Phosphine Substitution in Indenyl- and Cyclopentadienylruthenium Complexes. Effect of the η^5 Ligand in a Dissociative Pathway

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Received June 6, 1995[⊗]

The indenyl complex [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (**1**) reacts with monodentate (L: $PMePh_2$, PMe_2Ph, PMe_3) or bidentate [L−L: $Ph_2PCH_2PPh_2$ (dppm), $Ph_2P(CH_2)_2PPh_2$ (dppe)] phosphines to give monosubstituted [RuCl(η^5-C_9H_7)(PPh_3)(L)], bisubstituted [RuCl(η^5-C_9H_7)(L)$_2$], or chelated complexes [RuCl(η^5-C_9H_7)(L−L)] in toluene or tetrahydrofuran. The corresponding cyclopentadienyl complex [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (**2**) reacts similarly, at higher temperatures or longer reaction times. In refluxing toluene, PMe_3 and dppm give ionic products [Ru(η^5-C_9H_7)(L)$_3$]Cl. The kinetics of PPh_3 substitution by $PMePh_2$ and PMe_2Ph in tetrahydrofuran yield first-order rate constants that are independent of the concentration or the nature of phosphine. Rate decrease in the presence of added PPh_3 or saturation behavior at high [PPh_3] indicates that the reaction proceeds by a dissociative mechanism, in which extrusion of PPh_3 is rate determining. Kinetics for the reaction with $PMePh_2$ in the temperature range 12−40 °C for the indenyl and 20−50 °C for the cyclopentadienyl complex give the following activation parameters: $\Delta H^‡ = 26 \pm 1$ kcal mol^{-1} and $\Delta S^‡ = 11 \pm 2$ cal mol^{-1} K^{-1} for **1** and $\Delta H^‡ = 29 \pm 1$ kcal mol^{-1} and $\Delta S^‡ = 17 \pm 2$ cal mol^{-1} K^{-1} for **2**. Complex **1** is 1 order of magnitude more reactive than **2**, indicating more efficient stabilization of 16-electron intermediates RuCl(η^5-ligand)(PPh_3) by the indenyl group. Cyclic voltammetry measurements for [RuCl(η^5-ligand)(L)$_2$] in dichloromethane indicate that indenyl or pentamethylcyclopentadienyl complexes are oxidized at lower potentials than cyclopentadienyl complexes. Kinetics and electrochemistry suggest that indenyl is electron donating toward the metal fragment, with respect to cyclopentadienyl.

Introduction

Indenyl (Ind, C_9H_7) transition metal complexes are often characterized by greater reactivity with respect to their cyclopentadienyl (Cp, C_5H_5) analogues, either in stoichiometric[1] or in catalytic processes.[2] This evidence has prompted widespread interest regarding both the synthetic applications and the mechanistic features of indenyl complexes for a large number of transition metals. The chemistry of bis(phosphine)ruthenium auxiliaries η^5 bonded to ligands of the cyclopentadienyl family is an area of current active research.[3] We have recently reported on the preparation and reactivity of novel indenylruthenium complexes, mainly with respect to the chemistry of alkynyl, vinylidene, and carbene derivatives.[4] The synthetic features of metal−carbon unsaturated moieties are also displayed in the reactions of pentamethylcyclopentadienylruthenium (Cp*, C_5Me_5) complexes.[5] Moreover, the complex [RuCl(η^5-Ind)(PPh_3)$_2$] has shown enhanced catalytic activity in redox isomerizations of allylic alcohols.[6]

We intend to explore the properties of [RuCl(η^5-Ind)-

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1995.

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0276-7333/96/2315-0302$12.00/0

$(PPh_3)_2$] in basic reactions to understand the nature of the intimate steps occurring at the metal center and to describe in parallel the behavior of the corresponding cyclopentadienyl complex. The chemistry of [RuCl(η^5-Cp)$(PPh_3)_2$] is characterized by facile displacement of either chloride or one or both triphenylphosphine ligands, affording cationic or neutral compounds, respectively, depending on solvent and reaction conditions.[7] The synthesis of [RuCl(η^5-Ind)$(PPh_3)_2$] and the formation of ionic complexes have been reported.[8] Pentamethylcyclopentadienyl complexes [RuX(η^5-C_5Me_5)(phosphine)$_2$] have been described with regard to the kinetics for trimethylphosphine exchange[9] and with regard to the relative binding energies of sterically demanding phosphines.[10] The extrusion of a phosphine ligand to create coordinative unsaturation at the metal center and the effect of the spectator ligand on reactive 16-electron intermediates obviously are of central relevance.

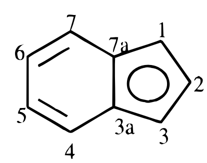
Ligand substitution reactions in indenyl transition metal complexes proceed at faster rates than in the corresponding cyclopentadienyl analogues. The higher reactivity has been explained as the result of facile metal ring slippage from η^5 to η^3 coordination of indenyl and the consequent creation of a vacant coordination site to host the entering ligand.[11a,b] In fact, the reactions generally proceed by associative pathways for complexes of the metals rhodium,[2e,11b,c] iridium,[12] rhenium,[13] and manganese.[14] On the other hand, carbonyl substitutions in [MoX(η^5-Ind)$(CO)_3$] (X = Cl, Br, I)[11a] and [WCl(η^5-Ind)$(CO)_3$][15] proceed by mixed associative and dissociative mechanisms and are still orders of magnitude faster than those of the Cp complexes. In the iron triad, the carbonyl substitution reaction of [FeI(η^5-Ind)$(CO)_2$] by phosphorus donors is characterized by rate-determining carbonyl dissociation and is independent of the incoming ligand.[16] The same reaction in the 19-electron radical [Fe(η^5-Ind)$(CO)_3$] is also dissociative, although slower than that of [Fe(η^5-Cp)$(CO)_3$] by 10^3 s^{-1}, displaying an "inverse indenyl effect".[17] With regard to cyclopentadienyl complexes, although Co(I) and Rh(I) prefer associative routes,[18] the majority of 18-electron metal complexes undergo ligand substitution by dissociative pathways.[19] For instance, substitution in [Co(η^5-Cp)$(PPh_3)_2$] proceeds by rate-determining loss of PPh_3.[20]

In this paper, we report on the exchange of PPh_3 in [RuCl(η^5-Ind)$(PPh_3)_2$] and [RuCl(η^5-Cp)$(PPh_3)_2$] by alkylarylphosphines and on the kinetics and mechanisms of some of these reactions.

Experimental Section

General Comments. The reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. The complex [RuCl(η^5-C_9H_7)$(PPh_3)_2$] and the phosphines $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2PCH_2CH_2PPh_2$ (dppe) were prepared by literature methods. The phosphines $PMePh_2$, PMe_2Ph, and PMe_3 were available commercially. PMe_2Ph used in the kinetic experiments was distilled over sodium under argon.

Cyclic voltammetry measurements (25 °C) were carried out with a three-electrode system. The working electrode was a platinum disk electrode, the counter electrode was a platinum spiral, and the reference electrode was an aqueous saturated calomel electrode (SCE) separated from the solution by a porous septum. Current and voltage parameters were controlled by using a PAR system M273. In a typical experiment, 10^{-2} mmol of complex was dissolved under a nitrogen atmosphere in 20 mL of recently distilled and deoxygenated dichloromethane containing 0.77 g of pure NBu_4PF_6 (0.2 mol) as electrolyte. The conductivities were measured at room temperature, in ca. 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. NMR spectra were recorded on a Bruker AC300 instrument at 300 (^{1}H), 121.5 (^{31}P), or 75.4 MHz (^{13}C) using $SiMe_4$ and 85% H_3PO_4 as standards. The following atom labels are used for the ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data.



The parameter $\Delta\delta$(C-3a,7a) is defined as the difference between δ(C-3a,7a) of the indenyl complex and δ(C-3a,7a) of sodium indenyl (δ = 130.70 ppm).[21] The term "Ind-6" in the NMR data is used for the undefined signals of carbon and hydrogen atoms at the 4, 5, 6 and 7 positions of the benzoid ring.

Synthesis of Indenyl Complexes. (a) Preparation of [RuCl(η^5-C_9H_7)(PPh_3)L] [L = $PMePh_2$ (3a), PMe_2Ph (3b), and PMe_3 (3c). General Procedure. A solution of the complex [RuCl(η^5-C_9H_7)$(PPh_3)_2$] (**1**) (776 mg, 1 mmol) and the corresponding phosphine (1 mmol) in toluene (80 mL) was heated until complete substitution of one triphenylphosphine ligand was achieved, as monitored by ^{31}P NMR. The toluene was then evaporated under vacuum and the solid residue was purified by column chromatography on silica, collecting the band eluted with dichlomethane. Yield (%), temperature of reaction (°C), reaction time, color, and electrochemical [$1/2(E_{p,a} + E_{p,c})$ in volts], analytical, and NMR spectroscopic data are as follows. L = $PMePh_2$ **(3a)**: 65, 45, 3.5 h, orange, 0.43. Anal. Calcd for $RuC_{40}H_{35}P_2Cl$: C, 67.27; H, 4.94. Found: C, 66.91; H, 4.85. ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 42.48 (d, J_{PP} = 41.5 Hz, $PMePh_2$), 45.61 (d, J_{PP} = 41.5 Hz, PPh_3). ^{1}H NMR ($CDCl_3$) δ: 1.13 (d, 3H, J_{HP} = 10.0 Hz, P*Me*Ph_2), 3.21 and 4.69 (br s, 1H each, H-1 and H-3), 4.85 (m, 1H, H-2), 6.43 (m, 1H, Ind-6), 6.8−8.0 (m, 28H, PPh_3, PMe*Ph*$_2$ and Ind-6). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 11.90 (d, J_{CP} = 29.3 Hz, PPh_2CH_3), 68.88 and 69.11 (C-1 and C-3), 89.49 (C-2), 109.13 and 111.73 (C-3a and C-7a),

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123.36 and 124.70 (Ind-6), 126.99−136.53 (m, Ph and Ind-6). $\Delta\delta$(C-3a,7a) = −20.27 (av.). L = PMe_2Ph **(3b):** 60, 50, 2 h, orange, 0.39; elemental analyses were unsatisfactory. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 25.72 (d, J_{PP} = 42.0 Hz, PMe_2Ph), 47.56 (d, J_{PP} = 42.0 Hz, PPh_3). ^1H NMR ($CDCl_3$) δ: 1.18 (d, 3H, J_{HP} = 10.0 Hz, P*Me*$_a$Me$_b$Ph), 1.49 (d, 3H, J_{HP} = 10.0 Hz, PMe$_a$*Me*$_b$Ph), 3.15 and 4.47 (2 s, 1H each, H-1 and H-3), 4.58 (m, 1H, H-2), 6.49 and 6.68 (m, 1H each, Ind-6), 7.10−7.62 (m, 22H, PPh_3, PMe_2*Ph*, and Ind-6). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 16.15 (d, J_{CP} = 30.2 Hz, P*Me*$_a$Me$_b$Ph), 17.05 (d, J_{CP} = 30.8 Hz, PMe$_a$*Me*$_b$Ph), 66.22 and 66.38 (C-1 and C-3), 88.65 (C-2), 107.64 and 111.94 (C-3a and C-7a), 124.0, 124.32, and 126.51 (Ind-6), 126.51−137.15 (m, Ph, Ind-6). $\Delta\delta$(C-3a,7a) = −20.91 (av.). L = PMe_3 **(3c):** 80, 30, 0.5 h, orange, 0.36. Anal. Calcd for $RuC_{30}H_{31}P_2Cl$: C, 61.07; H, 5.30. Found: C, 61.25; H, 5.28. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 16.30 (d, J_{PP} = 44.8 Hz, PMe_3), 50.10 (d, J_{PP} = 44.8 Hz, PPh_3). ^1H NMR ($CDCl_3$) δ: 1.15 (d, 9H, J_{HP} = 9.8 Hz, PMe_3), 3.47 and 4.91 (s, 1H each, H-1 and H-3), 5.19 (m, 1H, H-2), 6.74 and 7.01 (m, 1H each, Ind-6), 7.10−7.43 (m, 17H, PPh_3, Ind-6). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 19.05 (d, J_{CP} = 20.6 Hz, PMe_3), 63.75 and 63.98 (C-1 and C-3), 87.99 (C-2), 107.84 and 111.56 (C-3a and C-7a), 123.84, 124.09, 126.24, and 127.15 (C-4,5,6,7), 127.38−135.57 (m, PPh_3). $\Delta\delta$(C-3a,7a) = −22.86 (av.).

(b) Preparation of complexes [RuCl(η^5-C_9H_7)L_2] [L = $PMePh_2$ (4a), PMe_2Ph (4b), dppm (4c), dppe (4d)]. General Procedure. A solution of the complex [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (**1**) (776 mg, 1 mmol) and the corresponding phosphine (2 mmol of monodentate L, 1 mmol of bidentate L) in toluene (80 mL) was refluxed until complete substitution of triphenylphosphine was achieved (^{31}P NMR). The toluene was then evaporated under vacuum, and the solid residue was purified by column chromatography over silica, collecting the band eluted with diethyl ether for complexes **4a** and **4b** and that with dichloromethane for complexes **4c** and **4d**. Yield (%), reaction time, color, and electrochemical [1/2($E_{p,a}$ + $E_{p,c}$) in volts], analytical, and NMR spectroscopic data are as follows. L = $PMePh_2$ **(4a):** 80, 2 h, orange, 0.39. Anal. Calcd for $RuC_{35}H_{33}P_2Cl$: C, 64.46; H, 5.10. Found: C, 64.70; H, 5.38. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 36.02 ($PMePh_2$). ^1H NMR ($CDCl_3$) δ: 1.36 (vt, J = 9.1 Hz, 6H, P*Me*Ph_2), 4.39 (br s, 2H, H-1,3), 4.60 (br s, 1H, H-2), 6.98 and 7.09 (m, 2H each, H-4,7 and H-5,6), 7.14−7.41 (m, 20H, PMe*Ph*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 13.50 (vt, J = 30.3 Hz, P*Me*Ph_2), 64.14 (C-1,3), 89.20 (C-2), 109.80 (C-3a,7a), 123.91 and 126.83 (C-4,7 and C-5,6), 127.61−132.37 (m, Ph). $\Delta\delta$(C-3a,7a) = −20.90. L = PMe_2Ph **(4b):** 80, 1.5 h, orange, 0.31. Anal. Calcd for $RuC_{25}H_{29}P_2Cl$: C, 56.87; H, 5.54. Found: C, 57.10; H, 5.55. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 21.71 (PMe_2Ph). ^1H NMR ($CDCl_3$) δ: 1.37 (vt, J = 9.4 Hz, 6H, P*Me*$_a$Me$_b$Ph), 1.55 (vt, J = 8.7 Hz, 6H, PMe$_a$*Me*$_b$Ph), 4.41 (br s, 2H, H-1,3), 4.48 (br s, 1H, H-2), 7.12 and 7.26 (m, 2H each, H-4,7 and H-5,6), 7.33−7.46 (m, 10H, PMe_2*Ph*). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 15.93 (vt, J = 30.3 Hz, P*Me*$_a$Me$_b$Ph), 18.42 (vt, J = 29.6 Hz, PMe$_a$*Me*$_b$Ph), 61.99 (C-1,3), 87.06 (C-2), 109.62 (C-3a,7a), 124.02 and 126.07 (C-4,7 and C-5,6), 127.95−129.99 (m, Ph). $\Delta\delta$(C-3a,7a) = −21.08. L_2 = dppm **(4c):** 80, 2 h, red, 0.39. Anal. Calcd for $RuC_{34}H_{29}P_2Cl$: C, 64.14; H, 4.56. Found: C, 63.89; H, 4.80; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 15.37 (dppm). ^1H NMR ($CDCl_3$) δ: 4.25 (dt, J_{HH} = 14.2 Hz, J_{HP} = 11.4 Hz, PC*H*$_a$H$_b$P), 4.84 (br s, 3H, H-1,2,3), 4.96 (dt, J_{HH} = 14.2 Hz, J_{HP} = 10.2 Hz, PCH$_a$*H*$_b$P), 7.10−7.38 (m, 22H, PPh_2, Ind-6), 7.58 (m, 2H, Ind). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 48.23 (t, J_{CP} = 20.8 Hz, PCH_2P), 62.79 (t, J_{CP} = 3 Hz, C-1,3), 85.50 (C-2), 109.30 (t, J_{CP} = 2.5 Hz, C-3a,7a), 124.38 and 125.34 (C-4,7 and C-5,6), 127.82−138.15 (m, PPh_2). $\Delta\delta$(C-3a,7a) = −21.4. L_2 = dppe **(4d):** 80, 1.5 h, orange, 0.43. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 83.45 (dppe).

Synthesis of Cyclopentadienyl Complexes. (a) Preparation of [RuCl(η^5-C_5H_5)(PPh_3)L] [L = $PMePh_2$ (5a) and PMe_2Ph (5b)]. A solution of [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (**2**) (726 mg, 1 mmol) and the corresponding phosphine (1 mmol) in toluene (80 mL) was heated until complete substitution of one triphenylphosphine ligand was achieved. The toluene was then evaporated under vacuum and the solid residue was purified by column chromatography over silica, collecting the yellow band eluted with dichloromethane. Yield (%), temperature of reaction (°C), reaction time, and electrochemical [1/2($E_{p,a}$ + $E_{p,c}$) in volts], analytical, and NMR spectroscopic data are as follows. L = $PMePh_2$ **(5a)** (improvement of published method): 65, 45, 4.5 h, 0.54. ^1H NMR is in agreement with published data. Additional data: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 33.09 (d, J_{PP} = 42.0 Hz, PPh_2Me), 47.07 (d, J_{PP} = 42.0 Hz, PPh_3). L = PMe_2Ph **(5b):** 55, 50, 3 h, 0.50. Anal. Calcd for $RuC_{31}H_{31}P_2Cl$: C, 61.79; H, 5.15. Found: C, 61.51; H, 5.24. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 12.54 (d, J_{PP} = 44.9 Hz, $PPhMe_2$), 46.61 (d, J_{PP} = 44.9 Hz, PPh_3). ^1H NMR ($CDCl_3$) δ: 1.39 (d, 3H, J_{HP} = 8.8 Hz, P*Me*$_a$Me$_b$Ph), 1.48 (d, 9.0 Hz, J_{HP} = 8.8 Hz, PMe$_a$*Me*$_b$Ph), 4.12 (br s, 5H, Cp), 7.28−7.51 (m, 24H, Ph).

(b) Preparation of [RuCl(η^5-C_5H_5)L_2] [L = $PMePh_2$ (6a) and PMe_2Ph (6b)]. Improvement of Published Method. A solution of the complex [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (**2**) (726 mg, 1 mmol) and the corresponding phosphine (2 mmol) in toluene (80 mL) was refluxed until complete substitution of triphenylphosphine was achieved. Toluene was then evaporated under vacuum and the solid residue was purified by column chromatography over silica, collecting the band eluted with diethyl ether. Yield (%) and time of reaction are as follows (analytical and NMR spectroscopic data are in agreement with published values). L = $PMePh_2$ **(6a)**: 65, 2.5 h. L = PMe_2Ph **(6b):** 45, 1.5 h.

Synthesis of Cationic Derivatives. (a) Preparation of [Ru(η^5-C_9H_7)(PPh_3)(dppm)]Cl. A solution of [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (776 mg, 1 mmol) and bis(diphenylphosphine)methane (1 mmol) in toluene was refluxed for 15 min. A yellow precipitate appeared. The solution was decanted and the solid was washed with hexane (3 × 20 mL) and dried under vacuum. Yield (%), conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), and analytical and NMR spectroscopic data are as follows: 70, 115. Anal. Calcd for $RuC_{52}H_{44}P_3Cl$: C, 69.52; H, 4.93. Found: C, 69.34; H, 4.63. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 3.70 (d, J_{PP} = 28.9 Hz, dppm), 45.55 (d, J_{PP} = 28.9 Hz, PPh_3). ^1H NMR ($CDCl_3$) δ: 4.17 (dt, 1H, J_{HH} = 14.6 Hz, J_{HP} = 10.7 Hz, PC*H*$_a$H$_b$P), 4.9 (br s, 2H, H-1,3), 5.07 (dt, 1H, J_{HH} = 14.6 Hz, J_{HP} = 10.7 Hz, PCH$_a$*H*$_b$P), 5.23 (br s, 1H, H-2), 6.15−7.34 (m, 39H, PPh_2, PPh_3, and Ind-6).

(b) Preparation of [Ru(η^5-C_9H_7)(PMe_3)$_3$]Cl. A solution of [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (776 mg, 1 mmol) and trimethylphosphine (3 mmol) in toluene was refluxed for 15 min. A yellow precipitate appeared. The solution was decanted and the solid was washed with hexane (3 × 20 mL) and dried under vacuum. Yield (%), conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), and analytical and NMR spectroscopic data are as follows: 85, 127. Anal. Calcd for $RuC_{18}H_{34}P_3Cl$: C, 45.05; H, 7.14. Found: C, 45.33; H, 7.09. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 7.01 (PMe_3). ^1H NMR ($CDCl_3$) δ: 1.46 (m, 18H, PMe_3), 5.20 (d, 2H, J_{HH} = 2.7 Hz, H-1,3), 5.35 (d, 2H, J_{HH} = 2.7 Hz, H-2), 7.23 and 7.48 (m, 2H each, H-4,7 and H-6,7).

Kinetic Measurements. Manipulations were carried out under argon, and tetrahydrofuran was distilled over potassium/benzophenone. Kinetic experiments were carried out under pseudo-first-order conditions, using a large excess of phosphine, by UV−visible spectroscopy. The phosphines were added as neat liquids by syringe to solutions of the ruthenium complex in 1-cm quartz cells. Solutions of triphenylphosphine were mixed with solutions of the complex. Several kinetic runs were performed simultaneously in the instrument. The decrease in absorbance associated with the reaction was followed with time. Pseudo-first-order rate constants (k_{obs}) were obtained by fitting the exponential dependence of absorbance *vs* time data using a nonlinear least-squares regression program, which provides k_{obs} and A_∞. Values of A_∞ generally were well-defined in the experiments and in agreement with calculated ones. Fittings of k_{obs} to eq 2, to give the parameters k_1 and

(k_2/k_{-1}), were obtained with nonlinear least-squares calculations carried out by the program Kaleidagraph. Duplications of single kinetic runs were reproducible to within 6%. Activation parameters for the reaction with PPh_3 were obtained by linear least-squares analysis of the dependence of $\ln(k_2/T)$ on $1/T$. Blank experiments on solutions of the ruthenium complex (10^{-4} M) in the absence of phosphine showed no significant decomposition during the time required for the kinetic runs both in the dark and under irradiation.

Results

Reactions. The complex $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**1**) reacts with phosphines [L = $PMePh_2$, PMe_2Ph, PMe_3; L−L = $Ph_2PCH_2PPh_2$ (dppm), $Ph_2P(CH_2)_2PPh_2$ (dppe)] to give the products of mono- or disubstitution of PPh_3, depending on the reaction conditions, in either tetrahydrofuran or toluene (eq 1). A similar reaction pattern is displayed by the analogous cyclopentadienyl complex $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ (**2**), which, however, requires more vigorous conditions than **1**.

$$RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2 \xrightarrow[-PPh_3]{+L} RuCl(\eta^5\text{-}C_9H_7)(PPh_3)L \xrightarrow[-PPh_3]{+L}$$
$$L = PMePh_2\ (\mathbf{3a}) \quad L = PMe_2Ph\ (\mathbf{3b}) \quad L = PMe_3\ (\mathbf{3c})$$

$$RuCl(\eta^5\text{-}C_9H_7)L_2 \quad (1)$$
$$L = PMePh_2\ (\mathbf{4a}) \quad L = PMe_2Ph\ (\mathbf{4b}) \quad L_2 = \text{dppm}\ (\mathbf{4c}) \quad L_2 = \text{dppe}\ (\mathbf{4d})$$

The complexes $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)(L)]$ (**3a**, L = $PMePh_2$; **3b**, L = PMe_2Ph; **3c**, L = PMe_3) are obtained selectively with respect to further substitution upon reacting complex **1** with the appropriate phosphine in a 1:1 molar ratio, in toluene just above room temperature. The disubstituted complexes $[RuCl(\eta^5\text{-}C_9H_7)(L)_2]$ (**4a**, L = $PMePh_2$; **4b**, L = PMe_2Ph) are prepared in refluxing toluene (2 h) using a 2-fold molar ratio of L. Under the same reaction conditions, the two molecules of PPh_3 in **1** undergo substitution by either bis(diphenylphosphino)methane (dppm) or bis(diphenylphosphino)ethane (dppe) to give the chelated complexes $[RuCl(\eta^5\text{-}C_9H_7)(L\text{−}L)]$ (**4c**, L−L = dppm; **4d**, L−L = dppe). Instead, reaction of **1** with PMe_3 or with the chelating phosphine dppm proceeds to the formation of cationic trisubstituted complexes $[Ru(\eta^5\text{-}C_9H_7)(PMe_3)_3]$-Cl or $[Ru(\eta^5\text{-}C_9H_7)(dppm)(PPh_3)]Cl$ as insoluble ionic species after heating under reflux for 15 min, even in the presence of a 2-fold excess of PMe_3. When the mixture is heated for a longer time (2 h), complex $[Ru(\eta^5\text{-}C_9H_7)(dppm)(PPh_3)]Cl$ yields the neutral species **4c**.

The complexes $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)(L)]$ (**5a**, L = $PMePh_2$; **5b**, L = PMe_2Ph) and $[RuCl(\eta^5\text{-}C_5H_5)(L)_2]$ (**6a**, L = $PMePh_2$; **6b**, L = PMe_2Ph) have been prepared by heating compound **2** in the presence of phosphine either at 50 °C (monosubstituted) or at reflux (disubstituted) in toluene. Complexes **4d**, **5a**, **6a**, and **6b** have been previously described;[22,23] we report here an improved preparation or additional characterization.

(22) Lomprey, J. R.; Selegue, J. P. *J. Am. Chem. Soc.* **1992**, *111*, 5518.
(23) Treichel, P. M.; Komar, D. A.; Vincenti, P. J. *Synth. React. Inorg. Met.-Org. Chem.* **1984**, *14*, 383.

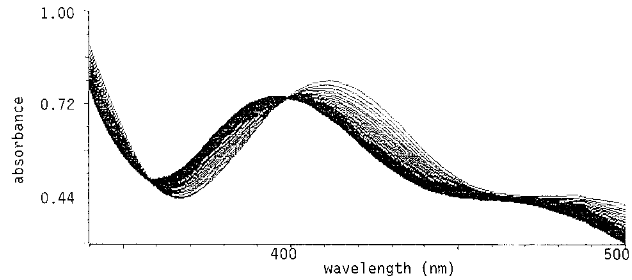


Figure 1. UV−vis spectral changes in the reaction of $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**1**) with PMe_2Ph in tetrahydrofuran at 22 °C (cycle time, 30 min).

Table 1. Reaction of $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (1) with $PMePh_2$ and PMe_2Ph

	tetrahydrofuran			toluene		
L[a]	T (°C)	time (h)	conversion[b] (%)	T (°C)	time (h)	conversion[c] (%)
$PMePh_2$	18	15	90	22	3	ca. 50:40:10
		20	100			
PMe_2Ph	18	18	80			
		24	100			

[a] [L] = 0.1−0.01 M. [b] With respect to the starting material. [c] **1**/**3a**(monosubstituted)/**4a**(disubstituted).

Table 2. Reaction of $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ (2) with $PMePh_2$ and PMe_2Ph in Tetrahydrofuran (Conversion to Monosubstituted Products 5a or 5b)

L[a]	T (°C)	time (h)	conversion[b] (%)
PMe_2Ph	22	24	ca. 1
$PMePh_2$	22	24	no reaction
PMe_2Ph or $PMePh_2$	35−40	3	ca. 50
		5	70
		7	80−90

[a] [L] = 0.01 M. [b] With respect to the starting material.

The progress of the reaction and consecutive formation of mono- and disubstitution products have been monitored conveniently by ^{31}P NMR. By choosing the appropriate temperature, it is possible to selectively obtain monosubstitution (also in the presence of excess phosphine). The conditions under which monosubstituted complexes are formed from $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**1**) or from $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ (**2**) are reported in Tables 1 and 2, respectively. Although reactions proceed similarly in tetrahydrofuran and in toluene, monosubstitution occurs more selectively at room temperature in the former solvent. Tetrahydrofuran therefore has been the solvent of choice to study the kinetics of triphenylphosphine exchange by $PMePh_2$ or PMe_2Ph in complexes **1** and **2** to yield **3a** or **3b** and **5a** or **5b**.

Kinetics. Both ^{31}P NMR and UV−vis spectroscopy have been used to follow the first step in eq 1. In the presence of at least a 10-fold excess of phosphine, the increase in the NMR signal of **3a**,**b** or the decrease in the absorbance of **1**, in the range 400−550 nm, exhibits first-order behavior when plotted *vs* time and gives similar values of half-life times (∼4 h, 20 °C). For convenience, UV−vis spectroscopy has been used to obtain most experimental data. The spectral changes observed in the reaction of **1** (8.5×10^{-4} M) with PMe_2-Ph (0.066 M) in tetrahydrofuran (22 °C) are shown in Figure 1. Absorbance increases between 360 and 400 nm and decreases at higher wavelengths clearly define an isosbestic point at 400 nm. Values (A) taken at 426 and 520 nm *vs* time yield observed rate constants (k_{obs})

Table 3. Observed Rate Constants (k_{obs}) for the Reaction of $RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2$ (1) with $PMePh_2$ at Different Temperatures in Tetrahydrofuran

T (°C)	[$PMePh_2$] (M)	[PPh_3] (M)	k_{obs} (s^{-1})
11.9	0.0663		1.31×10^{-5}
	0.131		1.28×10^{-5}
	0.256		1.25×10^{-5}
20.0	0.0111		4.13×10^{-5}
	0.0267		3.95×10^{-5}
	0.0663		4.34×10^{-5}
	0.131		4.61×10^{-5}
	0.256		4.43×10^{-5}
	0.375		4.30×10^{-5}
30.0	0.0663		2.04×10^{-4}
	0.131		2.10×10^{-4}
	0.256		2.05×10^{-4}
39.9	0.0663		8.65×10^{-4}
	0.131		8.28×10^{-4}
30.0	0.0132	0.51	1.39×10^{-5}
	0.0267	0.51	2.38×10^{-5}
	0.0663	0.51	4.72×10^{-5}
	0.131	0.51	7.43×10^{-5}
	0.192	0.51	9.08×10^{-5}
	0.256	0.51	10.3×10^{-5}
30.0	0.131	0.011	1.91×10^{-4}
	0.131	0.046	1.73×10^{-4}
	0.131	0.128	1.45×10^{-4}
	0.131	0.249	1.15×10^{-4}
	0.131	0.366	9.4×10^{-5}
	0.131	0.567	6.97×10^{-5}

Table 4. Observed Rate Constants (k_{obs}) for the Reaction of $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ (2) with $PMePh_2$ at Different Temperatures in Tetrahydrofuran

T (°C)	[$PMePh_2$] (M)	[PPh_3] (M)	k_{obs} (s^{-1})
20.6	0.066		4.5×10^{-6}
	0.131		5.6×10^{-6}
	0.256		4.7×10^{-6}
	0.375		5.5×10^{-6}
30.0	0.027		3.0×10^{-5}
	0.066		2.8×10^{-5}
	0.131		2.8×10^{-5}
	0.256		3.0×10^{-5}
	0.375		2.8×10^{-5}
40.1	0.066		1.30×10^{-4}
	0.192		1.37×10^{-4}
50.6	0.0663		5.75×10^{-4}
	0.131		5.67×10^{-4}
	0.256		5.93×10^{-4}
	0.375		6.03×10^{-4}
40.1	0.247	0.015	1.22×10^{-4}
	0.247	0.050	1.09×10^{-4}
	0.247	0.133	9.72×10^{-5}
	0.247	0.226	8.10×10^{-5}
	0.247	0.341	6.98×10^{-5}
	0.247	0.545	5.13×10^{-5}

of 4.9×10^{-5} and 4.8×10^{-5} s^{-1}, respectively, whereas data at 366 nm, where absorbance increases, do not give a clean first-order fit. Most experiments therefore have been carried out in the range 420−430 nm. Very similar spectral changes are displayed in the presence of $PMePh_2$.

Observed rate constants from measurements at different concentrations of phosphine and temperatures are reported in Table 3 for the reaction of **1** and in Table 4 for the reaction of **2** with $PMePh_2$. Data for the reactions of both **1** and **2** with PMe_2Ph are reported in Table 5. The effect of PPh_3 in large excess has been observed at increasing concentrations of $PMePh_2$ at 30 °C (Figure 2). Experiments have also been carried out for the reaction with $PMePh_2$ at different concentrations of PPh_3. The rate reduction that occurs upon increasing

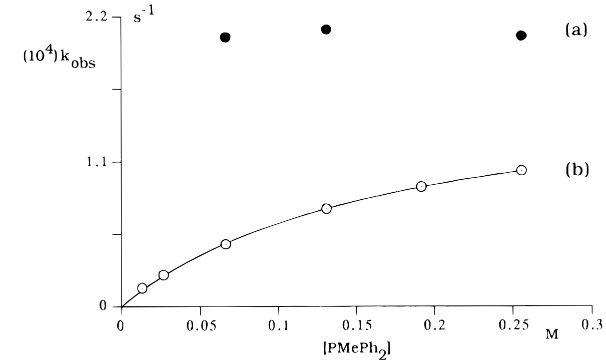


Figure 2. Observed rate constants (k_{obs}) for the reaction of $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**1**) with $PMePh_2$ (a) and with $PMePh_2$ (b) in the presence of PPh_3 (0.51 M) in tetrahydrofuran at 30 °C.

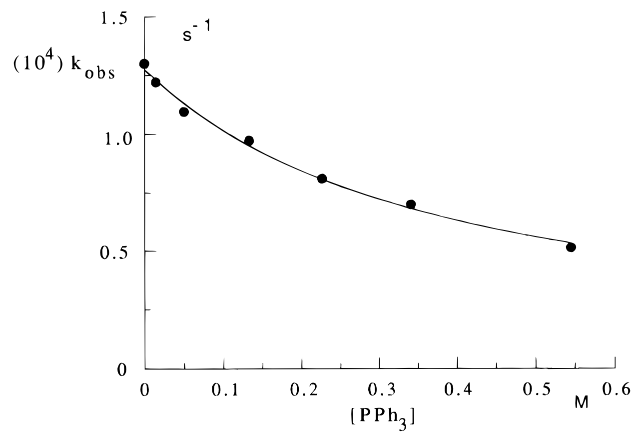


Figure 3. Observed rate constants (k_{obs}) for the reaction of $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ (**2**) with $PMePh_2$ (0.131 M) at increasing concentrations of PPh_3 in tetrahydrofuran at 40 °C.

Table 5. Observed Rate Constants (k_{obs}) for the Reaction of $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (1)[a] and $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ (2)[b] with PMe_2Ph in Tetrahydrofuran

Ind		Cp	
[PMe_2Ph] (M)	k_{obs} ($s^{-1} \times 10^5$)	[PMe_2Ph] (M)	k_{obs} ($s^{-1} \times 10^5$)
0.0024	4.33	0.035	2.72
0.0048	4.43	0.104	2.35
0.0091	4.35	0.205	2.67
0.0175	4.07	0.335	2.38
0.0523	4.33	0.490	2.37
0.138	4.52		
0.270	4.68		
0.490	4.60		

[a] T = 20.0 °C. [b] T = 30.0 °C.

[PPh_3] is shown graphically in Figure 3. Reaction rates appear to be independent of either the concentration or the nature of the reacting phosphine.

Electrochemistry. Different complexes $[RuCl(\eta^5\text{-}ligand)L_2]$ have been studied in CH_2Cl_2 solutions (25 °C) by cyclic voltammetry. Table 6 lists oxidation potential data for the novel indenyl mono- and disubstituted complexes, along with those of analogous cyclopentadienyl and pentamethylcyclopentadienyl[5a,23] complexes. The compounds undergo one-electron oxidation, which is chemically reversible under the experimental conditions.

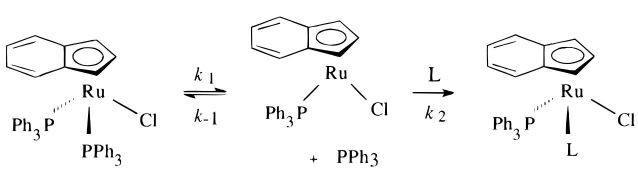
Table 6. Electrochemical Potentials for Redox Couples[a]

$$[RuCl(\eta^5\text{-ligand})(L_2)] \rightleftharpoons [RuCl(\eta^5\text{-ligand})(L_2)]^+ + e$$

compound	$^1/_2(E_{p,a} + E_{p,c})$ (V, *vs* SCE)	$E_{p,a} + E_{p,c}$ (mV)
$[RuCl(\eta^5-C_9H_7)(PPh_3)_2]$ (**1**)	0.45	66
$[RuCl(\eta^5-C_9H_7)(PPh_3)(PMePh_2)]$ (**3a**)	0.43	68
$[RuCl(\eta^5-C_9H_7)(PPh_3)(PMe_2Ph)]$ (**3b**)	0.39	64
$[RuCl(\eta^5-C_9H_7)(PPh_3)(PMe_3)]$ (**3c**)	0.36	64
$[RuCl(\eta^5-C_9H_7)(PPh_2Me)_2]$ (**4a**)	0.39	64
$[RuCl(\eta^5-C_9H_7)(PMe_2Ph)_2]$ (**4b**)	0.31	70
$[RuCl(\eta^5-C_9H_7)(dppm)]$ (**4c**)	0.39	62
$[RuCl(\eta^5-C_9H_7)(dppe)]$ (**4d**)	0.43	64
$[RuCl(\eta^5-C_5H_5)(PPh_3)_2]$ (**2**)	0.56	360[b]
$[RuCl(\eta^5-C_5H_5)(PPh_3)(PMePh_2)]$ (**5a**)	0.54	72
$[RuCl(\eta^5-C_5H_5)(PPh_3)(PMe_2Ph)]$ (**5b**)	0.50	70
$[RuCl(\eta^5-C_5H_5)(PMePh_2)_2]$ (**6a**)	0.52	110[b]
$[RuCl(\eta^5-C_5H_5)(PMe_2Ph)_2]$ (**6b**)	0.44	340[b]
$[RuCl(\eta^5-C_5H_5)(dppm)]$ (**6c**)	0.49	340[b]
$[RuCl(\eta^5-C_5H_5)(dppe)]$ (**6d**)	0.51	110[b]
$[RuCl(\eta^5-C_5Me_5)(PPh_3)_2]$ (**7**)	0.43	240[b]
$[RuCl(\eta^5-C_5Me_5)(PMe_2Ph)_2]$ (**7b**)	0.30	70[c]
$[RuCl(\eta^5-C_5Me_5)(dppe)]$ (**7d**)	0.33	270[b]

[a] Cyclic voltammetry in CH_2Cl_2. [b] Reference 23. [c] Reference 5a.

Scheme 1



Discussion

The driving force in the reactions of eq 1 is either stabilization of the product by chelation or formation of less congested complexes. There are in fact many examples showing that phosphine extrusion is governed by the steric bulk of the dissociating molecule.[10,24] For instance, loss of PMe_3 in $[RuX(\eta^5-C_5Me_5)(PMe_3)_2]$ is achieved only at temperatures around 100 °C.[9] The triphenylphosphine molecule in $[RuCl(\eta^5\text{-ligand})(PPh_3)(L)]$ is bound more tightly than in **1**, and displacement of chloride can effectively compete with PPh_3 dissociation in the presence of a chelating ligand. The electrochemical data $[1/2(E_{p,a} + E_{p,c})]$ reported in Table 6 for the redox couples $[RuCl(\eta^5\text{-ligand})L_2]/[RuCl(\eta^5\text{-ligand})L_2]^+$ indicate that 17-electron complexes are formed at lower potential from indenyl and pentamethylcyclopentadienyl species than from the cyclopentadienyl analogues. With respect to PPh_3-substituted complexes, coordination by chelating or by σ-donor alkylarylphosphines also reduces the oxidation potential.

The lack of rate dependence on the concentration or the nature of phosphine for the substitution of PPh_3 by $PMePh_2$ or PMe_2Ph (L) in $[RuCl(\eta^5\text{-Ind})(PPh_3)_2]$ and $[RuCl(\eta^5\text{-Cp})(PPh_3)_2]$ suggests that the reactions proceed by a dissociative mechanism, as indicated in Scheme 1 for complex **1**. This is described by the rate law shown in eq 2:

$$k_{obs} = \frac{k_1 k_2[L]}{k_{-1}[PPh_3] + k_2[L]} \quad (2)$$

(24) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113.

Table 7. Reaction Parameters for PPh_3 Substitution in $[RuCl(\eta^5-C_9H_7)(PPh_3)_2]$ (1) and $[RuCl(\eta^5-C_5H_5)(PPh_3)_2]$ (2) in Tetrahydrofuran

ligand	T (°C)	L	k_1 (×10^5) (s^{-1})	k_2/k_{-1}	$\Delta H^‡$ (kcal mol^{-1})	$\Delta S^‡$ (cal mol^{-1} K^{-1})
Ind	12.1	$PMePh_2$	1.3 ± 0.1		26 ± 1	11 ± 2
	20.0	$PMePh_2$	4.2 ± 0.2			
	30.0	$PMePh_2$	21 ± 1	2.0		
	39.9	$PMePh_2$	85 ± 3			
	20.0	PMe_2Ph	4.4 ± 0.2			
Cp	20.6	$PMePh_2$	0.50 ± 0.05		29 ± 1	17 ± 2
	30.0	$PMePh_2$	2.9 ± 0.2			
	40.1	$PMePh_2$	13.5 ± 1	1.6		
	50.6	$PMePh_2$	58 ± 2			
	30.0	PMe_2Ph	2.5 ± 0.2			

When $k_2[L]$ is larger than $k_{-1}[PPh_3]$, then the expression reduces to $k_{obs} = k_1$. This is infact the condition shown by the kinetic measurements which exhibit a first order dependence on **1** and **2**, and no dependence on L (Figure 2, Tables 3, 4, 5). The constant k_1 represents the rate of thermal ligand dissociation from $RuCl(\eta^5\text{-ligand})(PPh_3)_2$ to yield an intermediate species of empirical formula $RuCl(\eta^5\text{-ligand})(PPh_3)$, including solvation effects on the two species.

When the concentration of $PMePh_2$ is kept constant in different runs, the reaction rate is retarded by added PPh_3 (Figure 3), which competes with $PMePh_2$ for the intermediate $RuCl(\eta^5\text{-ligand})(PPh_3)$. A plot of $1/k_{obs}$ *vs* $[PPh_3]$ is linear, as predicted by eq 3. The ordinate

$$\frac{1}{k_{obs}} = \frac{k_{-1}[PPh_3]}{k_1 k_2[PMePh_2]} + \frac{1}{k_1} \quad (3)$$

intercept yields the k_1 value 2.04×10^{-4} s^{-1} for complex **1**, in good agreement with the directly observed rate constants obtained at 30 °C ($k_{obs} = k_1$, Table 3). In experiments at increasing $[PMePh_2]$ and a high constant concentration of PPh_3, a saturation effect is observed (Figure 2), as expected for a situation in which $k_{-1}[PPh_3] \simeq k_2[L]$, so that eq 2 holds in its extended form. Fitting of the experimental points with the equation also gives a ratio of rate constants (k_2/k_{-1}) = 2 at 30 °C, in agreement with a faster attack of $PMePh_2$ than PPh_3 on the intermediate $RuCl(\eta^5\text{-Ind})(PPh_3)$. The positive values of entropy of activation are consistent with the proposal that PPh_3 dissociation is rate limiting (k_1). The overall reaction parameters are listed in Table 7.

All of the experimental evidence therefore is in harmony with the dissociative mechanism depicted in Scheme 1. An alternative mechanism implying the formation of ring-slipped η^3 intermediates, which is very common in the reactions of indenyl complexes,[11−14] may be involved in the case of rate-determining solvent (S) coordination in **1** to give $(S)RuCl(\eta^3\text{-Ind})(PPh_3)_2$, followed by PPh_3 extrusion. This would also exhibit zero-order dependence on L, although a strong solvent effect (tetrahydrofuran *vs* toluene) should be expected, which is not the case in these reactions.

Group 9 metal−carbonyl complexes of the type $M(\eta^5\text{-ligand})(CO)_2$ (M = Co, Rh) have been known for years to undergo carbonyl substitution by an associative mechanism *via* the formation of ring-slipped η^3 intermediates or S_N2 type transition states. In the case of M = Rh, direct rate measurements of CO substitution by PPh_3 exhibited a tremendous difference in reactivity (10^8 M^{-1} s^{-1}) for the second-order rate constant between indenyl and cyclopentadienyl complexes, which has become known as the *indenyl ligand effect*.[11b] On the other hand, when the ligand is a weaker and sterically bulky triphenylphosphine instead of carbonyl, as in [Co(η^5-Cp)(PPh_3)$_2$], substitution of PPh_3 by PMe_3 proceeds by a clean dissociative mechanism (toluene, −60 °C), in a pattern very similar to that observed in the present study.[20] Competition between PMe_3 and PPh_3 for Co(η^5-Cp)(PPh_3) gave a ratio of rate constants (k_2/k_{-1}) = 4, which can be compared with the value (k_2/k_{-1}) = 2 for competition between $PMePh_2$ and PPh_3 in the indenylruthenium system, although at a different temperature.

In metals of group 8, a direct comparison for the reactivity of indenyl and cyclopentadienyl compounds is available from the measurements of carbonyl substitution by phosphites in the complexes Fe(η^5-ligand)-$(CO)_2$I (ligand = Cp, indenyl, and tetrahydroindenyl).[16] Although substitution involved strongly bound carbonyl ligands, the mechanism was found to be dissociative, and the indenyl complex was estimated to react 600 times faster than the cyclopentadienyl analogue. Such an effect in a dissociative mechanism was explained as the result of a favorable electronic interaction between the aromatic six-membered ring of indenyl and the metal to compensate for weakening of the metal−CO bond in the transition state. It has now been reported that the 19-electron radicals Fe(η^5-ligand)$(CO)_3$ exchange CO with P and As donors *via* a strictly dissociative mechanism, that ring slippage phenomena are not involved, and that the rate constant for the cyclopentadienyl species is 10^3 s^{-1} greater than that of indenyl, giving an *inverse* indenyl effect.[17]

In the present study, an indenylruthenium complex dissociates PPh_3 an order of magnitude faster than the corresponding cyclopentadienyl derivative to form transient 16-electron species RuCl(η^5-ligand)(PPh_3) through a mechanism that excludes the occurrence of η^3 intermediates. The small effect thus depends on different intrinsic properties of the indenyl group. The possibility of rate enhancements due to a less stable ground state in indenyl than in Cp complexes has been suggested.[25] It is also feasible that indenyl, acting as an electron reservoir toward the metal fragment RuCl$(PPh_3)_2$ in **1** or RuCl(PPh_3) in the transient, favors ruthenium−phosphorus bond rupture or stabilizes the 16-electron intermediate. The results of cyclic voltammetry are in agreement with this intepretation, since the easier oxidation of the indenyl complexes suggests higher electron density at the metal. Indenyl has already been described as a stronger donor than cyclopentadienyl from photoelectron spectroscopy studies of rhodium(I) complexes Rh(η^5-ligand)$(L)_2$ (L = ethylene, CO)[1] and from infrared data of iron(II) complexes Fe(η^5-ligand)-$(CO)_2$R.[26] From this work and from the literature, it is clear that the higher reactivity of indenyl complexes not only depends on ring slippage isomerizations but that more involved phenomena come into play.

Acknowledgment. Financial support from DGICYT (Project PB93-325), a fellowship from FICYT de Asturias (B.M.M.-V.), and a travel award from NATO (Collaborative Research Grant 950794) are gratefully acknowledged.

OM950428K

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