:3-d_3:3-d_6. Because the signals from 3-d_3:3-d_6 were identical, the peak ratio of the statistical distribution would be 0.58:2.25. Therefore, no crossover was observed after 2 days (Scheme 2). Minimal (<3%) decomposition of 3 and 3′ to 1 occurred during the crossover experiment.

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[12] Espensen, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: St. Louis, MO, 1981; pp 218.

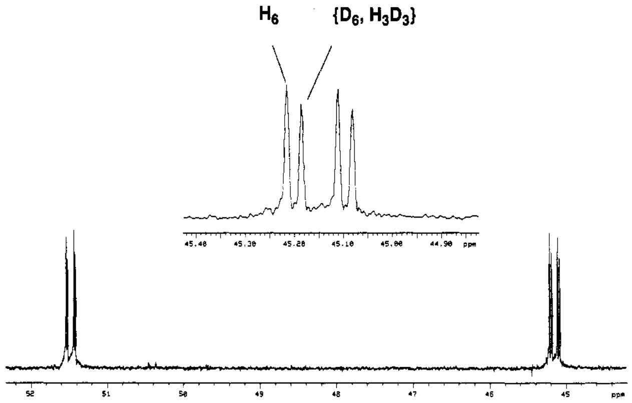
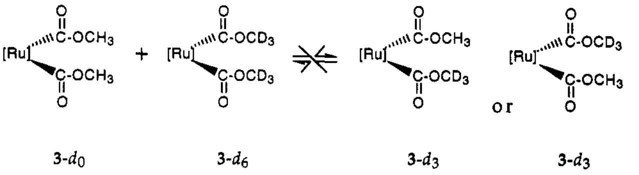


Figure 6. ^{31}P NMR spectrum of a 1.15 to 1 mixture of **3**-h_6 and **3′**-h_6 to **3**-d_6 and **3′**-d_6 after equilibrating for 2 days.

Scheme 2



This result was corroborated with that found by analyzing the solid mixture formed after removal of the solvent. Fast atom bombardment (FAB) and chemical ionization (CI) mass spectra of the pure compound **3** showed no molecular ion, and the highest observable mass was that of the parent molecule minus methoxide, $[M - OCH_3]^+$. Ionspray mass spectroscopy,[13] however, was successfully employed to observe the molecular ion plus sodium, $\{Ru(dppe)(CO)_2[C(O)OCH_3]_2Na\}^+$ (*m/z* 697, Figure 7b). The appearance of adventitious sodium is common in the ionspray technique. Figure 7a shows the isotope pattern for pure $\{Ru(dppe)(CO)_2[C(O)OCD_3]_2Na\}^+$ (*m/z* 703). The solid isolated after **3**-d_6 and **3′**-d_6 interacted with **3** and **3′** for 2 days at 21 °C gave the spectrum shown in Figure 7c. A calculated isotope abundance for these ions assuming that no crossover of methoxy groups had occurred is shown in Figure 7d, and Figure 7e depicts the calculated spectrum based on the relative isotope abundance for these ions if a statistical distribution of D_6 and H_6 methoxide had occurred.

^{13}CO Incorporation into 3 and 3′. To probe whether any of the carbonyl ligands in **3** or **3′** underwent exchange, a 25.0 mM solution of **3** in C_6D_6 was placed in the high-pressure NMR tube and pressurized with ^{13}CO (4 atm). No discernible incorporation of ^{13}CO was observed within the first 2 days. After the sample was allowed to stand undisturbed for 21 days, the ^{13}C NMR spectrum was again measured. Approximately 10% of the ^{13}CO was incorporated stereospecifically into sites *a* and *c* (Figure 1d). The degree of enrichment was estimated from the amount of $^{13}C-^{31}P$ coupling observed in the ^{31}P NMR spectrum. Some decomposition (8%) of **3** and **3′** generated ^{13}CO-labeled **1**. The resonance due to dissolved ^{13}CO was observed in the NMR spectrum at 185 ppm.

Characterization of 4. In a previous publication,[8] an intermediate was reported (observed by ^1H and ^{31}P NMR spectroscopy) in the reaction between CH_3OH and $Ru(dppe)(CO)_2[C(O)N(Ar)O]$ (**2**) to form $Ru(dppe)(CO)_2[C(O)OMe]_2$. The spectroscopic data and the apparently analogous reaction between $Ru(dppe)(CO)_2[C(O)N(Ar)O]$ and HCl to give $Ru(dppe)(CO)_2Cl_2$ caused us to formulate the structure of **4** as the bis(methanolato) species, $Ru(dppe)(CO)_2(OMe)_2$. In the current study, the synthesis of ^{13}CO-enriched **3** and **3′** allowed the determination of $^3J_{^{13}C-^1H}$ between the methoxy hydrogens and the carbonyl carbons (Scheme 1). Because we monitored the progress of the enrichment by NMR spectroscopy, we were able to observe that the ^1H NMR spectrum of **4** also clearly exhibited doublets ($^3J_{^{13}C-^1H} = 4.1$ Hz for the resonance at 3.38 ppm, $^3J_{^{13}C-^1H} = 4.3$ Hz for the resonance at 3.53 ppm) for both of the methoxy groups. This requires that the methoxy groups be coordinated as methoxycarbonyls rather than as metal-bound methoxides as previously suggested. We tentatively propose that the remaining two coordination sites on **4** are occupied by methanol. The previously unexplained broadening of the O–H resonance

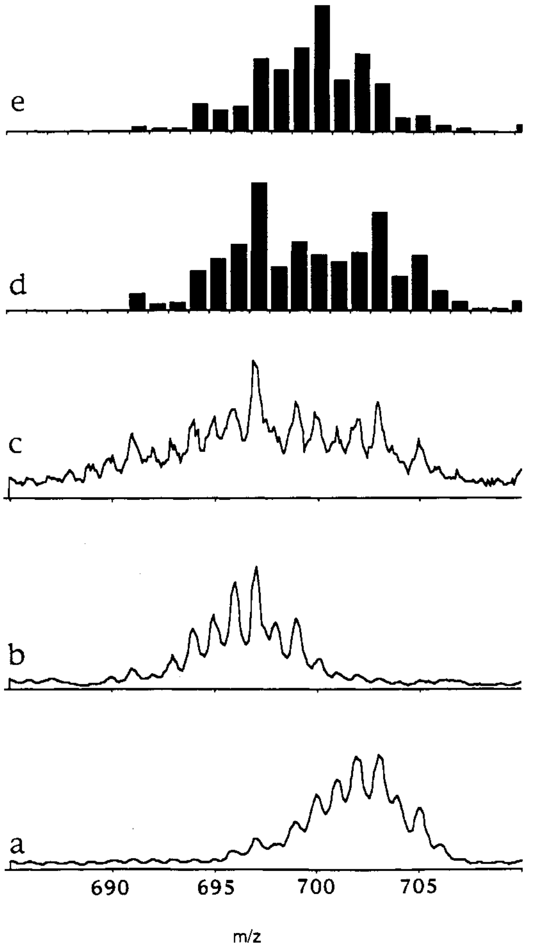
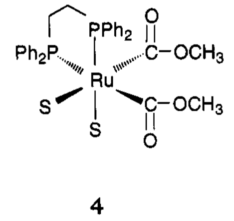


Figure 7. Ionspray mass spectra: (a) **3**-d_6 and **3′**-d_6; (b) **3**-h_6 and **3′**-h_6; (c) solid isolated from a 1.15 to 1 mixture of **3**-h_6 and **3′**-h_6 to **3**-d_6 and **3′**-d_6 after equilibrating for 2 days; (d) calculated spectrum assuming no crossover; (e) calculated spectrum assuming a statistical distribution of OCH_3 and OCD_3.



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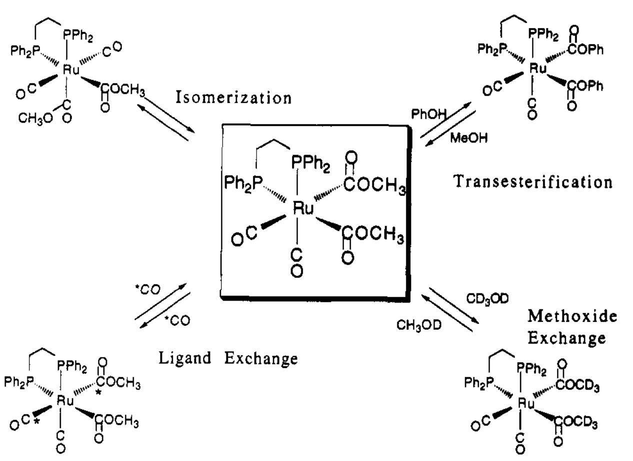
[13] Chapman, J. R.; Gallagher, R. T.; Barton, E. C.; Curtis, J. M.; Derrick, P. J. *Org. Mass. Spectrom.* **1992**, *23*, 195.

Scheme 3



of methanol observed during the formation of **4** that maximized at the highest concentrations of **4** (see Figure 2 in ref 8) could be due to rapid exchange between coordinated and free methanol.

The observation that the methoxycarbonyls of **4** are enriched to 41 and 28% in ^{13}C coupled with the fact that **2** undergoes no exchange with ^{13}CO means that **4** and/or an intermediate along the path to **4** can exchange with free CO. In this experiment, the initial molar ratio of ^{13}CO:**2** was nearly 10:1. That the enrichment of the methoxycarbonyls of **4** has not approached this mole ratio means that equilibration with the atmosphere was incomplete. In addition, no change in the enrichment of **4** occurs between 2 h (the first point acquired) and 31.5 h (almost completely converted to **3**). This suggests that the exchange with free CO occurred not with **4** itself but with an intermediate along the path to **4**.

Discussion

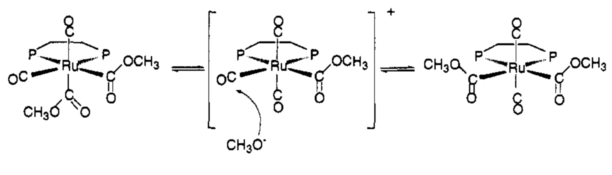
Formation of 3. The complete details on the formation of **3** from the reaction of **2** with MeOH and CO remain obscure. We know that the reaction proceeds through the intermediate **4**, whose set of ligands is comprised of two methoxycarbonyls, a chelating dppe ligand, and probably two methanols. The ^{13}CO studies establish that once **4** and **3** are formed further exchange with the gas is extremely slow at room temperature.

Mechanism of Isomerization of 3. Scheme 3 depicts the reactivity of **3**. One of the first discoveries made during our preliminary investigations of the reactivity of **3** was the isomerization of **3** in aromatic solvents to a symmetric form **3′**. The kinetic study of the isomerization indicated a first-order reaction that was not affected by the addition of CH_3OH to the solution. The equilibrium constant was found to be 0.24 at 21 °C. Scheme 4 outlines the possible routes by which this transformation could take place. Crossover experiments of **3** and **3′** with **3**-d_6 and **3′**-d_6 gave no mixed species, **3**-d_3 or **3′**-d_3, indicating methoxide was not leaving the coordination sphere of the complex. This rules out the mechanism shown in Scheme 4a.

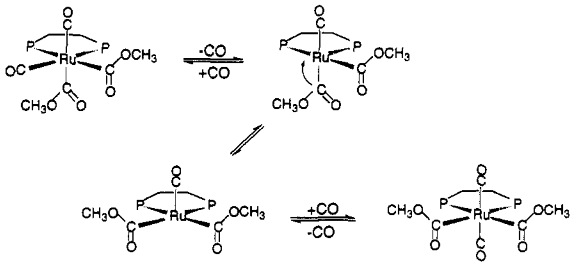
Another possible route for isomerization would involve CO dissociation to give stereochemically nonrigid, five-coordinate intermediates (Scheme 4b). Two observations rule out this mechanism. First, addition of carbon monoxide (3 atm) had no effect on the rate of isomerization, and second, the rate of exchange of gaseous ^{13}CO with **3** and **3′** was much slower (less than 10% complete over 3 weeks) than the rate of isomerization (complete in 3 h) under identical conditions. Dissociation of one end of the chelating phosphine ligand prior to isomerization would also yield a five-coordinate intermediate. If this intermediate were long-lived enough to isomerize, it is likely that it would also react with ^{13}CO present in solution.

Scheme 4. Possible Isomerization Mechanisms

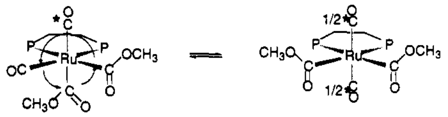
a. Methoxide dissociation



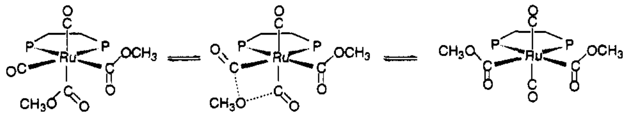
b. Carbonyl dissociation



c. Intramolecular trigonal twist



d. Intramolecular ligand-hopping



Although a fluxional process of the 6-coordinate species itself, such as a trigonal twist mechanism (Scheme 4c) is possible, it can be ruled out on the basis of the observed stereospecificity of ^{13}CO incorporation. If Scheme 4c were the mechanism, then ^{13}CO incorporated into position *c* would be rotated into position *a′*. By subsequent equivalent rotations, the label would be scrambled to all possible sites. No labeling of positions *b* or *d* is observed in **3** after standing for 3 weeks under ^{13}CO.

The mechanism that is consistent with all of the experimental results is shown in Scheme 4d. Specifically, we observe that the methoxy group bound to CO_a of **3** can move to CO_d to form **3′**. Exchange between CO_b and CO_d of **3** is invisible, whereas the shift of the methoxy from CO_b to CO_c on **3** would produce the unobserved isomer. The ligand-hopping process requires cis stereochemistry of the methoxycarbonyl and carbonyl ligands. In addition, the barrier to this mechanism will be very sensitive to the differences in bonding and size between a carbonyl and alkoxycarbonyl ligand. While a related facile fluxional process involving the transfer of oxygen among carbonyl groups in $Li_2[W(CO)_5(CO_2)]$ and $Li[Fe(\eta\text{-}C_5H_5)(CO)_2(CO_2)]$ has been observed by Cooper and co-workers,[14,15]

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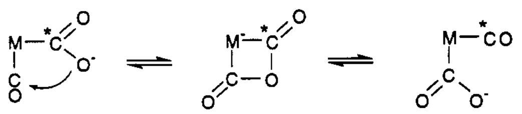
(14) Cooper, N. J.; Lee, G. R. *Organometallics* **1985**, *4*, 794.

(15) Cooper, N. J.; Lee, G. R.; Maher, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2956.

we could find no precedent for such a ligand-hopping mechanism among alkoxycarbonyls (eq 11).



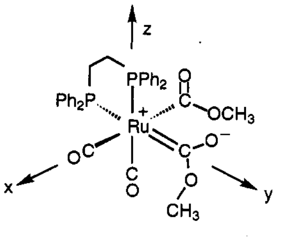
(11)

Transesterification. As shown in Scheme 3, **3** undergoes substitution of the alkoxy group, transesterification, when reacted with alcohols. While the transesterification of other alkoxycarbonyl complexes has been observed,[7,16,17] no quantitative study of the kinetics of alkoxy exchange has been reported.

The reaction of **3** with CD_3OD was found to follow second-order kinetics. Several of the initial steps of the possible mechanisms are the same as discussed for the isomerization process (Scheme 4) and can be ruled out for the same reasons. This leaves an associative mechanism as the only reasonable alternative. The kinetic data are consistent with this mechanism, but they cannot differentiate between nucleophilic attack at the methoxycarbonyl or the metal carbonyl ligand. Literature precedent does little to clarify the situation. In the consecutive reaction of two strong nucleophiles with metal carbonyls the first addition of an alkyllithium or Grignard reagent produces an acyl carbonyl which adds the second equivalent at a separate metal carbonyl group.[18] One can argue, however, that the methoxycarbonyl ligand should be more electrophilic than the acyl in the same way that organic esters are more susceptible to nucleophilic attack than ketones.

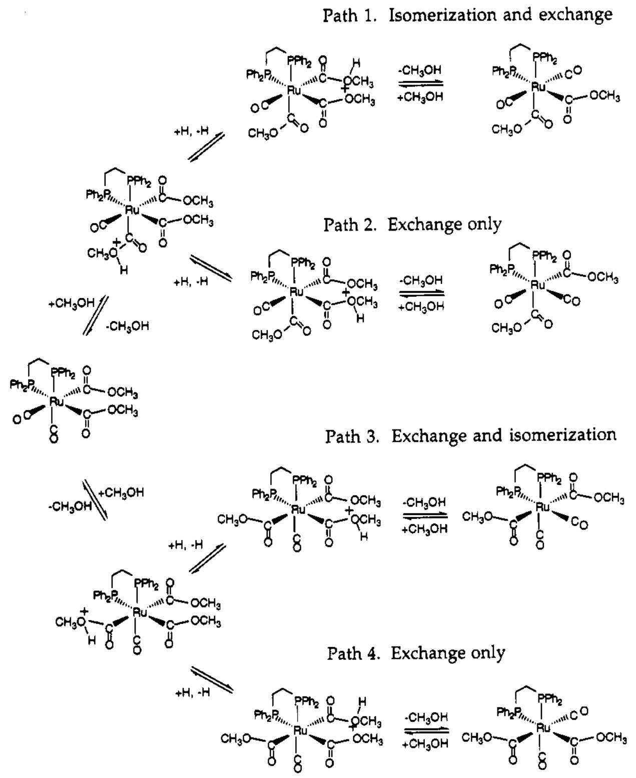
The most surprising outcome of the study of this substitution was the high selectivity observed for the exchange process. The rates of substitution of the two methoxycarbonyls of **3** differ by 1 order of magnitude, while no measurable, direct substitution occurs on **3′**. The interpretation of these results is dependent on which site is attacked by the entering alcohol, the methoxycarbonyl or the metal carbonyl. These are discussed separately in the following sections.

A. Nucleophilic Attack on the Methoxycarbonyl. The reactive methoxycarbonyl is trans to the phosphine, while the unreactive one is trans to CO. In the X-ray crystallographic study of the related carbamoyl complex, $Ru(dppe)(CO)_2[C(O)NH\text{-}i\text{-}Pr]_2$,[19] the identical stereochemistry to **3** was found, and the Ru–C bond of the carbamoyl ligand trans to the phosphine ligand was significantly (0.053(9) Å) shorter then the analogous bond trans to the CO. The reduced π-accepting ability of the alkyldiphenylphosphine ligand compared to CO allows the d_{yz} orbital to participate to a greater extent in back-bonding with the methoxycarbonyl ligand. The increasing importance of the resonance structure



is the result of this enhanced back-bonding. We would expect this resonance structure to decrease the susceptibility of this methoxycarbonyl toward nucleophilic attack.

Scheme 5



B. Nucleophilic Attack on the Metal Carbonyl. Alternatively, the increased positive charge on the ruthenium caused by the resonance hybrid shown above for **3** should increase the susceptibility of the ancillary CO ligands toward nucleophilic attack. This appears to us as a more reasonable explanation of the enhanced reactivity. Scheme 5 summarizes the possible intermediates and the structures that result from initial attack at the two different metal carbonyls and the subsequent dissociation of the two different methoxycarbonyl ligands. Path 1 would require isomerization to **3′** to occur at the same rate as exchange of the slower methoxycarbonyl group on **3**, and path 3 would produce an isomer that is not observed in the NMR spectrum. Paths 2 and 4 represent the most likely routes for exchange of the methoxy groups in both positions of **3**. The cause of the 1 order of magnitude difference in the substitution rates may be due to larger steric repulsion of the phenyl groups on both phosphorus atoms in the formation of the intermediate in path 4. The lack of direct substitution on **3′** may include this same steric argument because both carbonyls are located cis to both phosphines.

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OM930634X

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[16] Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627.

[17] Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927.

[18] Lukehart, C. M. *Acc. Chem. Res.* **1981**, *14*, 109.

[19] Gargulak, J. D.; Gladfelter, W. L. *Inorg. Chem.*, in press.