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Alkene Exchange Kinetics in Bis(η^2-alkene)(2,4-pentanedionato)rhodium(I) Investigated by NMR Spectroscopy[1]

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The alkene exchange kinetics in bis(η^2-alkene)(2,4-pentanedionato)rhodium(I) has been studied by ^{1}H and ^{13}C NMR line-broadening techniques for ethylene and *cis*-2-butene. The ethylene exchange goes by an overall second-order reaction, first order in both complex and ethylene. The value of the rate constant in $CDCl_3$ is 3000 ± 300 $M^{-1}\ s^{-1}$ at 298 K; the activation parameters are $\Delta H^* = 9.7 \pm 1.5$ kJ mol^{-1} and $\Delta S^* = -145 \pm 20$ J mol^{-1} K^{-1}. There is no large solvent effect on the rate, and the change in ^{103}Rh NMR shift for the complex in different solvents is small. Compared to ethylene, the exchange of the more weakly bound *cis*-2-butene is at least 2 orders of magnitude slower.

Introduction

The breaking and forming of metal–alkene bonds is a crucial step in many catalytic processes. Much fruitful research in this area has been generated by the Dewar–Chatt–Duncanson[2,3] bonding model. However, it is still not completely clear in what way the individual properties of the metal and alkene moiety affect the relative importance of the σ donation and the π back-donation.

The complex bis(η^2-ethylene)(2,4-pentanedionato)rhodium(I) = Rh(acac)(ethylene)$_2$ (1) and its derivatives constitute a class of compounds that have been used to probe these effects. Cramer pioneered these studies with investigations of exchange reactions and equilibria.[4] Studies of the metal–alkene bond by means of thermochemical methods and vibrational, NMR, and UV photoelectron spectroscopy have been presented in a number of papers by Jesse, Vrieze, Stufkens, and their co-workers.[5] A number of other researchers have also contributed to the understanding of the bonding in these complexes.[6]

Except for some studies on platinum–alkene complexes, alkene exchange kinetics seems to have attracted little attention.[7] Several years ago, Cramer used ^{1}H NMR spectroscopy to establish that the exchange is fast for the ethylene complex 1 (eq 1) and that the rate depends on

$$\mathrm{Rh(acac)(ethylene)_2 + ethylene^* \rightleftharpoons Rh(acac)(ethylene)(ethylene^*) + ethylene} \quad (1)$$

the concentrations of both the complex and ethylene.[4a] We felt that a more quantitative study would be valuable and decided to investigate the kinetics of the alkene exchange for some rhodium(I) complexes in more detail.

Rh(acac)(ethylene)$_2$ is a 16-electron, square-planar, four-coordinate complex, and thus the reaction is most likely associative.[8] We asked ourselves three questions: (1) Is the reaction purely associative, as found for ethylene exchange in Pt(acac)Cl(ethylene),[7a] or is there a competing pathway? (2) Is there a solvent influence? (3) How does the ethylene exchange in 1 compare to the butene exchange in 2, a complex where the metal–alkene bond is weaker?[4b]

The ethylene complex 1 was prepared by an established method,[9] while the *cis*-2-butene complex 2 was prepared by repeated alkene exchange between the ethylene complex and the butene. The complexes were then reacted in solution with the respective alkenes (in the case of ethylene, 99% ^{13}C-enriched ethylene was used in order to shorten the measuring time). The reaction was followed by means of NMR spectroscopy. The rotation of the alkenes around the metal–alkene bond contributes, together with the exchange, to the large broadening of the ^{1}H NMR signals, making them impractical for use in a kinetic study. Therefore, ^{13}C NMR methods were used to monitor the exchange. For the complex 1, the line broadenings of the ethylene peaks (free and coordinated) in the ^{13}C NMR spectra were used to determine the rate equation and activation parameters of the exchange process and thus to probe the mechanism. The solvent dependence of the rate and ^{103}Rh NMR chemical shifts were also studied to establish if solvent coordination to the "fifth coordination site" is important.

Experimental Section

Reagents and Solvents. All reagents were purchased from commercial sources and used without further purification. ^{13}C-enriched ethylene (99%) was purchased from ICON (Mt. Marion, NY). The deuterated solvents were dried over molecular sieves. THF was distilled from sodium-benzophenone before use, *n*-pentane and diethyl ether were distilled, acetone, dichloromethane, and acetonitrile were Aldrich-HPLC quality, and methanol was of purum quality.

NMR Measurements. ^{1}H, ^{13}C, and ^{103}Rh NMR spectra were recorded at a probe temperature of 25 ± 0.5 °C with a Bruker AM400 spectrometer. In order to obtain activation parameters, spectra were also recorded at −20 and −2 °C. The temperature was calibrated with use of a Pt(100) resistance. In order to assure that the ^{1}H NMR spectra were quantitative, a 35° pulse with a repetition time of 5 s was used. The ^{13}C NMR spectra were recorded with WALTZ-16 proton decoupling. ^{103}Rh NMR spectra were recorded with WALTZ-16 proton decoupling, an acquisition

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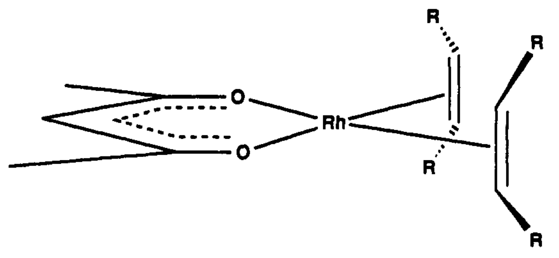

1 R = H

2 R = CH_3

Figure 1.

time of 0.5 s, and a pulse width of 12 μs (~60°). Chemical shifts (δ) are reported in ppm with the solvent as internal standard ($CHCl_3$ $\delta(^1H) = 7.26$, $CDCl_3$ $\delta(^{13}C) = 77.0$). For ^{103}Rh NMR spectra the shifts are referenced to $\Xi(^{103}Rh) = 3.16$ MHz.[10] The accuracy of the measured line widths is 5% and that of the ^{103}Rh NMR shifts 0.5 ppm.

Kinetic Measurements. Crystals of Rh(acac)(ethylene)$_2$ were dissolved in degassed (argon–vacuum cycles) solvent. The concentrations were calculated from the amount of Rh complex and solvent, and the density of the solvent ($CDCl_3$ 1.50, CD_2Cl_2 1.36, acetone-d_6 0.87 g/mL (99.5–99.8% D)). The sample tubes (5-mm outer diameter) were filled with 0.5 mL of the solution (diluted when appropriate), sealed with a rubber septum, and flushed with argon. The ^{13}C-enriched ethylene was added with a syringe and the concentration of free ethylene calculated from the integrated ^1H spectra. The line widths of the two overlapping peaks from coordinated ethylene (due to ^{103}Rh ($I = ^1/_2$) spin–spin coupling) and the free ethylene peak in the ^{13}C NMR spectra were measured by curve fitting with use of software from NMRi (Syracuse, NY) (assuming Lorentzian line shapes). For the higher exchange rates (broader lines) the rate parameters were also calculated by complete line-shape analysis. Least-squares fits were done to extract the rate constants. Since we have errors in both the line widths and the concentrations, this was done two times for each data set, with a change in the dependent variable, and the mean value was used. The error estimates of the fitted parameters were made by graphs and by fitting the lines with randomized estimated errors added to the experimental points.

Preparation of Bis(η^2-ethylene)(2,4-pentanedionato)rhodium(I) (1). This compound was prepared and purified according to literature methods.[9]

Preparation of Bis(η^2-*cis*-2-butene)(2,4-pentanedionato)rhodium(I) (2). Rh(acac)(ethylene)$_2$ (0.150 g, 0.58 mmol) was added to a round-bottom flask. The flask was evacuated, flushed with nitrogen, and then cooled to −70 °C (dry ice/ethanol). Gaseous *cis*-2-butene was added to a condensed volume of ca. 6 mL, the yellow solution was stirred at 0 °C for 3 h, and then the excess butene was evaporated. This process was repeated twice with 40-min reaction times and three times with 20-min reaction times. *n*-Hexane was then added to the yellow-brown solid, and the yellow solution plus dark precipitate were put in the freezer overnight. Then the precipitate was removed by filtration and the solvent evaporated to give bis(η^2-*cis*-2-butene)(2,4-pentanedionato)rhodium(I), pure according to NMR spectroscopy, as a yellow solid (0.038 g, 0.12 mmol, 21%). Recrystallization can be performed from *n*-pentane. ^1H NMR ($CDCl_3$, 25 °C): δ 1.44 (s, 6 H), 1.83 (s, 6 H), 2.6 (s, 4 H), 5.20 (s, 1 H). ^{13}C NMR ($CDCl_3$, 25 °C): δ 14.84 (s), 27.20 (s), 74.00 (d, $J_{C-Rh} = 12.8$ Hz (−60 °C)), 98.95 (d, $J_{C-Rh} \approx 2$ Hz), 185.48 (s). Anal. Calcd for $C_{13}H_{23}O_2Rh$: C, 49.7; H, 7.4. Found: C, 49.5; H, 7.0.

Results and Calculations

A rate equation including two terms was assumed:[11]

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{ligand}] \qquad (2)$$

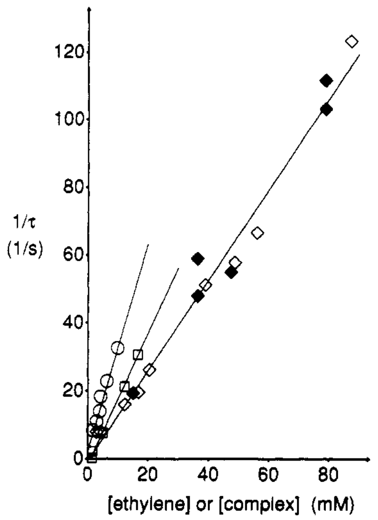

Figure 2. Reciprocal mean lifetime of coordinated ethylene in Rh(acac)(ethylene)$_2$ measured by ^{13}C NMR line broadening (○, 298 K; □, 271.5 K; ◇, 253 K) plotted against the free ethylene concentration and the reciprocal mean lifetime of free ethylene (◆, 253 K) plotted against the concentration of Rh(acac)(ethylene)$_2$. The slopes are the second-order rate constants, k_2 (eqs 3 and 4).

The rate parameter obtainable from NMR studies is the mean lifetime of (τ) of a particular site. For a ligand L, exchanging with a complex ML according to eq 2 we have

$$\tau_{ML}^{-1} = \text{rate}/[\text{ML}] = k_1 + k_2[\text{L}] \qquad (3)$$

$$\tau_{L}^{-1} = \text{rate}/[\text{L}] = k_1[\text{ML}]/[\text{L}] + k_2[\text{ML}] \qquad (4)$$

The value of τ can be extracted directly from the line widths, provided that the peaks do not overlap (slow exchange):[12]

$$\Delta\nu_{1/2}^{\text{exch}} = \Delta\nu_{1/2} - \Delta\nu_{1/2}^{0} = (\pi\tau)^{-1} \qquad (5)$$

Here, $\Delta\nu_{1/2}$ is the measured line width, $\Delta\nu_{1/2}^{0}$ is the nonexchange line width, and $\Delta\nu_{1/2}^{\text{exch}}$ is the exchange broadening. (Note that τ in this equation is the mean lifetime of a particular site and might thus differ from τ in eqs 3 and 4 by a stoichiometric factor.) In this case the nonexchange line widths were determined with the concentration of ligand or complex equal to zero, respectively.

Thus, for a reaction with a rate expression such as eq 2 (ligand = ethylene), a plot of the exchange broadening of the coordinated ligand times π (=τ^{-1}) against the concentration of the free ligand should give a straight line. This would then give k_2 as the slope, but we cannot extract k_1 from these data because the first-order process has already been subtracted (as the "nonexchange line width"). However, we can plot the broadening of the free ethylene signal in a corresponding way, but then we would only obtain a straight line if k_1 were equal to zero. The slope would again be the second-order rate constant, k_2.

In the present case, the attacking ligand can replace one of the two coordinated ethylenes. This means that the rate constants obtained from the broadening of the signal from the coordinated ethylenes must be multiplied by a stoichiometric factor of 2 to represent k_1 and k_2 in eq 2.

Plots of τ^{-1} (data for the coordinated ethylene multiplied by 2) against the appropriate concentration are shown in Figure 2. We were only able to measure the line width of the free ethylene for the relatively high concentrations used at the lowest temperature. This was due to the faster

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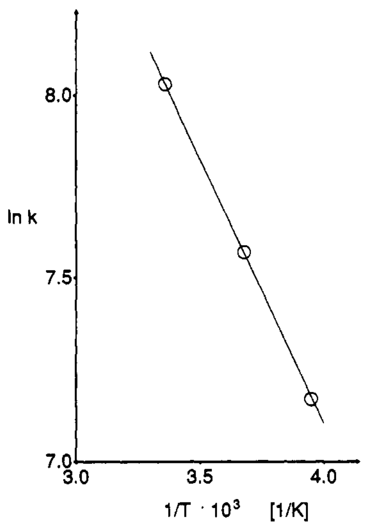

Figure 3. Arrhenius plot of the rate constants calculated from Figure 2. The activation energy is 12.1 ± 1.5 kJ mol^{-1}.

Table I. ^{103}Rh NMR Chemical Shifts (δ) for Rh(acac)(ethylene)$_2$ in Different Solvents (T = 298 K)

solvent	δ, ppm[a,b]	solvent	δ, ppm[a,b]
CH_2Cl_2 + H_2O[c]	1181.0	diethyl ether	1175.6[d]
CH_2Cl_2	1180.7	acetone	1175.4
$CDCl_3$	1180.3	acetonitrile	1171.7
THF	1178.3[d]	methanol	1167.2
n-pentane	1175.8		

[a] Concentration ~0.07 M. [b] Values are ±0.5 ppm, proton decoupled, referenced to [Ξ](^{103}Rh) = 3.16 MHz, and corrected for the different magnetic susceptibilities of the solvents with CH_2Cl_2 as reference point. (The corrections are on the order of 0.5 ppm.) [c] Saturated. [d] Not corrected for the magnetic susceptibility.

exchange and lower solubility of ethylene at higher temperatures. Another way to extract the rate constants from the line broadening of the free ethylene signal is to plot τ^{-1}[complex]$^{-1}$ against [ethylene]$^{-1}$. In this way, the same value as above is obtained for the constant k_2 and also the highest possible value for k_1 can be estimated; $k_1 \leq 0.3$ s^{-1} at 253 K.

The Arrhenius plot in Figure 3 gives the activation energy equal to 12.1 ± 1.5 kJ mol^{-1}, and the activation parameters were calculated as $\Delta H^{\ddagger}$ = 9.7 ± 1.5 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −145 ± 20 J mol^{-1} K^{-1}.

The rate constants (k_2 in eq 2) were measured at 298 K in $CDCl_3$ (3000 ± 300 M^{-1} s^{-1}), CD_2Cl_2 (3800 ± 500 M^{-1} s^{-1}), and acetone-d_6 (3800 ± 500 M^{-1} s^{-1}) (see Figure 4). Due to overlap from the solvent signals in the ^{1}H NMR spectra there is a large error for the acetone and CD_2Cl_2 solutions and thus a large error in the rate constants. In CD_2Cl_2 there is also an excessive line broadening of the free ethylene signal.[13] ^{103}Rh NMR chemical shifts for 1 in several solvents have been measured, and the results are shown in Table I. The values are corrected for the magnetic susceptibility of the different solvents with CH_2Cl_2 as a reference point.[14]

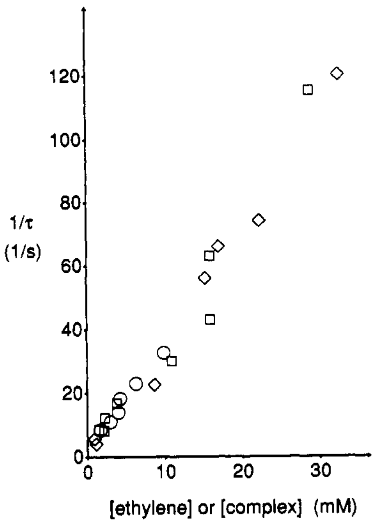

Figure 4. Reciprocal mean lifetime of coordinated ethylene in Rh(acac)(ethylene)$_2$ measured by ^{13}C NMR line broadening in different solvents (○, $CDCl_3$; ◇, CD_2Cl_2; □, acetone-d_6) at 298 K plotted against the free ethylene concentration and the reciprocal mean lifetime of free ethylene plotted against the concentration of Rh(acac)(ethylene)$_2$.

The exchange between *cis*-butene and the complex 2 in chloroform is so slow that even when a large excess of butene is added no extra broadening of the peaks can be detected. We therefore tried to use the spin saturation transfer method, which can detect rate constants 1 order of magnitude slower than those obtainable from line shape analysis.[15] A ^{1}H NMR experiment was performed where the olefinic protons in the complex (at 2.6 ppm) were selectively decoupled while the signal of the free olefinic protons (at 5.5 ppm) was measured for two butene concentrations. No decrease in signal integral of the free butene could be detected, and with use of the T_1 relaxation time of the alkene protons in coordinated butene (~2 s)[16] the exchange was calculated to have $k_2 \leq 10$ M^{-1} s^{-1} at 298 K. This experiment was impossible to perform at higher temperatures due to the increasing rate of isomerization of *cis*-butene.[17]

Discussion

The plot in Figure 2 clearly shows that the rate of ethylene exchange is a second-order process, first order in complex 1 and ethylene. Although a fairly large experimental error is inherent in the line width method, it seems safe to conclude that a first-order process (cf. eq 2) is negligible ($k_1 \leq 0.3$ s^{-1} at 253 K).

The activation energy obtained by Halloway and Fogelman[7a] for the ethylene exchange in Pt(acac)Cl(ethylene) (11.1 ± 0.8 kJ mol^{-1}) is not significantly different from the value (12.1 ± 1.5 kJ mol^{-1}) found in this investigation. If we accept the suggestion, made by several authors,[4a,7a] that the rate-determining step in the reaction is the formation of the σ bond (by donation of electron density from the ethylene double bond to the metal), one might expect a slightly higher value for the Rh complex because of the lower formal (and effective) charge on rhodium. The magnitude of this effect is hard to estimate, and therefore, comparison of the two studies neither supports nor contradicts this hypothesis. The activation entropies obtained for the two reactions have similar values: −145 ± 20 J mol^{-1} K^{-1} for the Rh complex vs −150 ± 20 J mol^{-1} K^{-1} for the Pt complex. Our results are in general agreement with the results of Cramer, though his estimate of the lifetime of

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(13) Line widths of free ethylene in CD_2Cl_2 do not agree with the results from the coordinated ethylene and are off by a factor of about 2. (The general relation $x_{coord}[\Delta\nu_{1/2}{}^{exch}(coord)] = x_{free}[\Delta\nu_{1/2}{}^{exch}(free)]$ does not hold). This might be due to a fast reaction of ethylene with some minor rhodium complex that we cannot detect.

(14) Becker, E. D. *High Resolution NMR*; Academic Press: New York, 1980; Chapter 4.

(15) Reference 12, Chapter 4.

(16) T_1 was measured by the inversion-recovery method, but due to broad signals and overlap only an approximate value was obtained.

(17) See for example: Tolman, C. A.; Scharpen, L. H. *J. Chem. Soc., Dalton Trans.* **1973**, 584 and references therein.

the coordinated ethylene ($<10^{-4}$ s at 298 K) is somewhat lower than the ones obtained in this study (10^{-1}–10^{-3} s at 298 K).[4a]

The solvent effects are not readily interpreted, but from the rate data it appears that they are not large. The ^{103}Rh NMR data do show a small solvent effect, but it does not correlate with, for example, the donor properties of the different solvents. Since metal shifts are known to be very sensitive even to weak interactions,[18] it seems fair to say that a solvent effect coming from the coordination of a solvent molecule to the metal is negligible. There are little data to compare this with, but for $[(n\text{-Bu})_4N^+]_2[PtCl_4^{2-}]$ this shift difference in various solvents is up to 200 ppm, and for aprotic solvents the shift decreases with increasing donor properties of the solvent.[19] On the other hand, for the complexes *trans*-$PtCl_2(AsBu_2)_2$, *trans*-$PtCl_2(SMe_2)_2$, $PtCl_3(PMe_3)^-$, and $Pt(PEt_3)_2H(m\text{-}MeC_6H_4CO_2)$ the solvent shifts are on the order of 2–30 ppm and are not easily correlated with any property of the solvent.[20] Thus, a large solvent shift that correlates with the donor properties of the solvent would indicate coordination of the solvent, whereas small shifts might arise from other effects such as electric fields from polar solvents or solvent magnetic anisotropy.

The second-order process and the large negative activation entropy suggest the presence of a five-coordinated transition state. If the solvent would participate in the transition state, we would probably observe different rates of ethylene exchange in the different solvents. Especially, the difference between chlorinated methane and acetone should be significant enough to be detected. However, no such effect is observed. Hence, the five-coordinated transition state may have the composition Rh(acac)(ethylene)$_3$. In fact, five-coordinated rhodium(I) complexes have been observed, e.g. in Rh(acac)$(C_2F_4)(PPh_3)_2$.[21]

The slow exchange in Rh(acac)(*cis*-2-butene)$_2$ ($k_2 \leq 10$ M^{-1} s^{-1} for the assumed associative pathway) is in agreement with the results on Rh(acac)(propene)$_2$[4b] (no line broadening when propene was added to the solution). This could be the result of two effects: (1) steric hindrance and (2) electronic effects. A study on distyrene complexes showed slow exchange in the acac complex but fast exchange in the corresponding acac F_6 (hfacac) compound.[22] There is no information on the mechanism for the exchange in the hfacac compound, but it seems reasonable to assume that it is closely related to the exchange mechanism in the acac compound. (In view of the electron-withdrawing properties of the hfacac group a dissociative mechanism seems unlikely.) The steric effects in the two (acac and hfacac complexes) transition states of the styrene exchange should therefore be of the same magnitude, and this leaves us with electronic effects as the most probable explanation. The reason for the slow exchange may be that ligands such as propene and butene (generally believed to be better σ donors than ethylene) "saturate" the metal center with electrons and thereby make it more difficult for an incoming donor ligand to form a five-coordinate intermediate/transition state.

If the butene exchange instead goes by a dissociative or solvent-assisted mechanism, the upper limit of the rate constant k_1 can be estimated as 0.2 s^{-1} (298 K). It can be noted that this is on the same order of magnitude as the detection limit for k_1 in the ethylene exchange (0.3 s^{-1}, 253 K).

Conclusions

The ethylene exchange in Rh(acac)(ethylene)$_2$ (**1**) is first order both in complex and in ethylene and has a large negative activation entropy. Thus, the exchange most likely takes place by an associative mechanism. The rate of ethylene exchange does not vary significantly in different solvents ($CDCl_3$, CD_2Cl_2, acetone-d_6). The changes of the ^{103}Rh NMR chemical shifts for the compound in several solvents are relatively small and do not correlate with the donor properties of the medium. It therefore seems unlikely that there is a solvent molecule coordinated to the metal in solution.

The slow exchange in Rh(acac)(*cis*-2-butene)$_2$ is ascribed mainly to electronic effects, but steric factors might contribute.

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Note Added in Proof. In a recent publication (Wickenheiser, E. B.; Cullen, W. R. *Inorg. Chem.* **1990**, *29*, 4671) Wickenheiser and Cullen claim evidence for a dissociative process for the ethylene exchange in the closely related complex bis(η^2-ethene)(2′-acetylphenoxy-*O*,*O*′)rhodium(I).

Supplementary Material Available: A table of concentrations and line width data for Figures 2 and 4 (1 page). Ordering information is given on any current masthead page.

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(18) Goodfellow, R. J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapter 20.

(19) ^{195}Pt shifts from: (a) Freeman, W.; Pregosin, P. S.; Sze, S. N.; Venanzi, L. M. *J. Magn. Reson.* **1976**, *22*, 473. (b) Pesek, J. J.; Mason, W. R. *J. Magn. Reson.* **1977**, *25*, 519. Donor strength (D_S) numbers from: (c) Sandström, M.; Persson, I.; Persson, P. *Acta Chem. Scand.* **1990**, *44*, 653.

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(21) Parshall, G. W.; Jones, F. N. *J. Am. Chem. Soc.* **1965**, *87*, 5356.

(22) Parker, D. *J. Organomet. Chem.* **1982**, *240*, 83.