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Pentadienyl–Metal–Phosphine Chemistry. 8.[1] Synthesis and Solution Dynamics of (η^3-2,4-Dimethylpentadienyl)Rh(PR_3)$_2$ Complexes

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(2,4-Dimethylpentadienyl)Rh(PR_3)$_2$ (R = Me, Et, *i*-Pr, *i*-Bu) complexes have been synthesized by reacting potassium 2,4-dimethylpentadienide–tetrahydrofuran with [(PR_3)$_2$RhCl]$_2$. These complexes are all ground-state 16e species in which the dimethylpentadienyl ligand (2,4-Me_2pd) is bonded to the rhodium center in an η^3-fashion. The dominant 2,4-Me_2pd geometry in each case is anti (U-shaped), but small quantities of the syn (W-shaped) isomers have been detected. In solution, the anti isomers undergo a fluxional process, which exchanges the ends of the 2,4-Me_2pd ligand via 18e (η^5-2,4-Me_2pd)Rh(PR_3)$_2$ intermediates. The free energy of activation for the exchange process, $\Delta G^{\ddagger}$, increases as the cone angle of the phosphine ligand increases. At higher temperatures, equilibration of anti and syn isomers is observed by NMR, and this process is believed to involve intermediates with sickle-shaped 2,4-Me_2pd ligands.

Introduction

Electron-rich polyenyl–transition-metal complexes have recently generated a good deal of interest because of their ability to react with bonds which are normally difficult to activate[2] and their ability to stabilize unusual bonding interactions.[3] Our efforts in this area have focussed on pentadienyl–metal–phosphine complexes, a class of electron-rich molecules whose reactivity is further enhanced by the ability of the acyclic pentadienyl ligand to interconvert between η^5, η^3, and η^1-bonding modes.[4,5]

Recently, we reported the synthesis, structure, and reaction chemistry of (2,4-dimethylpentadienyl)Co(PEt_3)$_2$.[1c,e] In the ground state of this complex, the 2,4-dimethylpentadienyl ligand (2,4-Me_2pd) is bonded in an η^5-fashion; however, many of its reactions clearly involve the 16e η^3-2,4-Me_2pd isomer (η^3-2,4-Me_2pd)Co(PEt_3)$_2$ as an intermediate.

We now describe the synthesis and solution dynamics of a family of analogous rhodium complexes, (2,4-dimethylpentadienyl)Rh(PR_3)$_2$. Interestingly, these complexes are *ground-state* 16e species containing η^3-2,4-Me_2pd ligands. In solution they undergo a fluxional process, which exchanges the ends of the 2,4-Me_2pd ligands via 18e (η^5-2,4-Me_2pd)Rh(PR_3)$_2$ intermediates.

Experimental Section

A. General Data. All manipulations were carried out under

(1) The previous papers in this series are: (a) Bleeke, J. R.; Kotyk, J. J. *Organometallics* **1983**, *2*, 1263. (b) Bleeke, J. R.; Hays, M. K. *Ibid.* **1984**, *3*, 506. (c) Bleeke, J. R.; Peng, W.-J. *Ibid.* **1984**, *3*, 1422. (d) Bleeke, J. R.; Kotyk, J. J. *Ibid.* **1985**, *4*, 194. (e) Bleeke, J. R.; Peng, W.-J. *Ibid.* **1986**, *5*, 635. (f) Bleeke, J. R.; Stanley, G. G.; Kotyk, J. J. *Ibid.* **1986**, *5*, 1642. (g) Bleeke, J. R.; Moore, D. A. *Inorg. Chem.* **1986**, *25*, 3522.

(2) See, for example: (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (b) Jones, W. D.; Feher, F. *Ibid.* **1984**, *106*, 1650. (c) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *Ibid.* **1985**, *107*, 4358. (d) Green, M. L. H.; Joyner, D. S.; Wallis, J.; Bell, J. P. Presented at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 1985.

(3) See, for example: (a) Ittel, S. D.; Van-Catledge, F. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 6905. (b) Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *Ibid.* **1981**, *103*, 169. (c) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 1410. (d) Cracknell, R. B.; Orpen, A. G.; Spencer, J. L. *Ibid.* **1984**, *326*. (e) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395 and references cited therein.

(4) See papers cited in ref 1. See also: (a) Paz-Sandoval, M. A.; Powell, P.; Drew, M. G. B.; Perutz, R. N. *Organometallics* **1984**, *3*, 1026. (b) Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56 and references cited therein.

(5) Haptotropic rearrangements involving the related indenyl[5a–d] and cyclopentadienyl[5e–l] ligands have also attracted considerable recent attention: (a) Ji, L-N.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740. (b) Casey, C. P.; O'Connor, J. M. *Ibid.* **1985**, *4*, 384. (c) Faller, J. W.; Crabtree, R. H.; Habib, A. *Ibid.* **1985**, *4*, 929. (d) Merola, J. S.; Kacmarcik, R. T.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 329. (e) Casey, C. P.; Jones, W. D. *Ibid.* **1980**, *102*, 6154. (f) Casey, C. P.; O'Connor, J. M.; Jones, W. D.; Haller, K. J. *Organometallics* **1983**, *2*, 535. (g) Casey, C. P.; O'Connor, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 2920. (h) Casey, C. P.; O'Connor, J. M.; Haller, K. J. *Ibid.* **1985**, *107*, 1241. (i) Rerek, M. E.; Basolo, F. *Organometallics* **1983**, *2*, 372. (j) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908. (k) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Chem. Commun.* **1984**, 624. (l) Yang, G. K.; Bergman, R. G. *Organometallics* **1985**, *4*, 129.

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inert atmosphere, using either drybox or Schlenk techniques. Tetrahydrofuran was dried with sodium/benzophenone and distilled before use. Pentane was dried over calcium hydride and distilled. Trimethylphosphine, triethylphosphine, tri-isopropylphosphine, and tri-isobutylphosphine were obtained from Strem Chemicals; 2,4-dimethylpentadiene was purchased from Wiley Organics; $RhCl_3 \cdot 3H_2O$ was obtained from Pressure Chemical Co. All reagents were used without further purification. NMR experiments were performed on a Varian XL-300 NMR spectrometer. ^1H (300-MHz) and ^{13}C (75-MHz) spectra were referenced to tetramethylsilane, while ^{31}P (121-MHz) spectra were referenced to external H_3PO_4. In general, ^{13}C NMR peak assignments were made from gated decoupled spectra. ^1H NMR peak assignments were then obtained from ^{13}C–^1H shift-correlated (HETCOR) 2D spectra. Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer. Mass spectra were obtained on a Finnigan 3200 GC/MS. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or Schwarzkopf Laboratory, Inc., Woodside, NY.

B. Synthesis of (η^3-2,4-Dimethylpentadienyl)Rh(PR_3)$_2$ Complexes. Four equivalents of PR_3 (R = methyl, ethyl, isopropyl, or isobutyl) were added quickly to a freshly prepared solution of $[(cis\text{-cyclooctene})_2RhCl]_2$[6] in tetrahydrofuran (THF). The solution was swirled briefly, and the volatiles were then removed under vacuum, leaving solid $[(PR_3)_2RhCl]_2$.[7] In a typical reaction, 1.0 g (1.4×10^{-3} mol) of $[(cis\text{-cyclooctene})_2RhCl]_2$ in 60 mL of THF was reacted with 0.43 g (5.6×10^{-3} mol) of PMe_3, producing 0.80 g (1.4×10^{-3} mol) of $[(PMe_3)_2RhCl]_2$ (98% yield). Similar yields were obtained for the reactions involving the other phosphines.

A solution of potassium 2,4-dimethylpentadienide–tetrahydrofuran[8a] in THF was added slowly to a stirred solution of $[(PR_3)_2RhCl]_2$ in THF, maintained at −78 °C. The resulting red solution was then allowed to warm to 25 °C while being stirred, filtered through Celite, and evaporated to dryness. The oily red residue was extracted with pentane, filtered through Celite, and evaporated to dryness. In a typical reaction, 0.73 g (1.3×10^{-3} mol) of $[(PMe_3)_2RhCl]_2$ in 40 mL of THF was reacted with 0.50 g (2.7×10^{-3} mol) of $K^+C_7H_{11}^- \cdot 0.7THF$[8b] in 20 mL of THF to produce 0.89 g (2.5×10^{-3} mol) of (η^3-2,4-Me_2pd)Rh(PMe_3)$_2$ (**1**; 98%). The yields of (η^3-2,4-Me_2pd)Rh(PEt_3)$_2$ (**2**), (η^3-2,4-Me_2pd)Rh[P(*i*-Pr)$_3$]$_2$ (**3**), and (η^3-2,4-Me_2pd)Rh[P(*i*-Bu)$_3$]$_2$ (**4**) were 95–98%.

Each product was extremely soluble in THF and very soluble in pentane. Attempts to crystallize the compounds from a variety of solvents yielded oils or low-melting solids. Analytically pure samples of **1**–**4** were obtained by repeated precipitation from saturated pentane solutions at −30 °C. Anal. Calcd for **1** ($C_{13}H_{29}RhP_2$): C, 44.57; H, 8.36. Found: C, 44.26; H, 8.52. Anal. Calcd for **2** ($C_{19}H_{41}RhP_2$): C, 52.52; H, 9.53. Found: C, 52.04; H, 9.46. Anal. Calcd for **3** ($C_{25}H_{53}RhP_2$): C, 57.89; H, 10.32. Found: C, 57.41; H, 10.17. Anal. Calcd for **4** ($C_{31}H_{65}RhP_2$): C, 61.76; H, 10.78. Found: C, 61.25; H, 10.63. MS (electron impact, solid probe, 70 eV) for **1**: M^+ at 350, $(M - PMe_3)^+$ at 274, $(M - C_7H_{11})^+$ at 255. MS for **2**: M^+ at 434, $(M - Et)^+$ at 405, $(M - C_7H_{11} - H_2)^+$ at 337, $(M - PEt_3)^+$ at 316. MS for **3**: $[M - P(i\text{-}Pr)_3]^+$ at 358. MS for **4**: $(M - C_7H_{11})^+$ at 507, $[M - P(i\text{-}Bu)_3]^+$ at 400. IR (selected peaks in benzene) for **1**: 1606 (C=C), 936 cm^{-1} (P—C). IR for **2**: 1601 (C=C), 1023 cm^{-1} (P—C). IR for **3**: 1608 (C=C), 1029 cm^{-1} (P—C). IR for **4**: 1603 (C=C), 1066 cm^{-1} (P—C). NMR data for complexes **1**–**4** are reported in Table I.

C. Solution Dynamics of Compounds 1–4. Samples were dissolved in toluene-d_8, tetrahydrofuran-d_8, or dimethyl-d_6 ether[9] and NMR spectra were recorded over the temperature range −110 to 90 °C. Probe temperatures were calibrated by using the temperature dependence of the difference in chemical shift between the ^1H resonances of the methyl and hydroxyl groups of methanol below ambient temperatures and between the ^1H resonances of the methylene and hydroxyl groups of ethylene glycol above ambient temperatures.[10]

Exchange rate constants, k_c, at the coalescence temperature were calculated by using the formula

$$k_c = \pi(\Delta\nu)/2^{1/2}$$

where $\Delta\nu$ is the difference in frequencies between the two exchanging sites in the stopped-exchange limit.[11] These exchange rate constants were then used to determine the free energy of activation, $\Delta G^\ddagger$, at the coalescence temperature, T_c, from the Eyring equation

$$k_c = \frac{k'}{h} T_c e^{-\Delta G^\ddagger/RT_c}$$

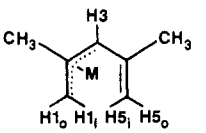
where k' = Boltzmann's constant, h = Planck's constant, and R = ideal gas constant.[12]

Rate constants for anti-$\eta^3 \rightleftharpoons$ anti-η^3 (end-to-end) exchange were calculated by using the C1/C5 signals and C2/C4 signals in the ^{13}C NMR spectra, while those for anti-$\eta^3 \rightleftharpoons$ syn-η^3 isomerization were determined from P1 (anti)/P1 (syn) signals and P2 (anti)/P2 (syn) signals in the ^{31}P NMR spectra. Since stopped exchange spectra for **1a** and **2a** were not obtained, $\Delta\nu$'s for these compounds were estimated from the ^{13}C NMR data for **3a** and **4a**.

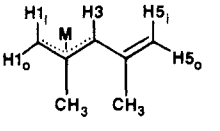
Results and Discussion

A. Syntheses of (η^3-2,4-Dimethylpentadienyl)Rh(PR_3)$_2$ Complexes. (2,4-Dimethylpentadienyl)Rh(PR_3)$_2$ compounds [R = Me (compound **1**), R = Et (**2**), R = *i*-Pr (**3**), R = *i*-Bu (**4**)] are produced in essentially quantitative yield from the reaction of 2 equiv of potassium 2,4-dimethylpentadienide–tetrahydrofuran with the chloro-bridged dimers $[(PR_3)_2RhCl]_2$. These phosphine-containing dimers can, in turn, be conveniently synthesized by reacting $[(cis\text{-cyclooctene})_2RhCl]_2$ with 4 equiv of PR_3.

Complexes **1**–**4** are all ground-state 16e complexes in which the dimethylpentadienyl ligand (2,4-Me_2pd) is bonded to the rhodium center in an η^3-fashion.[13] The infrared spectra of complexes **1**–**4** show C–C double-bond stretches for the uncoordinated isopropenyl groups around 1600 cm^{-1}. The dominant geometry of the η^3-2,4-Me_2pd ligand in each case is anti (U-shaped), but small quantities (~10%) of the syn (W-shaped) isomers are observed for the PMe_3 and P(*i*-Bu)$_3$ complexes (**1s** and **4s**, respectively). Even smaller quantities of the syn isomers are observed for the PEt_3 and P(*i*-Pr)$_3$ complexes.[14]



anti isomer



syn isomer

(6) Van der Ent, A.; Onderdelinden, O. *Inorg. Synth.* **1973**, *14*, 92.

(7) Werner has reported the synthesis of $[(PMe_3)_2RhCl]_2$ from the reaction of $[(ethylene)_2RhCl]_2$ with 4 equiv of PMe_3. This compound was used as a starting material for the synthesis of (indenyl)Rh(PMe_3)$_2$ which, interestingly, has an η^5 ground state: Werner, H.; Feser, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 689.

(8) (a) Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036. (b) When the volatiles were removed by vacuum from a solution of potassium 2,4-dimethylpentadienide in THF, the composition of the residual solid product was approximately $K^+C_7H_{11}^- \cdot 0.7THF$. This value was used for all stoichiometric calculations and yielded essentially quantitative formation of 2,4-Me_2pd complexes.

(9) Dimethyl-d_6 ether was prepared by addition of 5 mL of concentrated H_2SO_4 to 5 g of cold methanol-d_4, reflux, and collection of the product in a liquid N_2 trap.

(10) Von Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227.

(11) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High Resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959; p 223.

(12) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1976; p 194.

(13) These complexes are closely related to (η^3-allyl)Rh(PR_3)$_2$ (PR_3 = phosphines and phosphites) complexes first reported by Muetterties, et al.: Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878.

(14) The anti and syn isomers can be readily distinguished by the chemical shift of the H3 proton. H3 for the anti isomer typically appears at δ 4.1–4.2, while H3 for the syn isomers (where it is more shielded) appears at δ 3.1–3.3 (see Table I).

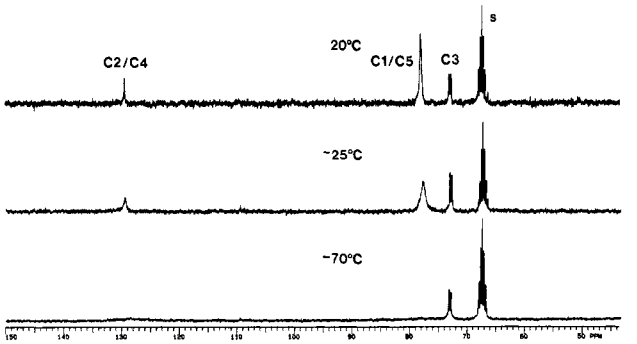


Figure 1. $^{13}C\{^1H\}$ NMR spectrum of (*anti*-η^3-2,4-Me_2pd)Rh(PEt_3)$_2$ (**2a**) at 20 °C (top), −25 °C (middle), and −70 °C (bottom). At 20 °C, the two ends of the 2,4-Me_2pd ligands are exchanging rapidly, giving rise to time averaged signals for C1/C5 and C2/C4. As the sample is cooled, exchange is slowed and the time averaged signals begin to broaden and split. At −70 °C, the system is in intermediate exchange, and the signals for C1/C5 and C2/C4 have disappeared into the base line. We have been unable to obtain the stopped exchange spectrum. Note that the signal for C3 is unaffected by the exchange process. Tetrahydrofuran-d_8 peaks are labeled "s".

B. End-to-End Exchange of (*anti*-η^3-2,4-Dimethylpentadienyl)Rh(PR_3)$_2$ Complexes in Solution. In solution, the anti isomers, complexes **1a**–**4a**, exhibit a common fluxional process involving exchange of the ends of the 2,4-Me_2pd ligand. This process is clearly manifested in the variable-temperature $^{13}C\{^1H\}$ NMR spectra. Under stopped-exchange conditions, all of the pentadienyl carbon nuclei give rise to separate signals. However, as the temperature is raised, the exchange rate increases, causing coalescence of the signals due to C1 and C5 and of the signals due to C2 and C4. The C3 signal remains unchanged.[15] The ^1H NMR spectra are also temperature-dependent. Under stopped-exchange conditions, distinct signals due to $H1_{outer}$, $H1_{inner}$, H3, $H5_{outer}$, and $H5_{inner}$ are observed (see labeling scheme for anti isomer above). However, as the temperature is raised, the signals due to $H1_{outer}$ and $H5_{outer}$ and those due to $H1_{inner}$ and $H5_{inner}$ broaden and coalesce. H3 remains unaffected.

The free energy of activation, $\Delta G^{\ddagger}$, for this exchange process depends on the steric bulk of the trialkylphosphine ligands. As the cone angle of the phosphine[16] increases, $\Delta G^{\ddagger}$ increases. Hence, for the PMe_3 (cone angle = 118°) and PEt_3 (cone angle = 132°) complexes (**1a** and **2a**), $\Delta G^{\ddagger}$ is 7.5 ± 0.2 and 7.9 ± 0.2 kcal, respectively.[17] These complexes are in fast exchange at room temperature, and although their NMR signals broaden upon cooling, we are unable to reach the stopped-exchange limit[18] (see Figure 1). The P(*i*-Bu)$_3$ (cone angle = 143°) complex (**4a**) has a $\Delta G^{\ddagger}$ of 14.9 ± 0.2 kcal.[17] It is in intermediate exchange at room temperature, and the slow-exchange limit is reached at −20 °C (see Figure 2). Fast exchange is not observed before decomposition above 90 °C. Finally, the P(*i*-Pr)$_3$ (cone angle = 160°) complex (**3a**) exhibits a $\Delta G^{\ddagger}$ of 15.9 ± 0.5 kcal[17] and is in stopped exchange at room temperature. As in the case of **4a**, fast exchange is not reached before the sample decomposes.

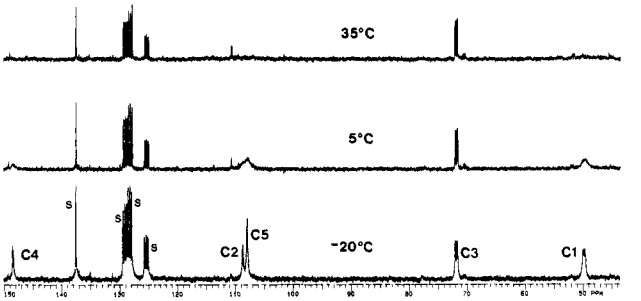
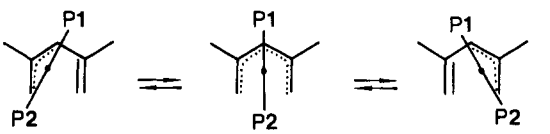


Figure 2. $^{13}C\{^1H\}$ NMR spectrum of (η^3-2,4-Me_2pd)Rh[P(*i*-Bu)$_3$]$_2$ (**4**) at 35 °C (top), 5 °C (middle), and −20 °C (bottom). The anti isomer **4a** predominates, but small peaks due to the syn isomer **4s** are present at each temperature and are most evident in the 35 °C (top) spectrum at δ 149.0 (C4), 113.6 (C2), 110.5 (C5), 70.2 (C3), and 51.6 (C1). At 35 °C, **4a** is in intermediate exchange and the situation is similar to that described in Figure 1 for **2a** at T = −70 °C. At −20 °C, exchange of the two ends of the 2,4-Me_2pd ligand in **4a** is stopped and all of the 2,4-Me_2pd carbon atoms give rise to separate signals. **4s** is not fluxional over this temperature regime. Toluene-d_8 peaks are labeled "s".

Scheme I



The $^{31}P\{^1H\}$ NMR spectra of complexes **1a**–**4a** all consist of two signals which are split into doublets of doublets by rhodium and phosphorus coupling.[19] In all cases, J_{Rh-P} is 180–190 Hz, while J_{P-P} is 20–30 Hz. Unlike the ^{13}C and ^1H NMR spectra, the ^{31}P spectra do not change with temperature until anti–syn interconversion becomes observable (vide infra).

C. Mechanism of End-to-End Exchange in (*anti*-η^3-2,4-Dimethylpentadienyl)Rh(PR_3)$_2$ Complexes. We propose that the fluxional process which exchanges the ends of the *anti*-η^3-2,4-Me_2pd ligand in compounds **1a**–**4a** proceeds through an 18e (η^5-2,4-Me_2pd)Rh(PR_3)$_2$ intermediate as shown in Scheme I. This mechanism is fully consistent with the variable-temperature NMR data. In particular, it accounts for the observation that the two phosphine ligands remain inequivalent throughout the process; one remains under the mouth of the 2,4-Me_2pd ligand while the other remains under the backbone. An analogous η^3–η^5–η^3 interchange has been cited by Maitlis[20] to explain the dynamic behavior in a series of isoelectronic (η^3-cycloheptadienyl)PdL_2^+ complexes. Furthermore, theoretical calculations by Mingos on (η-cyclohexadienyl)Pt$(PH_3)_2^+$[21a] and by Albright on (η-pentadienyl)Pt$(PH_3)_2^+$[21b] confirm the energetic feasibility of this mechanism.

The alternative mechanism involving a 14e (η^1-2,4-Me_2pd)Rh(PR_3)$_2$ intermediate in which the rhodium center

(15) Under stopped exchange conditions, the metal-bound carbon atom C1 is a doublet with a coupling constant, $^1J_{C-Rh}$, of 20–30 Hz, and the signal for vinylic carbon atom C5 is a singlet ($^3J_{Rh-C} \approx 0$). However, when end-to-end exchange is rapid, C1 and C5 give rise to a single signal whose coupling constant, J_{C-Rh}, is equal to the average of the coupling constants cited above, i.e., $J_{C-Rh} = {}^1/_2({}^1J_{C-Rh} + {}^3J_{C-Rh}) \approx {}^1/_2({}^1J_{C-Rh})$. The coupling of C3 to Rh is unaffected by the end-to-end exchange process.

(16) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(17) $\Delta G^{\ddagger}$'s have been calculated at the coalescence temperatures.

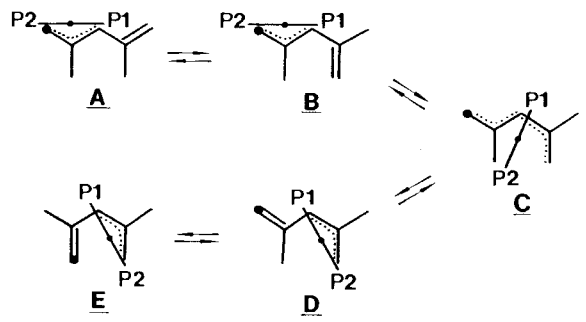
(18) At −110 °C in dimethyl-d_6 ether, the ^{13}C NMR signals due to C1 and C5 of the PEt_3 complex **2a** begin to grow in as very broad humps.

(19) For each compound, the lower field ^{31}P peak, δ(P1), is assigned to the phosphine under the backbone of the 2,4-Me_2pd ligand and δ(P2) is assigned to the phosphine under the mouth of the 2,4-Me_2pd ligand: Bleeke, J. R.; Peng, W.-J., unpublished results for analogous cobalt complexes.

(20) Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1976**, 1058.

(21) (a) Extended Hückel calculations by Mingos and Nurse have shown that for isoelectronic (but hypothetical) (η-cyclohexadienyl)Pt$(PH_3)_2^+$ complexes, the η^5-geometry lies 12 kcal higher in energy than the ground-state η^3-geometry: Mingos, D. M. P.; Nurse, C. R. *J. Organomet. Chem.* **1980**, *184*, 281. (b) More recent calculations by Albright and Silvestre for (η-pentadienyl)Pt$(PH_3)_2^+$ have found the η^5-complex to be 9 kcal higher in energy than the η^3 ground state: Silvestre, J.; Albright, T. A. *J. Am. Chem. Soc.* **1985**, *107*, 6829.

Scheme II



Scheme III

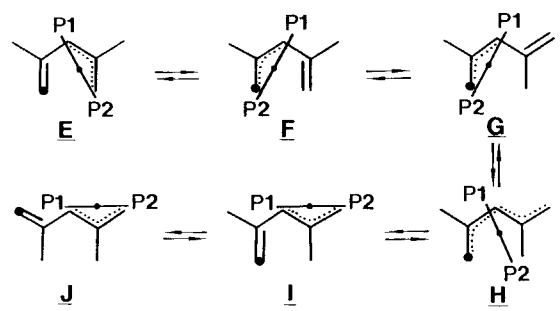


Table I. NMR Data on (η^3-Me_2pd)$Rh(PR_3)_2$ Complexes[a]

Dimethylpentadienyl Signals: $^{13}C\{^1H\}$ and ^1H

complex	no.	temp, °C	δ(C1) (J_{CRh})	δ(H1)'s (J)	δ(C2)	δ(C3) (J_{CRh}, J_{CP2}, J_{CP1})	δ(H3) (J)	δ(C4)	δ(C5)	δ(H5)'s	δ(C6)[d]	δ(H6)	δ(C7)[d]	δ(H7)
(*anti*-η^3-Me_2pd)-$Rh(PMe_3)_2$	**1a**	18[b]	77.22, d (13.5)	3.65, 3.55	127.2	72.29, d of d (28.1, 8.5)	4.1	127.2	77.22	3.65, 3.55	26.80	1.75	26.80	1.75
(*syn*-η^3-Me_2pd)-$Rh(PMe_3)_2$	**1s**	−25[c]	54.13, d (24)	2.67, t; 2.28, d (4.0, 7.0)	116.38	70.44, d of d (26, 6.7)	3.29, d (7.3)	149.51	110.48	5.03; 4.93	u	2.07	24.98	1.93
(*anti*-η^3-Me_2pd)-$Rh(PEt_3)_2$	**2a**	18[b]	78.24, d (13.1)	3.73, d; 3.63 (3.9)	129.06	72.87, d of d of d (28.1, 8.5, 2.0)	4.18, t	129.06	78.24	3.73; 3.63	27.32	1.82	27.32	1.82
(*anti*-η^3-Me_2pd)-$Rh(P\text{-}i\text{-}Pr_3)_2$	**3a**	18[c]	48.1, m (30)	2.56, d; 2.44 (6.8)	105.4	69.83, d of d of d (24.9, 9.2, 5.4)	4.16	148.8	109.07	4.81; 4.64	27.9	1.78	25.2	1.70
(*anti*-η^3-Me_2pd)-$Rh(P\text{-}i\text{-}Bu_3)_2$	**4a**	−46[c]	49.86, d (22.4)	2.62; 2.43	108.71	71.89, d of d (25.3, 6.0)	4.14	148.36	107.99	4.78; 4.49	29.77	1.73	24.04	1.73
(*syn*-η^3-Me_2pd)-$Rh(P\text{-}i\text{-}Bu_3)_2$	**4s**	17[c]	51.6, d (25)	2.44; u	113.6	70.24, d of d of d (25.5, 5.5, 2.2)	3.12, d (6)	148.95	110.46	4.95; u	u	u	u	u

Trialkylphosphine Signals: $^{13}C\{^1H\}$, ^1H, and $^{31}P\{^1H\}$

no.	temp, °C	δ(CH) (J_{CP})	δ(C*H*)	δ(CH_2) (J_{CP})	δ(CH_2) (J_{HH})	δ(CH_3) (J_{CP})	δ(CH_3) (J_{HP}, J)	δ(P1) (J_{PRh}, J_{PP2})	δ(P2) (J_{PRh}, J_{PP1})
1a	18					21.98, d; 20.61, d (22, 22)	1.27, d of d; 1.24, d of d (6.8, 2; 8.4, 2)	−9.2 (187, 29)	−13.4 (189, 29)
1s	−25					22.94, d; 19.62, d (24, 21)	u	−8.1 (192, 29)	−16.7 (189, 29)
2a	18			21.90, d; 20.09, d (20.3, 19.1)	1.47, q; 1.58 q (7.3, 7.8)	9.20, 9.04	0.96, m	29.1 (190, 29)	23.2 (188, 29)
3a	18	28.95, d; 27.65, d (13.1, 13.2)	2.2, m			21, m	1.23, d; 1.19, d (7.3, 6.7)	53.9 (186, 20)	50.2 (186, 20)
4a	17	26.47	1.96	41.25, d; 38.31, d (16.6, 17.6)	1.62, t (6.5)	26.00, d; 25.51, d (7.8, 7.5)	1.01, d; 0.99, d (6.2; 7.0)	22.6 (187, 25)	14.6 (188, 25)
4s	19	u	u	u	u	u	u	23.4 (199, 25)	9.9 (188, 25)

[a] ^{13}C and ^1H chemical shifts referenced to Me_4Si; ^{31}P chemical shifts referenced to external H_3PO_4; solvent = toluene-d_8; d = doublet, t = triplet, m = multiplet, u = unobserved or obscured; J = absolute value of coupling constant in hertz. [b] Fast exchange. [c] Stopped exchange. [d] C6 and C7 refer to the methyl carbon atoms bonded to C2 and C4, respectively.

is bonded to C3 of the 2,4-Me_2pd ligand can be ruled out because the two phosphine ligands would become equivalent in such an intermediate, assuming free rotation about the Rh–C3 bond. Furthermore, (*anti*-η^3-2,4-Me_2pd)Rh(PR_3)$_2$ would be expected to convert to (*syn*-η^3-2,4-Me_2pd)Rh(PR_3)$_2$ at the same rate that one anti isomer converts to the other, assuming free rotation about single bonds C2–C3 and C3–C4 in the (η^1-2,4-Me_2pd)Rh(PR_3)$_2$ intermediate. This is not the case: anti $\rightleftharpoons$ anti interconversion occurs much more readily than anti $\rightleftharpoons$ syn interconversion (vide infra). Molecular orbital calculations by Albright on haptotropic shifts in isoelectronic (η-pentadienyl)Pt(PH_3)$_2^+$ complexes support our contention that (η^1-2,4-Me_2pd)Rh(PR_3)$_2$ intermediates are not involved in the fluxional process.[22]

The observed increase in $\Delta G^\ddagger$ with increasing cone angle of the phosphine ligand must result primarily from unfavorable steric interactions in the (η^5-2,4-Me_2pd)Rh(PR_3)$_2$ intermediate. The electronic features of the trialkylphosphine ligands are all very similar[16] and cannot have a significant effect on $\Delta G^\ddagger$.

D. Syn–Anti Isomerization in (η^3-2,4-Dimethylpentadienyl)Rh(PR_3)$_2$ Complexes. The (*syn*-η^3-2,4-Me_2pd)Rh(PR_3)$_2$ complexes, **1s** and **4s**, are much more rigid in solution than their anti isomers. For example, (*syn*-η^3-2,4-Me_2pd)Rh(PMe_3)$_2$ (**1s**) exhibits ^{13}C and ^1H NMR spectra in stopped exchange at room temperature while **1a** displays the time averaged signals of fast end-to-end exchange. However, as the mixture of **1s** and **1a** is heated above room temperature, equilibration of the two isomers becomes rapid on the NMR time scale. The ^{13}C NMR signals due to C1 and C5 of **1s** broaden and then coalesce with the C1/C5 signal of **1a**. Similarly, peaks C2 and C4 of **1s** coalesce with the C2/C4 peak of **1a**, and peak C3 of **1s** coalesces with peak C3 of **1a**. Furthermore, the ^{31}P signal due to P1 of **1s** coalesces with the signal due to P1 of **1a**, and signal P2 of **1s** coalesces with signal P2 of **1a**, but, significantly, the signals due to P1 and P2 do *not* coalesce.

As with the anti–anti interconversion, the syn–anti interconversion is slowed down by increasing the cone angle of the phosphine. Using ^{31}P NMR data, we have determined $\Delta G^\ddagger$ for this process to be 16.1 ± 0.2 kcal for **1** and 18.5 ± 0.4 kcal for **4**.[17]

E. Mechanism of Syn–Anti Isomerization in (η^3-2,4-Dimethylpentadienyl)Rh(PR_3)$_2$. We propose that the (*syn*-η^3-2,4-Me_2pd)Rh(PR_3)$_2$ complexes equilibrate with their anti-η^3-isomers via sickle-shaped 2,4-Me_2pd intermediates, as shown in Scheme II. This process exchanges carbon atom C1 of the syn isomer (highlighted in A, Scheme II) with C5 of the anti isomer (highlighted in E). Furthermore, when this sequence is coupled with fast end-to-end exchange in the anti isomers, as shown in Scheme III, it leads to inclusion of C1 (anti) and C5 (syn) in the exchange process (see highlighted atoms in intermediates F and J, Scheme III). Similarly, C2 (syn) is exchanged with C2 (anti), C4 (anti), and C4 (syn), while C3 (syn) is exchanged with C3 (anti).

Hence, the sequence shown in Schemes II and III is fully consistent with our ^{13}C NMR data; it provides a mechanism for equilibration of syn and anti isomers with concomitant exchange of C1 (syn), C1 (anti), C5 (syn), and C5 (anti), exchange of C2 (syn), C2 (anti), C4 (syn), and C4 (anti), and exchange of C3 (syn) and C3 (anti).

The proposed mechanism is also consistent with our ^{31}P NMR data. In particular, it accounts for our observation that P1 (syn) exchanges with P1 (anti) while P2 (syn) exchanges with P2 (anti), but P1 and P2 remain inequivalent throughout the process; P2 is always trans to C3.

Again, molecular orbital calculations by Albright on haptotropic shifts in isoelectronic (η-pentadienyl)Pt(PH_3)$_2^+$ complexes confirm that the mechanism described in Scheme II is the lowest energy pathway for interconverting syn and anti-η^3-isomers.[23]

Conclusion

(2,4-Dimethylpentadienyl)Rh(PR_3)$_2$ complexes can be readily synthesized from the reaction of potassium 2,4-dimethylpentadienide with [(PR_3)$_2$RhCl]$_2$. These complexes have a 16e ground state in which the 2,4-Me_2pd ligand is bonded to the rhodium center in an η^3-fashion. In all cases, the dominant η^3-2,4-Me_2pd geometry is anti (U-shaped), but small quantities of the syn (W-shaped) isomers have been detected. In solution, the (*anti*-η^3-2,4-Me_2pd)Rh(PR_3)$_2$ complexes undergo a rapid fluxional process, which exchanges the ends of the 2,4-Me_2pd ligands. The 18e (η^5-2,4-Me_2pd)Rh(PR_3)$_2$ complexes are involved as intermediates in this fluxional process. At higher temperatures, equilibration of anti and syn isomers is observed, and this process is believed to involve intermediates with sickle-shaped 2,4-Me_2pd ligands.

We have begun to study the reaction chemistry of these (η^3-2,4-Me_2pd)Rh(PR_3)$_2$ complexes and are particularly interested in comparing their reactivity with that exhibited by their cobalt analogues, (2,4-dimethylpentadienyl)Co(PR_3)$_2$, whose *ground states* are 18e η^5-2,4-Me_2pd complexes.

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Registry No. **1**, 104779-56-8; **2**, 104779-57-9; **3**, 104779-58-0; **4**, 104779-59-1; [(*cis*-cyclooctene)$_2$RhCl]$_2$, 12279-09-3; [(PMe_3)$_2$RhCl]$_2$, 75094-83-6; [(PEt_3)$_2$RhCl]$_2$, 79075-69-7; [(P(*i*-Pr)$_3$)$_2$RhCl]$_2$, 104807-13-8; [(P(*i*-Bu)$_3$)$_2$RhCl]$_2$, 104807-14-9; PMe_3, 594-09-2; PEt_3, 554-70-1; P(*i*-Pr)$_3$, 6476-36-4; P(*i*-Bu)$_3$, 4125-25-1; (2,4-Me_2pd)K(THF), 72013-05-9.

Supplementary Material Available: ^{13}C–^1H shift correlated (HETCOR) 2D NMR spectrum of (η^3-2,4-dimethylpentadienyl)Rh[P(*i*-Bu)$_3$]$_2$ (**4**) at −25 °C (2 pages). Ordering information is given on any current masthead page.

(22) The calculations show that the 14e η^1-pd species, (η^1-pentadienyl)Pt(PH_3)$_2^+$, lies in a high energy region of the potential energy surface for (η-pentadienyl)Pt(PH_3)$_2^+$: see ref 21b.

(23) The haptotropic rearrangement of (*syn*-η^3-pentadienyl)Pt(PH_3)$_2^+$ to its anti-η^3-isomer via a sickle-shaped pd intermediate is accompanied by a barrier of 22 kcal: see ref 21b.