

Kinetics and mechanism of CO ligand substitution in the ring-substituted indenyl rhodium complexes $[(\eta^5\text{-C}_9\text{R}_n\text{H}_{7-n})\text{Rh}(\text{CO})_2]$

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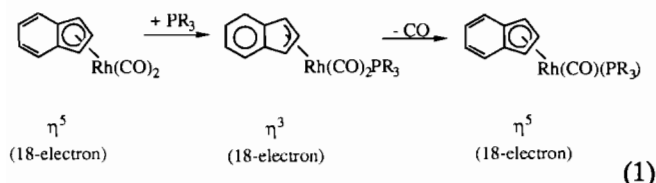
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Abstract

Effects of controlled electronics and sterics at the metal centre on the kinetics of associative (S_N2)CO substitutions by a number of phosphine and phosphite ligands in a series of indenyl ring-substituted rhodium bis(carbonyl) complexes, $[(\eta\text{-C}_9\text{R}_n\text{H}_{7-n})\text{Rh}(\text{CO})_2]$ ($\text{R} = \text{Cl}, \text{CH}_3, \text{OCH}_3, \text{OCH}_2\text{O}, \text{C}_4\text{H}_9; n = 1\text{--}7$), are reported. The reaction is first order in the indenyl complex and first order in the incoming nucleophile. Comparison of the molecular structure of $[(\eta\text{-}4,5,6,7\text{-Me}_4\text{C}_9\text{H}_3)\text{Rh}(\text{CO})_2]$ with that of the unsubstituted analogue shows that although the steric bulk of the indenyl ligand is increased by alkylation, there is no effect on the ground state structure of these molecules. Rates of CO substitution are dependent on both the nature of incoming nucleophile and the rhodium complex (electron richness of the metal centre, perturbations to the lowest unoccupied molecular orbital (LUMO), and the steric demands of the indenyl ligand). An alternative η^5 - to η^3 -*exo*- to η^5 -indenyl ligand slippage mechanism is suggested as being one plausible explanation of the kinetic results.

Introduction

Transition metal indenyl complexes are known to display enhanced reactivity in ligand substitution reactions [1, 2] as well as catalytic processes [3] compared with their cyclopentadienyl analogues. In S_N2 replacement reactions, it has been demonstrated [2d, e] that $[(\eta\text{-C}_9\text{H}_7)\text{Rh}(\text{CO})_2]$ reacts 3.8×10^8 times faster than the corresponding $[(\eta\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2]$ complex. This has been attributed to the flexibility of the indenyl ligand to undergo facile η^5 to η^3 coordinative isomerizations known as the kinetic indenyl ligand effect.



Such a low energy associative pathway is possible because a pair of electrons are localized on the ring in the transition state allowing the complex to maintain a stable 18-electron count at the metal [4]. Complete aromatization of benzene in the transition state would

impart enhanced stability and, hence, could be responsible for this huge effect [2e]. Evidence of such rearomatization has recently been obtained [5a] from analysis of the ring C–C distances in the series of indenyl sandwich complexes $[(\eta\text{-C}_9\text{H}_7)_2\text{M}]$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$). As would be expected on the basis of electron counting rules, the $\text{M} = \text{Fe}$ complex is essentially undistorted η^5 , whereas gradual slip-fold distortion toward η^3 coordination was found for $\text{M} = \text{Co}, \text{Ni}$. In the nickel case, the indenyl rings are best described as being halfway between true η^5 and η^3 coordination. The butadiene-like distribution of C–C bond distances for C(4)–C(5), C(5)–C(6), C(6)–C(7) in the Fe complex begins to disappear as the metal approaches η^3 coordination in the Ni complex. All ring C–C distances of the six-membered portion of the indenyl ring are essentially equal in the $[(\eta^3\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]^-$ complex [5b].

Recent isolation and structural characterization [6] of the complex $[(\eta^3\text{-C}_9\text{H}_7)\text{Ir}(\text{PPh}_2\text{Me})_3]$ lends further support to the ring slippage mechanism. It has also been shown that all $d^8\text{-}[(\eta\text{-C}_9\text{H}_7)\text{RhL}_2]$ complexes show a small but significant slip-fold distortion from η^5 towards η^3 coordination even in the ground state [7, 8].

There is ample evidence from kinetic studies that the substituents on the cyclopentadienyl ring affect the rates of ligand substitution in the $[(\eta\text{-C}_5\text{H}_5)\text{ML}_2]$ com-

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plexes. For example, electron donating groups, as in $[(\eta\text{-C}_5(\text{CH}_3)_5)\text{Rh}(\text{CO})_2]$, which make the ring more electron rich, slow down the associative replacement of CO [9]. Similar results were reported for ethylene displacement reactions in $[(\eta\text{-C}_5(\text{CH}_3)_5)\text{Rh}(\text{C}_2\text{H}_4)_2]$ relative to $[(\eta\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)]$ [10]. This is explained on the basis of unwillingness of the electron rich $[\eta\text{-C}_5(\text{CH}_3)_5]$ ring to accept electron density from the metal on attack by a nucleophile. The rate decrease could also be due to steric factors. However, the differentiation between steric and electronic effects has not been made quantitatively. Electron withdrawing groups on the ring have been shown [9, 10] to accelerate $\text{S}_{\text{N}}2$ displacement reaction in cyclopentadienyl RhL_2 systems.

In our continuing effort to examine the reactivity of $[(\eta\text{-C}_9\text{H}_7)\text{RhL}_2]$ systems in ligand substitution reactions [2f, 2g] and in catalytic process [3a], we have prepared a series of substituted indenyl rhodium complexes, $[(\eta\text{-C}_9\text{R}_7\text{H}_{7-n})\text{Rh}(\text{CO})_2]$. We were interested in determining the effects of degree and position of the indenyl ring substitution on the structure, the electron density at the metal center, and the rates of CO ligand substitution. The results of these investigations, including a comparison of the relative donor abilities of these ligands, are reported here. Stepwise alkylation of the indenyl ligand helps tailor the electron density and steric environment at the metal center. It was reported previously [2b] that complete methylation of the indenyl ligand to give $[(\eta\text{-C}_9(\text{CH}_3)_7)\text{Rh}(\text{CO})_2]$ leads to a rate reduction for CO substitution of $\sim 5 \times 10^2$ relative to the indenyl complex. This reduction may once again be due to the increased negative charge on the ring, increased congestion, or a combination of both factors. The synthesis of a variety of substituted indenyl complexes allowed us to carry out a more complete study of substitution kinetics in order to determine whether steric or electronic factors predominate in influencing substitution rates in these systems.

Experimental

Preparation of ring-substituted indenyl rhodium dicarbonyl complexes: general

All reactions were carried out under a nitrogen atmosphere, either in a glove box or using Schlenk techniques. Solvents were predried and distilled from Na/benzophenone (THF) or K/benzophenone (hexane), and all deuterated solvents were freeze-pump-thaw degassed and distilled on a high vacuum line. The NMR spectra were recorded on a Bruker AC200 or AM250 spectrometer. The IR spectra were recorded (in hexane solutions) on a Nicolet DX-20 FT-IR spectrometer.

Synthesis: general procedure for the synthesis of 1–11

Carbon monoxide was bubbled through a solution of the appropriate $[(\eta\text{-C}_9\text{R}_n\text{H}_{7-n})\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$ complex (c. 20 ml) for 0.5–2.0 h. The solvent was removed *in vacuo* yielding the desired $[(\eta\text{-C}_9\text{R}_n\text{H}_{7-n})\text{Rh}(\text{CO})_2]$ complexes as orange solids. Yields, reaction times and ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are given below. (For IR spectra see Tables 1 and 2.) Full details of the synthesis of the substituted indenyl ligands and their $\text{Rh}(\eta\text{-C}_2\text{H}_4)_2$ complexes will be published elsewhere [11].

$[(\eta\text{-5,6-Cl}_2\text{C}_9\text{H}_5)\text{Rh}(\text{CO})_2]$ (1)

Using $[(\eta\text{-5,6-Cl}_2\text{C}_9\text{H}_5)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$ (150 mg, 0.4 mmol) and a reaction time of 1 h, 150 mg of 1 was obtained, 100% yield.

^1H (C_6D_6 , 200 MHz) δ 4.85 (d, $J(\text{H-H})=3$ Hz, 2H, H(1,3)), 5.4 (q, $J(\text{H-H})=J(\text{Rh-H})=3$ Hz, 1H, H(2)), 6.70 (s, 2H, H(4,7)).

$^{13}\text{C}\{^1\text{H}\}$ (C_6D_6 , 50.3 MHz) δ 74.3 (d, $J(\text{Rh-C})=3$ Hz, C(1,3)), 100.0 (s, C(2)), 117.4 (s, C(3a,7a)), 119.7 (s, C(4,7)), 129.3 (s, C(5,6)), 189.1 (d, $J(\text{Rh-C})=86$ Hz, CO).

$[(\eta\text{-4,7-(MeO)}_2\text{C}_9\text{H}_5)\text{Rh}(\text{CO})_2]$ (3)

Carbon monoxide gas was bubbled through $[(\eta\text{-4,7-(MeO)}_2\text{C}_9\text{H}_5)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$ (200 mg, 0.6 mmol) in hexane (15 ml) for 1 h. The hexane solution was concentrated and then cooled to -40 °C. The compound $[(\eta\text{-4,7-(MeO)}_2\text{C}_9\text{H}_5)\text{Rh}(\text{CO})_2]$ (3) was obtained as a yellow solid in 75% yield (150 mg).

^1H (C_6D_6 , 200 MHz) δ 3.37 (s, 6H, OCH₃), 5.47 (q, $J=3$ Hz, 1H, H(2)), 5.78 (d, $J(\text{H-H})=J(\text{Rh-H})=3$ Hz, 2H, H(1,3)), 6.12 (s, 2H, H(5,6)).

$^{13}\text{C}\{^1\text{H}\}$ (C_6D_6 , 50.3 Hz) δ 55.1 (s, OCH₃), 74.0 (d, $J(\text{Rh-C})=3$ Hz, C(1,3)), 95.9 (d, $J(\text{Rh-C})=5$ Hz, C(2)), 104.2 (s, C(5,6)), 109.2 (s, C(3a,7a)), 145.7 (s, C(4,7)), 190.7 (d, $J(\text{Rh-C})=86$ Hz, CO).

$[(\eta\text{-4,7-Me}_2\text{C}_9\text{H}_5)\text{Rh}(\text{CO})_2]$ (4)

Using $[(\eta\text{-4,7-Me}_2\text{C}_9\text{H}_5)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$ (50 mg, 0.16 mmol) and a reaction time of 2 h, 50 mg of 4 was obtained, 100% yield.

^1H (C_6D_6 , 200 MHz) δ 2.10 (s, 6H, CH₃), 5.29 (d, $J(\text{H-H})=3$ Hz, 2H, H(1,3)), 5.50 (q, $J(\text{H-H})=J(\text{Rh-H})=3$ Hz, 1H, H(2)), 6.66 (s, 2H, H(5,6)).

$^{13}\text{C}\{^1\text{H}\}$ (C_6D_6 , 50.3 Hz) δ 17.9 (s, CH₃), 74.8 (d, $J(\text{Rh-C})=4$ Hz, C(1,3)), 96.2 (d, $J(\text{Rh-C})=6$ Hz, C(2)), 116.5 (s, C(3a,7a)), 125.5 (s, C(4,7)), 125.9 (s, C(5,6)), 190.8 (d, $J(\text{Rh-C})=86$ Hz, CO).

$[(\eta\text{-5,6-(}\mu\text{-OCH}_2\text{O)}\text{C}_9\text{H}_5)\text{Rh}(\text{CO})_2]$ (5)

Using $[(\eta\text{-5,6-(}\mu\text{-OCH}_2\text{O)}\text{C}_9\text{H}_5)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$ (50 mg, 0.16 mmol) and a reaction time of 0.5 h, 50 mg of 5 was obtained, 100% yield.

^1H (C_6D_6 , 250 MHz) δ 5.04 (d, $J(\text{H-H})=3$ Hz, 2H, H(1,3)), 5.12 (AB q, $J(\text{H-H})=1.2$ Hz, 2H, CH_2O), 5.44 (q, $J(\text{H-H})=J(\text{Rh-H})=3$ Hz, 1H, H(2)), 6.25 (s, 2H, H(4,7)).

$^{13}\text{C}\{^1\text{H}\}$ (C_6D_6 , 62.9 MHz) δ 75.2 (d, $J(\text{Rh-C})=3$ Hz, C(1,3)), 95.1 (d, $J(\text{Rh-C})=7$ Hz, C(2)), 97.3 (s, CH_2O), 100.9 (s, C(4,7)), 113.9 (s, C(3a,7a)), 147.4 (s, C(5,6)), 191.3 (d, $J(\text{Rh-C})=89$ Hz, CO).

$[(\eta\text{-}5,6\text{-Me}_2\text{C}_9\text{H}_5)\text{Rh}(\text{CO})_2]$ (6)

Using $[(\eta\text{-}5,6\text{-Me}_2\text{C}_9\text{H}_5)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$ (50 mg, 0.2 mmol) and a reaction time of 2 h, 50 mg of 6 was obtained, 100% yield.

^1H (C_6D_6 , 200 MHz) δ 1.62 (s, 6H, CH_3), 4.98 (d, $J(\text{H-H})=3$ Hz, 2H, H(1,3)), 5.28 (q, $J(\text{H-H})=J(\text{Rh-H})=3$ Hz, 1H, H(2)), 6.38 (s, 2H, H(4,7)).

$^{13}\text{C}\{^1\text{H}\}$ (C_6D_6 , 50.3 MHz) δ 20.2 (s, CH_3), 75.1 (d, $J(\text{Rh-C})=3$ Hz, C(1,3)), 96.4 (d, $J(\text{Rh-C})=6$ Hz, C(2)), 117.1 (s, C(3a,7a)), 119.1 (s, C(4,7)), 134.5 (s, C(5,6)), 191.2 (d, $J(\text{Rh-C})=86$ Hz, CO).

$[(\eta\text{-}1\text{-MeC}_9\text{H}_6)\text{Rh}(\text{CO})_2]$ (7)

Using $[(\eta\text{-}1\text{-MeC}_9\text{H}_6)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$ (29 mg, 0.1 mmol) and a reaction time of 0.5 h, 24 mg of 7 was obtained, 80% yield.

^1H (CD_2Cl_2 , 250 MHz) δ 2.31 (s, 3H, CH_3), 5.54 (d, $J(\text{H-H})=2.5$ Hz, 1H, H(3)), 5.97 (t, $J(\text{H-H})=J(\text{Rh-H})=2.5$ Hz, 1H, H(2)), 7.14 (m, 4H, H(4-7)).

$^{13}\text{C}\{^1\text{H}\}$ (CD_2Cl_2 , 50.3 MHz) δ 12.9 (s, CH_3), 72.1 (d, $J(\text{Rh-C})=4$ Hz, C(3)), 93.7 (s, C(1)), 98.7 (d, $J(\text{Rh-C})=6$ Hz, C(2)), 117.0, 118.8 (s, C(3a,7a)), 117.6, 119.3, 125.0, 125.2 (s, C(4-7)), 191.0 (d, $J(\text{Rh-C})=86$ Hz, CO).

$[(\eta\text{-}5,6\text{-}(\text{MeO})_2\text{C}_9\text{H}_5)\text{Rh}(\text{CO})_2]$ (8)

Using $[(\eta\text{-}5,6\text{-}(\text{MeO})_2\text{C}_9\text{H}_5)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$ (50 mg, 0.15 mmol) and a reaction time of 2 h, 50 mg of 8 was obtained, 100% yield.

^1H (C_6D_6 , 200 MHz) δ 3.26 (s, 6H, CH_3O), 5.26 (d, $J(\text{H-H})=3$ Hz, 2H, H(1,3)), 5.58 (q, $J(\text{H-H})=J(\text{Rh-H})=3$ Hz, 1H, H(2)), 6.22 (s, 2H, H(4,7)).

$^{13}\text{C}\{^1\text{H}\}$ (C_6D_6 , 50.3 MHz) δ 55.3 (s, CH_3O), 75.4 (s, C(1,3)), 94.6 (s, C(2)), 100.0 (s, C(4,7)), 113.1 (s, C(3a,7a)), 150.3 (s, C(5,6)), 191.8 (d, $J(\text{Rh-C})=86$ Hz, CO).

$[(\eta\text{-}4,5,6,7\text{-Me}_4\text{C}_9\text{H}_3)\text{Rh}(\text{CO})_2]$ (9)

Using $[(\eta\text{-}4,5,6,7\text{-Me}_4\text{C}_9\text{H}_3)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$ (50 mg, 0.15 mmol) and a reaction time of 1 h, 50 mg of 9 was obtained, 100% yield.

^1H (C_6D_6 , 250 MHz) δ 1.86, 2.03 (s, 12H, CH_3), 5.36 (d, $J(\text{H-H})=3$ Hz, 2H, H(1,3)), 5.55 (q, $J(\text{H-H})=J(\text{Rh-H})=3$ Hz, 1H, H(2)).

$^{13}\text{C}\{^1\text{H}\}$ (C_6D_6 , 62.9 MHz) δ 15.5, 16.2 (s, CH_3), 75.2 (s, C(1,3)), 95.2 (s, C(2)), 116.1 (s, C(3a,7a)), 122.6 (s,

C(4,7)), 132.5 (s, C(5,6)), 191.5 (d, $J(\text{Rh-C})=85$ Hz, CO).

$[(\eta\text{-}1,2,3\text{-Me}_3\text{C}_9\text{H}_4)\text{Rh}(\text{CO})_2]$ (10)

Using $[(\eta\text{-}1,2,3\text{-Me}_3\text{C}_9\text{H}_4)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$ (50 mg, 0.16 mmol) and a reaction time of 0.25 h, 40 mg of 10 was obtained, 80% yield.

^1H (C_6D_6 , 250 Hz) δ 1.83 (d, $J(\text{Rh-H})=2.4$ Hz, 3H, CH_3), 1.95 (s, 6H, CH_3), 6.4 (m, 4H, H(4-7)).

$^{13}\text{C}\{^1\text{H}\}$ (C_6D_6 , 62.9 MHz) δ 10.6, 11.7 (s, CH_3), 88.4 (s, C(1,3)), 114.7 (d, $J(\text{Rh-C})=6$ Hz, C(2)), 116.6 (s, C(4,7)), 117.1 (s, C(3a,7a)), 124.4 (s, C(5,6)), 192.0 (d, $J(\text{Rh-C})=86.0$ Hz, CO).

$[(\eta\text{-}1,2,3,4,5,6,7\text{-Me}_7\text{C}_9)\text{Rh}(\text{CO})_2]$ (11)

Using $[(\eta\text{-}1,2,3,4,5,6,7\text{-Me}_7\text{C}_9)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$ (40 mg, 0.11 mmol) and a reaction time of 1 h, 32 mg of 11 was obtained (80% yield).

^1H (C_6D_6 , 200 MHz) δ 1.85 (d, $J(\text{Rh-H})=2.2$ Hz, 3H, CH_3), 1.97 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 2.33 (s, 6H, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 50.3 MHz) δ 11.6, 14.2, 15.8, 16.1 (s, CH_3), 88.5 (s, C(1,3)), 106.0 (s, C(2)), 112.8 (s, C(3a,7a)), 122.6, 131.6 (s, C(4-7)), 191.4 (d, $J(\text{Rh-C})=87$ Hz, CO).

$[(\eta\text{-}1\text{-}(\text{C}_4\text{H}_9)\text{-}2,3,4,5,6,7\text{-Me}_6\text{C}_9)\text{Rh}(\text{CO})_2]$ (12)

To a solution of $[1\text{-C}_4\text{H}_9\text{-}2,3,4,5,6,7\text{-Me}_6\text{C}_9\text{H}]$ (128 mg, 0.5 mmol) in THF (20 ml), *n*-BuLi in hexane (0.89 M, 0.6 ml, 0.5 mmol) was added. The yellow solution obtained was stirred overnight and then added dropwise to a solution suspension of $[\text{Rh}(\text{CO})_2(\mu\text{-Cl})_2]$ (100 mg, 0.25 mmol) in THF (25 ml) under a CO atmosphere. After stirring for 1 h, the THF was removed *in vacuo* and the resulting solid was extracted with hexane. On removal of hexane and recrystallization from a hexane/THF mixture at -35 °C, 12 (195 mg, 94% yield based on Rh) was obtained as a yellow-orange solid.

^1H (C_6D_6 , 200 MHz) δ 0.86 (m, 3H, $\text{CH}_3(\text{C}_4\text{H}_9)$), 1.32 (m, 6H, $\text{CH}_2(\text{C}_4\text{H}_9)$), 1.94 (d, $J(\text{Rh-H})=2.2$ Hz, 3H, CH_3), 1.97 (s, 6H, CH_3), 2.13 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.36 (s, 3H, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ (C_6D_6 , 62.9 MHz) δ 14.1, 16.5, 16.7 (s, $\text{CH}_2(\text{C}_4\text{H}_9)$), 23.2, 23.5, 25.3, 27.9, 28.4, 28.6, 32.6 (s, CH_3), 90.3 (s, C(1)), 94.7 (s, C(3)), 111.1 (s, C(2)), 112.6, 114.9 (C(3a,7a)), 123.0, 123.3, 132.2, 132.4 (s, C(4-7)).

Kinetics experiments: general procedure

Compounds and solvents

All experimental operations (apart from kinetics) were carried out under a nitrogen atmosphere. Toluene was distilled from Na/benzophenone and then bubbled with N_2 for 1 h, when used for kinetic measurements.

Triphenylphosphine (PPh₃), [tri(*p*-methoxyphenyl)-phosphine] ([P(*p*-MeO-Ph)₃]) and tricyclohexylphosphine (PCy₃) were recrystallized from ethanol before use in kinetic experiments. The other phosphines were distilled from Na prior to use.

Instrumentation

A Nicolet SPC FT-IR spectrometer was used to record IR spectra in toluene solutions, and a CARY 219 spectrophotometer was used to record UV-Vis spectra. Kinetic data were collected using a Durrum stopped-flow instrument interfaced to an OLIS (on-line instrument service) data collection and analysis system. The instrument was not adapted for air-sensitive work, but preliminary studies with solutions of the complexes in toluene showed that they were sufficiently air stable over several minutes to allow accurate kinetic studies.

Kinetic measurements

All reactions were studied by near-UV spectrometry in toluene at room temperature (~25 °C (298 K)). Rate constants were determined by monitoring the increase in absorption at λ_{max} of the appropriate substituted product as a function of time (wavelengths given in Table 2). Correlation coefficients of least-squares lines ($R^2 > 0.995$) were good. All kinetic experiments were carried out under pseudo-first-order conditions with at least a ten-fold excess of nucleophile. All reactions proceeded to completion to give the appropriate substituted product.

Crystal data, data collection and reduction, solution and refinement for 9

Crystal of **9**, C₁₅H₁₅O₂Rh, molecular weight = 330.2 are triclinic, $a = 7.698(2)$, $b = 8.929(3)$, $c = 20.386(6)$ Å, $\alpha = 91.26(2)$, $\beta = 91.83(2)$, $\gamma = 92.72(2)^\circ$, $V = 1398.4(7)$ Å³, space group $P\bar{1}$, $Z = 4$, $\rho_c = 1.568$ g cm⁻³, $F(000) = 664$, $\lambda = 0.71073$ Å, $T = 295$ K, $\mu(\text{Mo K}\alpha) = 11.92$ cm⁻¹.

Data were collected from an orange prism of dimensions 0.27 × 0.29 × 0.32 mm mounted on a Nicolet-Siemens R3m/V diffractometer equipped with graphite-monochromated Mo K α radiation. Accurate unit-cell parameters were derived from 25 general reflections ($22 < 2\theta < 32^\circ$) well distributed in reciprocal space. Data were measured by the ω -scan method ($\Delta\omega = 1.2^\circ$) in the hemisphere $h \pm k \pm l$ with $2\theta \leq 50^\circ$ using variable scan rates (2.25 to 29–30 ° min⁻¹ in ω). Background measurements were made at the beginning and end of each scan for a total time equal to half the scan time. Crystal stability was monitored by measuring two standard reflections every 100 measurements; only statistical fluctuations ($\pm 2\%$) were observed. Data were corrected for Lorentz and polarization effects and absorption (Ψ -

scan, semi-empirical, transmission factors 0.55–0.68). From a total of 4941 independent reflections measured, 3700 with $F \geq 6\sigma(F)$ were considered observed and used in the solution and refinement.

The structure was solved by Patterson and Fourier techniques for two independent molecules in the asymmetric unit and refined by full-matrix least-squares using Siemens SHELXTL PLUS software, the function minimized being $\sum_w (|F_o| - |F_c|)^2$. Difference Fourier synthesis provided the location of all hydrogen atoms which were included in the refinement with isotropic thermal parameters. A total of 446 parameters was refined with a data: parameter ratio of 8:3:1. Final R and R_w values were 2.94 and 3.21% with a GOF of 1.24*. During the final cycles of refinement a weighting scheme of the form $w^{-1} = \sigma(F) + aF^2$ was included with $a = 0.0004$. A final difference map was featureless with maximum residuals of +0.41 (at Rh) and -0.24 e Å⁻³. Scattering factors used including the anomalous dispersion corrections for rhodium were taken from the International Tables, Vol. 4.

Results and discussion

With the exception of **12**, all [(indenyl)Rh(CO)₂] complexes (**1–11**) (Fig. 1) were prepared by carbonylation of the corresponding bis(ethylene) derivatives [11] using CO at ambient temperature and pressure. Complex **12** was prepared by direct reaction of [1-ⁿBu-2,3,4,5,6,7-Me₆C₉]⁻ with [Rh(CO)₂(μ-Cl)]₂ under a CO atmosphere. Table 1 lists the CO stretching frequencies for [(η-C₉R_nH_{7-n})Rh(CO)₂], [(η-C₉R_nH_{7-n})Rh(PPh₃)(CO)] and [(η-C₅H₅)Rh(CO)₂] complexes. All data for each given solvent were obtained on a single digital IR spectrometer under identical conditions. For comparative purposes, we have averaged the values for the symmetric and asymmetric CO stretching frequen-

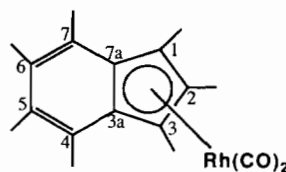


Fig. 1. Ring substituted [(Indenyl)Rh(CO)₂] complexes: (η-5,6-Cl₂C₉H₃Rh(CO)₂) (**1**), η-C₉H₇Rh(CO)₂ (**2**), η-4,7-(MeO)₂-C₉H₅Rh(CO)₂ (**3**), η-4,7-Me₂C₉H₅Rh(CO)₂ (**4**), η-5,6-(μ-CH₂O)₂C₉H₅Rh(CO)₂ (**5**), η-5,6-Me₂C₉H₅Rh(CO)₂ (**6**), η-1-Me-C₉H₆Rh(CO)₂ (**7**), η-5,6-(MeO)₂C₉H₅Rh(CO)₂ (**8**), η-4,5,6,7-Me₄C₉H₃Rh(CO)₂ (**9**), η-1,2,3-Me₃C₉H₄Rh(CO)₂ (**10**), η-1,2,3,4,5,6,7-Me₇C₉Rh(CO)₂ (**11**), η-1-(C₄H₉)-2,3,4,5,6,7-Me₆C₉-Rh(CO)₂ (**12**).

$$*R = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}; \quad R_w = \frac{[\sum (|F_o| - |F_c|)^2 \sum w F_o^2]^{1/2}}{GOF = [\sum w (|F_o| - |F_c|)^2 / N_{obs} - N_{var}]^{1/2}}$$

TABLE 1. CO stretching frequencies for $[(\eta\text{-C}_9\text{R}_n\text{H}_{7-n})\text{Rh}(\text{CO})_2]$, $[(\eta\text{-C}_9\text{R}_n\text{H}_{7-n})\text{Rh}(\text{PPh}_3)(\text{CO})]$ and $[(\eta\text{-C}_5\text{R}_5)\text{Rh}(\text{CO})_2]$ complexes

Compound number	Ligand	Rh(CO) ₂			Rh(PPh ₃)(CO)
		$\nu(\text{CO})^a$	Av. $\nu(\text{CO})^a$	$\Delta\nu(\text{CO})^{a,b}$	$\nu(\text{CO})^c$
1	$\eta\text{-5,6-Cl}_2\text{C}_9\text{H}_5$	2056, 2001	2028.5	-10.0	2050, 1993
2	$\eta\text{-C}_9\text{H}_7$	2046, 1991	2018.5		2044, 1984
3	$\eta\text{-4,7-(OMe)}_2\text{C}_9\text{H}_5$	2048, 1990	2019.0	-0.5	2043, 1982
4	$\eta\text{-4,7-Me}_2\text{C}_9\text{H}_5$	2045, 1988	2016.5	2.0	2040, 1980
5	$\eta\text{-5,6-(}\mu\text{-CH}_2\text{O}_2\text{)C}_9\text{H}_5$	2045, 1988	2016.5	2.0	
6	$\eta\text{-5,6-Me}_2\text{C}_9\text{H}_5$	2045, 1987	2016.0	2.5	2039, 1979
7	$\eta\text{-1-MeC}_9\text{H}_6$	2043, 1985	2014.0	4.5	2039, 1979
8	$\eta\text{-5,6-(MeO)}_2\text{C}_9\text{H}_5$	2042, 1984	2013.0	5.5	2037, 1975
9	$\eta\text{-4,5,6,7-Me}_4\text{C}_9\text{H}_3$	2041, 1982	2011.5	7.0	2037, 1975
10	$\eta\text{-1,2,3-Me}_3\text{C}_9\text{H}_4$	2035, 1978	2006.5	12.0	2031, 1973
11	$\eta\text{-1,2,3,4,5,6,7-Me}_7\text{C}_9$	2028, 1969	1998.5	20.0	2024, 1965
12	$\eta\text{-1-(C}_4\text{H}_9\text{)-2,3,4,5,6,7-Me}_6\text{C}_9$	2027, 1968	1997.5	21.0	2024, 1964
	$(\eta\text{-C}_5\text{H}_5)$	2047, 1984	2015.5	3.0	
	$(\eta\text{-C}_5\text{Me}_5)$	2024, 1962	1993.0	25.5	

^aIn hexane, cm^{-1} . ^b $\Delta\nu = \text{av. } \nu(\text{CO}) - \text{av. } \nu(\text{CO})$ of $\text{IndRh}(\text{CO})_2$. ^cIn toluene, cm^{-1} .

cies (av. $\nu(\text{CO})$). These values, for hexane solutions, are given in Table 1, and for toluene solutions, in Table 2. Also listed in Table 1 are the difference in av. $\nu(\text{CO})$ ($\Delta\nu(\text{CO})$) for each compound with respect to $(\eta\text{-C}_9\text{H}_7)\text{Rh}(\text{CO})_2$.

Estimation of electron density at Rh and the relative donor abilities of the η^5 ligands from IR data

For a series of analogous metal carbonyl complexes, CO stretching frequencies are often employed [12–14] as a means by which to assess relative electron density at the metal center. The assumption made is that increased electron density at M will be reflected by increased backdonation into $\text{CO-}\pi^*$ orbitals resulting in lower values of $\nu(\text{CO})$. A degree of caution must be applied to the interpretation of data for indenyl versus cyclopentadienyl rhodium complexes, insofar as there are differences in the frontier orbitals of the two

ligands which may affect the degree of electron donation into specific d orbitals on M [15]. It should, however, be possible to correlate electron density at Rh with $\nu(\text{CO})$ for the series of ring-substituted indenyl complexes.

The $\text{Rh}(\text{CO})_2$ complexes in Table 1 are listed in order of decreasing average $\nu(\text{CO})$. Several important conclusions can be drawn from these data. Substitution at remote positions on the six-membered ring does affect electron density at Rh, although substitution of the five-membered ring is more efficient in this regard. The indenyl anion HOMO has its maximum coefficients on C(1,3), significant coefficients on C(4,5,6,7), and a node at C(2) [7c]. The second HOMO has its maximum coefficient on C(2), significant contributions from C(1,3,5,6), and is essentially vanishing on C(4,7) [7c]. Thus, the two most efficient π -donor orbitals have some contributions from the six-membered ring.

Interestingly, $[\text{5,6-Cl}_2\text{C}_9\text{H}_5]^-$ is a poorer π -donor than $[\text{C}_9\text{H}_7]^-$. The chlorines must be acting as inductively withdrawing groups, as they are formally π -donors. In contrast, $[\text{5,6-(MeO)}_2\text{C}_9\text{H}_5]^-$ is a better donor than $[\text{C}_9\text{H}_7]^-$. Here, the methoxy groups are serving as π -donors and this effect outweighs the inductive one. We were surprised to find that the 5,6-methylenedioxy substituent was not more efficient than two methoxy groups as a π -donor, since the relatively rigid ring should enhance oxygen p orbital to ring π conjugation. It seems likely that ring-methyl substituents enhance electron density via a hyperconjugative effect. Methyl substitution at either C(4,7) or C(5,6) alone has a small effect whereas methylation at all four positions C(4,5,6,7) has a greater effect ($\Delta\nu(\text{CO}) = 7.0 \text{ cm}^{-1}$). Methylation at C(1,2,3) is more effective ($\Delta\nu(\text{CO}) = 12.0 \text{ cm}^{-1}$), as expected, and permethylation gives $\Delta\nu(\text{CO}) = 20.0 \text{ cm}^{-1}$,

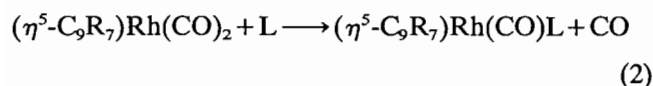
TABLE 2. Second-order rate constants for reaction of 1–10 with PPh_3 in toluene at 22 °C

Compound number	Average $\nu(\text{CO})$ (cm^{-1})	Observed λ (nm)	k_2 ($\text{M}^{-1} \text{s}^{-1}$)
1	2021.5	390	$(1.47 \pm 0.2) \times 10^4$
2	2014	385	$(6.28 \pm 0.1) \times 10^3$
3	2013	405	$(1.25 \pm 0.05) \times 10^3$
4	2010	385	$(1.48 \pm 0.06) \times 10^3$
6	2009	375	$(9.4 \pm 0.5) \times 10^3$
7	2009	395	$(4.17 \pm 0.26) \times 10^3$
8	2006	374	$(1.24 \pm 0.05) \times 10^3$
9	2006	395	$(3.56 \pm 0.03) \times 10^2$
10	2002	395	$(1.22 \pm 0.02) \times 10^3$
11	1994.5	405	46 ± 0.45
12	1994	405	31.9 ± 1.2

comparable to the sum of the effects at C(4–7) and C(1–3). Finally, the [1-Bu-2,3,4,5,6,7-Me₆C₉][−] ligand is similar to [C₉M₇][−] in its donor ability, but can be used to break the C_s symmetry of the RhL₂ complexes for dynamic FT NMR studies [7a–c, 8] of hindered indenyl ring rotation.

Kinetics of CO substitution

The original studies of [(η⁵-C₅H₅)Rh(CO)₂] reported [4] that the rates of CO substitution are first-order in complex and first-order in nucleophile. This behavior is followed by all of the complexes examined in the present study. Except for the reactions of PPh₂H with complexes 9–11, and of P(OEt)₃ with 9, all other reactions studied give monosubstituted products under the experimental conditions used. The dependence of the rate of reaction (eqn. (2)) on the concentration of PPh₃ is given in Fig. 2. A straight line with a zero intercept is obtained, indicating no detectable dissociative substitution.



(R = H, Cl, MeO, or CH₃; L = PPh₃, PCyPh₂, PCy₂Ph, PCy₃, P(n-Bu)₃, P(OEt)₃, PMePh₂, P(C₆H₄-p-OMe)₃, PPh₂H)

Table 2 contains the kinetic data for the reaction (eqn. (2)) with PPh₃. This reaction was also investigated with a variety of other ligands. Kinetic data as a function of L are given in Table 3. Because disubstituted products were obtained for the reactions of PPh₂H with 9–11, and P(OEt)₃ with 9, the rate constants for these reactions

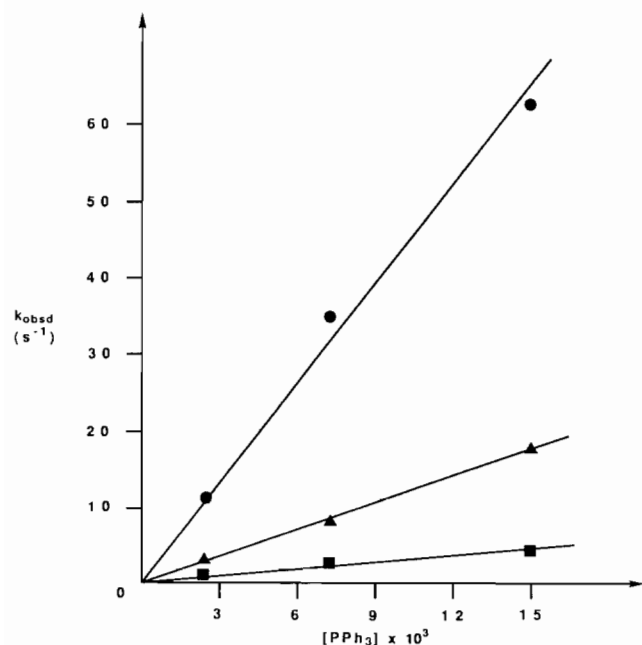


Fig. 2. Plot of k_{obs} vs. PPh₃ concentrations for the reaction of PPh₃ with 7 (●), 9 (▲) and 10 (■) in toluene at room temperature.

were not obtained since the absorption peaks in the UV spectra were overlapping. In addition to the electronic effect, the substituted indenyl ligands will exert a greater steric demand than the parent indenyl ligand. The observation is obvious on examining the data in Table 3, where different ligands are employed. It is clear from the study of phosphine ligand size on the size on the CO substitution reactions of 8–11, that there is a pronounced steric retardation with increasing cone angle, regardless of phosphine basicity. For all of the complexes studied, the rate of substitution of the larger but more basic PCy₃ is slower than that of PPh₃. Although P(n-Bu)₃ has approximately the same basicity as PCy₃, P(n-Bu)₃ with its much smaller cone angle reacts two orders of magnitude faster than PCy₃. In addition, the smallest cone angle ligand studied reacts only slightly slower than the much more basic P(n-Bu)₃. This behavior appears to contrast with that observed for reactions of the corresponding cyclopentadienyl systems [4], where the dominant factor contributing to the nucleophilic strength of the entering ligand is its basicity. This has also generally been the case for associative displacement reactions in other transition metal organometallic compounds [19, 20]. However, for the permethylated cyclopentadienyl moiety, ligand basicity has been shown to be of secondary importance and behavior similar to that observed here has been reported [2b].

Thus, the steric demands of the substituted indenyl ligands do have a profound effect on the course of carbonyl substitution in these compounds. As shown in Table 3, when the size of the ligand becomes very large, as for PCy₃, the reaction rate shows a dramatic decrease. This is consistent with an associative process. A correlation between the rate of reaction and the cone angle of the incoming ligand can be drawn (Figs. 3 and 4) for complexes 10 and 11. Apart from P(OEt)₃, the other ligands show a reasonable correlation. However, the Tolman cone angle [16] of 109° for P(OEt)₃ has been revised by Stahl and Ernst [17] to a value of 134°, and using this value the point for P(OEt)₃ falls much closer to the lines obtained with the other ligands.

As expected, the strength of a nucleophile depends on its size and basicity, and, depending on the substrate, one or the other of these factors may dominate. Quantitative assessment of steric and electronic factors for other systems have been carried out and, though the data in this study is limited, an attempt can be made to delineate the contribution of basicity and steric effects.

Poë and co-workers [21, 22] and Giering and co-workers [23, 24], have developed several equations in order to construct steric profiles for associative substitution reactions of metal carbonyls. These involve subtracting the electronic effect of the ligand from k_2

TABLE 3. Second-order rate constants for the reactions of 8–11 with PR_3 in toluene at 22 °C

L	θ^a	pK_a^c	k_2 ($M^{-1} s^{-1}$)			
			8	9	10	11
PPh ₂	126	0.03	13.3 ± 0.6			
P(n-Bu) ₃	132	8.43	$(2.0 \pm 0.2) \times 10^4$	$(1.35 \pm 0.1) \times 10^4$	$(2.77 \pm 0.05) \times 10^4$	$(4.07 \pm 0.43) \times 10^3$
P(OEt) ₃	134 [b]	3.31	$(1.49 \pm 0.1) \times 10^2$		$(4.58 \pm 0.1) \times 10^3$	$(4.09 \pm 0.36) \times 10^2$
PMePh ₂	136	4.57	$(2.43 \pm 0.02) \times 10^4$			
PPh ₃	145	2.73	$(1.24 \pm 0.05) \times 10^3$	$(3.56 \pm 0.03) \times 10^2$	$(1.22 \pm 0.02) \times 10^3$	46 ± 0.45
P(C ₆ H ₄ pOMe) ₃	145	4.59	$(3.0 \pm 0.1) \times 10^3$	$(7.00 \pm 0.05) \times 10^2$		
PCyPh ₂	153	(5.05)	$(1.5 \pm 0.2) \times 10^3$	$(1.89 \pm 0.03) \times 10^2$	$(1.5 \pm 0.1) \times 10^3$	59.9 ± 0.5
PCy ₂ Ph	162	(7.38)	$(2.22 \pm 0.04) \times 10^2$	74 ± 1	$(1.2 \pm 0.1) \times 10^2$	12.4 ± 0.6
PCy ₃	170	9.70	$(1.40 \pm 0.2) \times 10^2$	78 ± 4	$(2.55 \pm 0.16) \times 10^2$	17 ± 0.8

^aRef. 16. ^bRef. 17. ^cRef. 18.

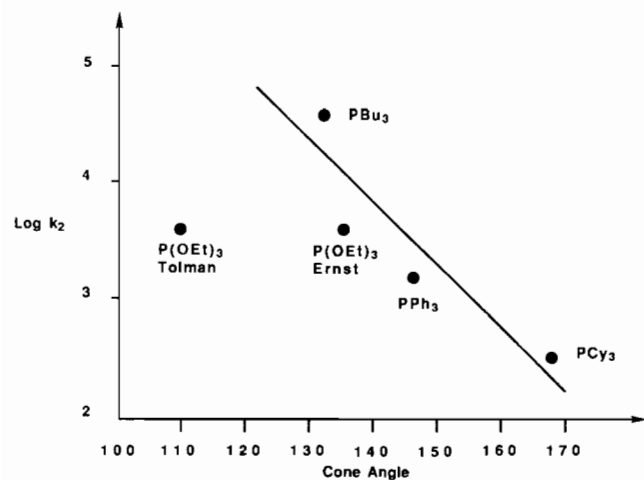


Fig. 3. Plot of $\log k_2$ vs. cone angle for the reaction of **10** with PR_3 in toluene at room temperature.

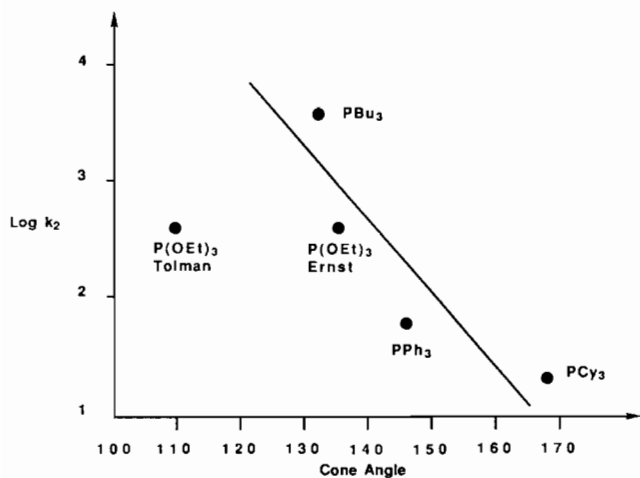


Fig. 4. Plot of $\log k_2$ vs. cone angle for the reaction of **11** with PR_3 in toluene at room temperature.

so that the resultant k_2° should be a function of ligand size only. One such equation is eqn. (3)

$$\log k_2^\circ = \log k_2 - \beta(pK_a + 4) \quad (3)$$

where β is an electronic selectivity parameter derived from the slopes of the linear free energy relation. The $(pK_a + 4)$ term standardizes the nucleophile in question relative to a hypothetical weak nucleophile with $pK_a = -4$. The β values employed in this study for **8** (0.21) and **9** (0.16) were obtained from the $\log k_2$ values for PPh₃ ($\theta = 145^\circ$) and P(*p*-MeO-Ph)₃ ($\theta = 145^\circ$), using their respective pK_a values. For examples **10** (0.16) and **11** (0.19), the corresponding β values were obtained from the $\log k_2$ values for P(n-Bu)₃ ($\theta = 132^\circ$) and P(OEt)₃ ($\theta = 134^\circ$), making allowances for small differences in cone angles. These β values are close to that of $[(\eta^5-C_5H_5)Rh(CO)_2]$ (0.19) [21]. Applying eqn. (3) to complex **11** gives a linear plot with excellent correlation (Fig. 5). A plot of this type suggests that large steric effects are in operation because, even as

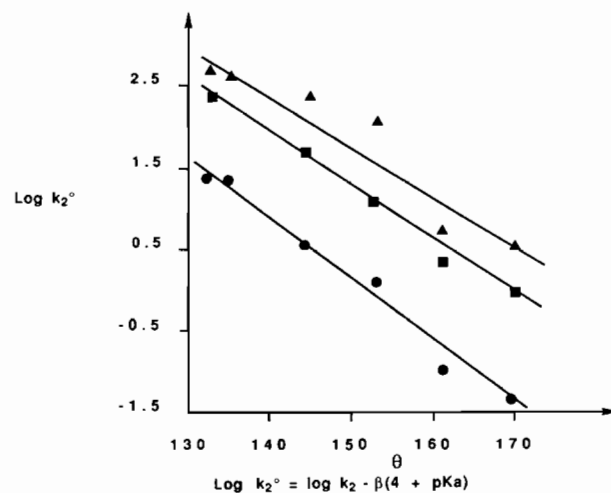


Fig. 5. Steric profile for the reaction of **9** (■), **10** (▲) and **11** (●).

one goes to smaller nucleophiles, the plot does not start curving. If steric effects get much smaller with smaller cone angles, then the dependence of $\log k_2^\circ$ on cone angle should diminish and the plot would deviate from linearity. Thus, the linear plot obtained suggests that **11** is very crowded.

Applying eqn. (3) to complex **10** gives a similar plot (Fig. 5). The two lines have similar slopes which implies that the two complexes may have similar sensitivities to the steric effect of the ligands. Because of the limitation of the equipment (reactions became too fast for the stopped-flow apparatus), it was not possible to obtain rate constants for the reactions of **10** with smaller ligands. For the small and less basic ligands, such as PPh_2H , disubstitution occurs easily, and the results are not reliable. Although the intercept of the sloping and horizontal lines, which, in part, also reflects the steric effect, was not observed, it is reasonable to believe that complex **10**, which has its five-membered ring fully substituted, has about the same steric effect as does complex **11**.

The steric profile for the reaction of complex **9** with PR_3 is also shown in Fig. 5. The difference between this complex and **10** or **11** is that its reaction with $\text{P}(\text{OEt})_3$ gives disubstituted product. Although a conclusion about the steric effect cannot be made from these results, it was not expected that the rates for **9** would be slower than those for **10** on either electronic or steric grounds.

Complex **8**, which is believed to be less crowded than complexes **10** and **11**, was examined. For **8**, the rate of the reaction depends only on ligand basicity when the cone angle is smaller than 135° (Fig. 6). When $\theta > 135^\circ$, it also shows a strong steric effect. This again

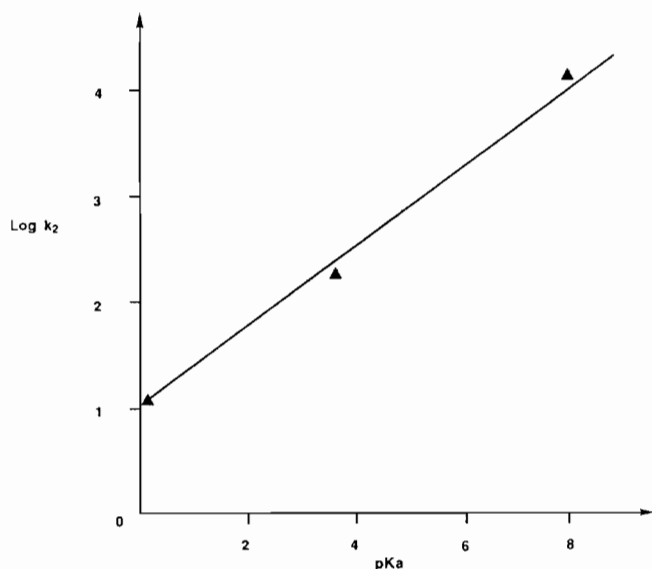
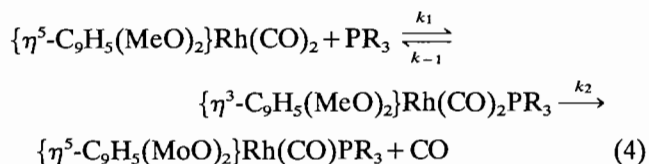


Fig. 6. Plot of $\log k_2$ vs. $\text{p}K_a$ for the reaction of **8** with PR_3 in toluene at room temperature.

suggests that the indenyl system is more crowded than the corresponding cyclopentadienyl system. It is not understood why ligands with $\theta < 135^\circ$ react slower than expected. One possible reason is that in the transition states for these small ligands, bond making is much further advanced than for the large ligands. This will produce a very negative ΔS^\ddagger , and retard the reaction. Note that the slope of Fig. 6 is 0.38, which is almost twice the value of β used in Fig. 7.

Another reason might be that the intermediates $[\{\eta^3\text{-C}_9\text{H}_5(\text{MeO})_2\}\text{Rh}(\text{CO})_2\text{PR}_3]$ are relatively stable, the dissociation of CO from these intermediates to the products being slower than for the reaction of the complex with large ligands. If this is the case, the rate law for reaction (4) becomes $R = (k_2 k_1 / (k_{-1} + k_2))$ -



[complex][PR_3]. Thus, the rate constant obtained from the experiment is $k_2 k_1 / (k_{-1} + k_2)$. If the above mechanism is followed, the rate of CO substitution will be retarded under CO atmosphere. Unfortunately, such an experiment could not be performed with the stopped-flow instrument employed for this study.

Last, the results show that there is a linear relation among the effects of methyl groups on the rates of the reaction. Note that: $\log(k_2/k_9) = 1.3$, $\log(k_2/k_{10}) = 0.71$, $\log(k_2/k_{11}) = 2.1$, $\log(k_2 k_{11}) = \log(k_2/k_9) + \log(k_2/k_{10})$, where the subscripts refer to the compounds **2** and **9-11**. This is another example of linear free energy relation of substituents.

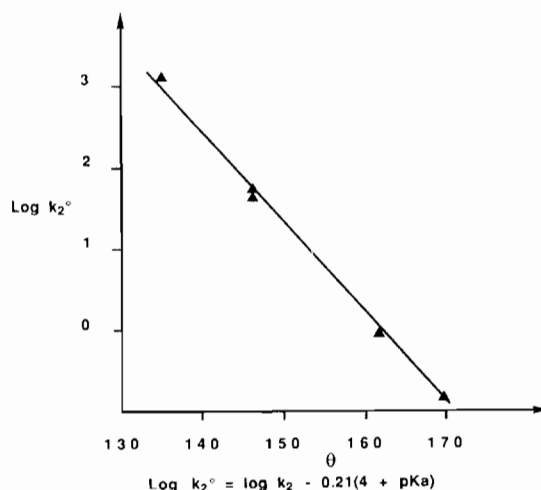


Fig. 7. Steric profile for the reaction of **7** with PR_3 in toluene at room temperature.

Molecular structure of $[(\eta\text{-}4,5,6,7\text{-Me}_4\text{C}_9\text{H}_3)\text{Rh}(\text{CO})_2]$: a comparison of the ground state structure of indenyl vs. substituted $[(\text{Ind})\text{RhL}_2]$ complexes

We were intrigued by the lower rates of ligand substitution in **3**, **4** and **9** versus **10**. In order to investigate the effect of indenyl ring alkylation at positions 4, 5, 6 and 7, on the ground state structure of the resulting $(\eta\text{-}4,5,6,7\text{-Me}_4\text{C}_9\text{H}_3)\text{Rh}(\text{CO})_2$ complex, we have carried out a single crystal X-ray structure investigation on **9**.

It is well documented [2a, b, 5a, 7a–d, 8a–d] that all $(\eta\text{-indenyl})\text{ML}_n$ complexes show significant slip distortions from η^5 towards η^3 coordination in the ground state. Structural characterization of several of these complexes has indicated that the metal to carbon distances for the carbons (1–3) (M–C(1), M–C(2), M–C(3)) are shorter than those to the bridgehead carbons (M–C(3a), M–C(7a)). The degree of distortion in the solid state in these complexes has been discussed [5a] in terms of three parameters: (i) slip distortion (Δ) which is defined as the difference in the average metal to carbon distances of C(3a,7a) and C(1,3) ($\Delta = d\{(\text{M}-\text{C}(3\text{a},7\text{a})) - (\text{M}-\text{C}(1,3))\}$); (ii) hinge angle (HA), which is the angle between normals to the least-squares planes defined by [C(1), C(2), C(3)] and [C(1), C(7a), C(3a), C(3)]; and (iii) fold angle (FA), which is the angle between normals to least-square planes defined by [C(1), C(2), C(3)] and [C(3a), C(4), C(5), C(6), C(7), C(7a)]. The values for these parameters range [5a] from 0.030 Å (Δ), 2.5° (HA), 4.4° (FA) for true η^5 complexes, 0.11–0.42 Å (Δ), 7–14° (HA), 6–13° (FA) for distorted η^5 complexes to 0.8 Å (Δ), 28° (FA) for true η^3 complexes.

The solid state structure of **9** is shown in Fig. 8. Selected bond lengths and angles and positional and thermal parameters are listed in Tables 4 and 5. Slip-fold distortion parameters for **9** and the analogous unsubstituted complex **2** [7a], together with the selected bond lengths for the two complexes, are given in Table 6.

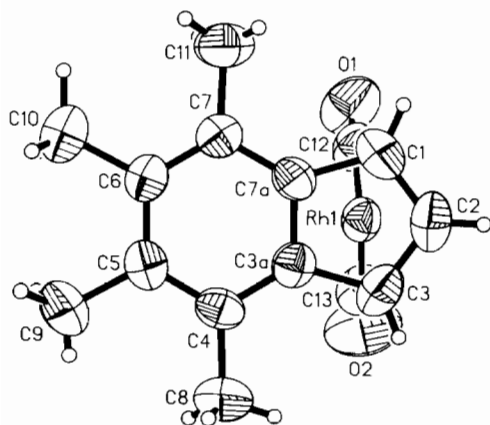


Fig. 8. Molecular structure of $(\eta\text{-}4,5,6,7\text{-Me}_4\text{C}_9\text{H}_3)\text{Rh}(\text{CO})_2$ (**9**).

TABLE 4. Selected bond distances (Å) and angles (°) for $[(\eta\text{-}4,5,6,7\text{-Me}_4\text{C}_9\text{H}_3)\text{Rh}(\text{CO})_2]$ (**9**)

Molecule A			
Rh(1)–C(1)	2.194(5)	Rh(1)–C(2)	2.232(5)
Rh(1)–C(3)	2.221(5)	Rh(1)–C(3A)	2.424(4)
Rh(1)–C(7A)	2.400(4)	Rh(1)–C(12)	1.866(5)
Rh(1)–C(13)	1.857(5)	O(1)–C(12)	1.127(7)
O(2)–C(13)	1.127(7)	C(1)–C(2)	1.393(7)
C(1)–C(7A)	1.466(6)	C(2)–C(3)	1.391(8)
C(3)–C(3A)	1.459(6)	C(3A)–C(4)	1.395(5)
C(3A)–C(7A)	1.417(5)	C(4)–C(5)	1.385(6)
C(4)–C(8)	1.511(7)	C(5)–C(6)	1.424(5)
C(5)–C(9)	1.489(7)	C(6)–C(7)	1.375(5)
C(6)–C(10)	1.510(6)	C(7)–C(7A)	1.404(5)
C(7)–C(11)	1.519(7)		
Molecule B			
Rh(2)–C(1)	2.203(5)	Rh(2)–C(2)	2.224(5)
Rh(2)–C(3)	2.199(5)	Rh(2)–C(3A)	2.419(4)
Rh(2)–C(7A)	2.396(4)	Rh(2)–C(12)	1.860(5)
Rh(2)–C(13)	1.842(5)	O(1)–C(12)	1.119(7)
O(2)–C(13)	1.136(7)	C(1)–C(2)	1.389(8)
C(1)–C(7A)	1.460(7)	C(2)–C(3)	1.402(8)
C(3)–C(3A)	1.461(6)	C(3A)–C(4)	1.399(6)
C(3A)–C(7A)	1.401(6)	C(4)–C(5)	1.397(6)
C(4)–C(8)	1.495(8)	C(5)–C(6)	1.419(6)
C(5)–C(9)	1.500(8)	C(6)–C(7)	1.398(6)
C(6)–C(10)	1.525(7)	C(7)–C(7A)	1.403(6)
C(7)–C(11)	1.500(8)		
Molecule A			
Rh(1)–C(12)–O(1)		179.5(5)	
Rh(1)–C(13)–O(2)		178.2(5)	
C(12)–Rh(1)–C(13)		92.2(2)	
Molecule B			
Rh(2)–C(12)–O(1)		178.8(4)	
Rh(2)–C(13)–O(2)		178.0(5)	
C(12)–Rh(2)–C(13)		92.8(2)	

The unit cell consists of two chemically equivalent, but crystallographically independent, molecules of $[(\eta\text{-}4,5,6,7\text{-Me}_4\text{C}_9\text{H}_3)\text{Rh}(\text{CO})_2]$. The coordination of the metal to the indenyl ligand is unsymmetrical. The Rh–C distances to the ring junction carbons (C(3a,7a)) (av. 2.410(4) Å) are longer than the Rh–C(1,3) distances (av. 2.205(5) Å). The values of the slip-fold parameters for **9** are: $\Delta = 0.205(5)$ Å; FA = 10.9°, and HA = 9.2°.

It has been demonstrated [7d] that the peralkylation of the indenyl ligand in $[(\eta\text{-C}_9\text{R}_7)\text{Rh}(\eta^4\text{-}1,5\text{-COD})]$ (R = H, Me) has no effect on the ground state structure of these molecules. Similar findings were obtained [7e] for the solid state structures of $[(\eta\text{-}4,5,6,7\text{-Me}_4\text{-C}_9\text{H}_3)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$ and $[(\eta\text{-}1\text{-}^n\text{Bu-}2,3,4,5,6,7\text{-Me}_6\text{C}_9)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$ compared with that of the unsubstituted complex, $[(\eta\text{-C}_9\text{H}_7)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$ [7a, 8a]. Slip-fold parameters for these complexes are essentially equivalent.

TABLE 5. Positional and thermal parameters for $[(\eta\text{-}4,5,6,7\text{-Me}_4\text{C}_9\text{H}_3)\text{Rh}(\text{CO})_2]$ (**9**)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Molecule A				
Rh(1)	6611.8(4)	2239.1(4)	8261.0(1)	59.2(1)
O(1)	4163(6)	4709(5)	8444(2)	124(2)
O(2)	4052(7)	514(6)	7372(2)	150(2)
C(1)	9014(6)	3195(6)	8744(3)	72(2)
C(2)	9500(6)	2415(6)	8185(3)	76(2)
C(3)	8981(6)	914(6)	8248(2)	70(2)
C(3A)	8440(5)	674(4)	8918(2)	53(1)
C(4)	7953(5)	−615(4)	9254(2)	55(1)
C(5)	7525(4)	−464(4)	9907(2)	54(1)
C(6)	7492(5)	983(5)	10213(2)	53(1)
C(7)	7911(5)	2266(4)	9880(2)	55(1)
C(7A)	8445(5)	2108(4)	9231(2)	53(1)
C(8)	7936(9)	−2114(6)	8894(4)	81(2)
C(9)	7032(8)	−1800(7)	10297(3)	76(2)
C(10)	6988(8)	1092(7)	10921(2)	76(2)
C(11)	7767(10)	3846(6)	10157(4)	84(2)
C(12)	5079(7)	3775(6)	8375(2)	79(2)
C(13)	5030(7)	1144(6)	7710(3)	87(2)
Molecule B				
Rh(2)	1472.7(4)	2679.0(4)	3237.9(1)	61.1(1)
O(1)	−761(6)	−51(5)	3488(2)	119(2)
O(2)	−1269(6)	3935(6)	2377(2)	143(2)
C(1)	4023(6)	2140(7)	3668(3)	73(2)
C(2)	4322(6)	2885(7)	3089(3)	81(2)
C(3)	3674(7)	4319(7)	3157(2)	76(2)
C(3A)	3254(5)	4576(5)	3843(2)	59(1)
C(4)	2709(5)	5853(4)	4173(2)	61(1)
C(5)	2418(5)	5725(5)	4843(2)	63(1)
C(6)	2582(5)	4340(5)	5162(2)	58(1)
C(7)	3081(5)	3059(4)	4823(2)	59(1)
C(7A)	3442(5)	3210(4)	4157(2)	58(1)
C(8)	2486(9)	7269(7)	3808(4)	90(2)
C(9)	1875(8)	7052(7)	5237(3)	83(2)
C(10)	2201(9)	4260(9)	5890(3)	83(2)
C(11)	3178(10)	1549(7)	5127(3)	93(2)
C(12)	92(7)	969(6)	3399(2)	77(2)
C(13)	−226(7)	3476(6)	2714(3)	88(2)

^aEquivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

An inspection of Table 6 indicates that a similar situation exists for **9** versus **2**. The structures of these two molecules are virtually identical. All Rh–C(indenyl ring), Rh–C(CO) distances, and C–O distances, are statistically equivalent at the 3σ level in both molecules. In fact, the numbers rarely deviate by more than 1σ .

These results clearly demonstrate that specific modifications of the indenyl ligand by alkylation, have no effect on the ground state structure of the resulting $[(\text{indenyl})\text{RhL}_2]$ complexes. Hence, the reasons for slower rates of CO substitution in **9** cannot possibly be explained on the basis of ground state structural effects.

TABLE 6. Slip-fold parameters and selected bond lengths for $[(\eta\text{-}4,5,6,7\text{-Me}_4\text{C}_9\text{H}_3)\text{Rh}(\text{CO})_2]$ (**9**) and **2**

	Complex 2	Complex 9	
Δ (Å)	0.200(7)	Mol. A	0.204(5)
		Mol. B	0.207(5)
		av.	0.205(5)
HA (°)	9.2	Mol. A	10.2
		Mol. B	10.5
		av.	10.3
FA (°)	10.9	Mol. A	10.4
		Mol. B	10.8
		av.	10.6
$d[\text{M}-\text{C}(1,3)]$ (av.) (Å)	2.211(7)	Mol. A	2.208(5)
		Mol. B	2.201(5)
		av.	2.205(5)
$d[\text{M}-\text{C}_2]$ (av.) (Å)	2.222(8)	Mol. A	2.232(5)
		Mol. B	2.224(5)
		av.	2.228(5)
$d[\text{M}-\text{C}(3a,7a)]$ (av.) (Å)	2.411(7)	Mol. A	2.412(4)
		Mol. B	2.408(4)
		av.	2.410(4)
$d[\text{Rh}-\text{C}(\text{CO})]$ (av.) (Å)	1.857(10)	Mol. A	1.862(5)
		Mol. B	1.851(5)
		av.	1.857(5)
$d[\text{C}-\text{O}]$ (av.) (Å)	1.132(12)	Mol. A	1.127(7)
		Mol. B	1.128(7)
		av.	1.128(7)

Proposed mechanism

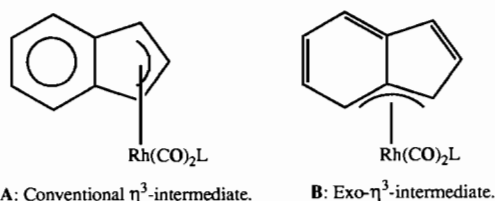
On the basis of electronic factors, it was expected that the second-order rate constants for CO substitution would in fact parallel the trends observed in the IR spectra of the $[(\text{indenyl})\text{Rh}(\text{CO})_2]$ complexes. Thus, we anticipated that increased electron density at Rh, reflected in decreasing values for $\nu(\text{CO})$ (increasing $\Delta\nu(\text{CO})$), would result in decreased rates for CO substitution. For the most part, this trend is in fact followed. For example, the rate for CO substitution in $[(5,6\text{-Cl}_2\text{C}_9\text{H}_5)\text{Rh}(\text{CO})_2]$ (**1**) is 2.3 times faster than that in the parent complex **2**, and that for $[(\eta\text{-C}_9\text{Me}_7)\text{Rh}(\text{CO})_2]$ (**11**) is 137 times slower than in **2**. Previous studies [2d] indicated a factor of $c. 5 \times 10^2$ for the relative rates of CO substitution in **11** versus **2**, which is not far from that found in the present study. However, the rate constant for **9** was found to be lower than that for **10**, which is not in keeping with the $\Delta\nu(\text{CO})$ values. In addition, steric arguments, based on a conventional $[(\eta^3\text{-M}(\text{CO})_2\text{L})]$ intermediate, would also predict lower rates for **10** versus **9**. An examination of **6** and **4** indicated that methylation at carbons 5 and 6 had little effect on either k_2 or $\Delta\nu(\text{CO})$, whereas methylation at

carbons 4 and 7 significantly decreased k_2 but had little influence on $\Delta\nu(\text{CO})$.

For an $\text{S}_{\text{N}}2$ substitution process, the LUMO of the complex must also be considered in addition to electron density at the metal centre. Changes in the energy of the LUMO will not necessarily be reflected in the values of $\Delta\nu(\text{CO})$ as the latter will be influenced only by the energies of filled molecular orbitals. Destabilization of the LUMO by substitution with π -donor groups is expected to result in decreased rates for the $\text{S}_{\text{N}}2$ substitution processes. Extended Hückel molecular orbital calculations [25, 26] on **2**, employing a model planar indenyl ligand, indicate that the molecular LUMO has a significant contribution from the LUMO of the indenyl anion, which in turn has its largest coefficients at carbons 4 and 7. Thus, substitution with π -donors at these carbons would be expected to destabilize the LUMO of the anion as well as the LUMO of the $\text{Rh}(\text{CO})_2$ complex. The HOMO will also be destabilized, but to a much lesser extent than the LUMO. In fact, preliminary EHMO calculations on the model anion $[4,7\text{-HO})_2\text{C}_9\text{H}_5]^-$ and the complex $\eta\text{-}4,7\text{-(HO)}_2\text{C}_9\text{H}_5\text{Rh}(\text{CO})_2$ bear out these predictions. A similar situation would be expected for substitution at carbons 5 and 6 but the effect will be smaller due to the lesser contribution of the p_z orbitals on C(5,6) to the molecular LUMO. In addition, one would anticipate that MeO groups would cause a significantly greater perturbation than methyl groups. This is in keeping with the order of the substitution rate constants for **3** versus **4**. What is surprising is that the observed effect is not larger and that methylation at positions C(4,5,6,7) (and especially at C(4,7)) does cause such a large decrease in substitution rates. Attempts to correlate the rate constants, taken as $\log(k_2(\text{complex})/k_2(\mathbf{2}))$, with any Hammett constants also failed to produce meaningful plots. Thus, we are forced to consider possible steric constraints in addition to electronic factors.

It should also be borne in mind that in a conventional $[\eta^3\text{-M}(\text{CO})_2\text{L}]$ intermediate, the hinge angle between the allylic-C(3) group and the six-membered ring will be in the order of 22–28°. This serves to partially decouple the two π -systems as the six-membered ring rearomatizes. Thus, one might expect that the electronic influence of substituents at C(4,7) might not be felt as strongly in this intermediate as they might in the transition state. Similar arguments would apply to steric demands of substituents at C(4,7): these would have a greater influence on the transition state than on the η^3 -intermediate.

In any event, we find it difficult to explain the large perturbation in k_2 caused by methylation at positions 4–7 (cf. **9** versus **2** or **11** versus **10** in Table 2). Again, methylation at C(5,6) actually *increases* the value of k_2



A: Conventional η^3 -intermediate. B: Exo- η^3 -intermediate.

Fig. 9. η^3 -Indenyl intermediates.

slightly (**6** versus **2**) and thus, positions 4 and 7 seem most important. These factors lead us to consider the possibility of an unexpected *exo- η^3* species B (Fig. 9) lying along the reaction pathway for ligand substitution.

Clearly B would be expected to be higher in energy than A, and it is A that has been documented crystallographically in previous work [5b, 6]. However, if a structure such as B is involved anywhere along the positional surface for the substitution reaction, it would serve to explain the apparent steric hindrance observed at positions 4 and 7 which are now π -bonded to Rh. Such a structure has yet to be observed spectroscopically, although similar *exo*-structures have been proposed as intermediates or transition states for haptotropic rearrangements in indenyl, fluorenyl and naphthalene complexes [27, 28].

We must exercise due caution in our assessment of the reaction mechanism. There seems to be ample reason to be suspicious of a conventional pathway, but there may be energetic problems associated with the *exo- η^3* species. In summary, an unusual and unexpected influence of methyl and methoxy groups at C(4,7) was observed in the CO substitution reactions. As a proposal, we put forth a novel mechanism involving an *exo- η^3* intermediate which would be consistent with steric constraints caused by CH_3 and OCH_3 moieties at C(4,7). It is also possible that orbital constraints force the nucleophile to attack Rh via a trajectory which takes it towards Rh from under the six-membered ring. This would still allow for a steric effect at positions 4 and 7, and the possibility of a conventional *endo- η^3* intermediate. Further molecular orbital calculations will be required to address the relative importance of these issues in more detail.

Conclusions

This study shows that changes in (i) the nature of the indenyl ligand and (ii) the nature of the incoming ligand (L) have an effect on the rate of substitution reactions of these complexes. The effect of incoming ligand can be separated into electronic and steric com-

ponents. The $[C_9H_{7-x}(CH_3)_x]$ ligands are more electron donating than the $[C_9H_7]$ ligand, and are also larger creating a greater steric demand in associative substitutions. Both of these factors contribute to the slower rates of substitution observed for the methyl substituted indenyl complexes. In contrast, substitution with inductively withdrawing Cl at remote carbons 5 and 6 significantly enhances CO substitution rates. A linear free energy relation exists among the effects of substituent groups. The indenyl system has a greater steric demand than the corresponding cyclopentadienyl system.

Supplementary material

Structure determination summary, atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, anisotropic displacement parameters, hydrogen atom coordinates and isotropic displacement parameters, observed and calculated structure factors and a complete listing of bond distance and bond angle data are available from the authors on request. These will also be deposited at the Cambridge Crystallographic Data Centre.

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