We have found that nonrelativistic calculations on binuclear metal complexes uniformly afford the order $\Delta E_{MM}(5d) < \Delta E_{MM}(4d)$. This order might, however, be reversed by relativistic effects, provided that the $(n + 1)$s metal orbitals have a substantial contribution to the metal–metal bond as in Ag_2 and Au_2[8] or Mo_2H_6 and W_2H_6.[5b] A modest participation from $(n + 1)$s in the metal–metal bond will on the other hand result in too small a contribution from the relativistic effects to reverse the nonrelativistic order $\Delta E_{MM}(5d) < \Delta E_{MM}(4d)$, as in the case of the $M_2Cl_4(PH_3)_4$ systems.

We would expect that the contribution to the metal–metal bond from the relatively diffuse $(n + 1)$s orbital is considerably increased and the contribution from the more contracted nd orbitals decreased in metal–bulk compared to $M_2Cl_4(PH_3)_4$, since the metal–metal bond distance R_{MM} is much longer in bulk than in $M_2Cl_4(PH_3)_4$ (note that R_{MM} in Mo–bulk is 1 Å longer than in $M_2Cl_4(PH_3)_4$!) Our analysis above would thus suggest that the order $\Delta E_{MM}(4d) < \Delta E_{MM}$ observed in bulk is a relativistic effect, brought about by the substantial contribution from the $(n + 1)$s orbital to the metal–metal bond in bulk.

It is hoped that additional theoretical calculations will provide a simple qualitative method by which the involvement of $(n + 1)$s in the metal–metal bond, and thus the order of $\Delta E_{MM}(4d)$ and $E_{MM}(5d)$, can be predicted for any class of binuclear complexes.

Acknowledgment. This investigation was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). We thank Dr. E. J. Baerends and Dr. J. G. Snijders, both from the Free University of Amsterdam, for providing us with the newest version of their HFS-program system and Mr. P. Vernooijs (The Free University of Amsterdam) for installing the HFS-program system on the Cyber-175 installation at the University of Calgary.

Registry No. $Mn_2Cl_4(PH_3)_4$, 91550-28-6; $Mn_2Cl_4(PH_3)_4^+$, 91550-29-7; $Mn_2Cl_4(PH_3)_4^{2+}$, 91550-30-0; $Tc_2Cl_4(PH_3)_4$, 91550-31-1; $Tc_2Cl_4(PH_3)_4^+$, 91550-32-2; $Tc_2Cl_4(PH_3)_4^{2+}$, 91550-33-3; $Re_2Cl_4(PH_3)_4$, 91604-62-5; $Re_2Cl_4(PH_3)_4^+$, 91550-34-4; $Re_2Cl_4(PH_3)_4^{2+}$, 91550-35-5; $Mo_2Cl_4(PH_3)_4$, 80485-12-7; $Mo_2Cl_4(PH_3)_4^+$, 91550-36-6; $Cr_2Cl_4(PH_3)_4$, 91550-37-7; $W_2Cl_4(PH_3)_4$, 80485-13-8.

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(18) The corresponding overlaps for $M_2Cl_4(PH_3)_4$ with M = Cr, Mo, W were the following: Cr [$S_\sigma = 0.168$, $S_\delta = 0.053$, $S_\pi = 0.212$] at $R_{MM} = 1.9$ Å; Mo [$S_\sigma = 0.256$, $S_\delta = 0.081$, $S_\pi = 0.301$] at 2.15 Å; W [$S_\sigma = 0.265$, $S_\delta = 0.075$, $S_\pi = 0.305$] at $R_{MM} = 2.28$ Å. The overlaps of Cr, Mo, and W are larger than the corresponding overlaps with Mn, Tc, and Re, respectively, since the d orbitals on Cr, Mo, and W are more diffuse than the corresponding d orbitals on Mn, Tc, and Re.

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Kinetics and Mechanism of Substitution Reactions of η^5-Cyclopentadienyldicarbonylrhodium(I) Derivatives. Rate Enhancement of Associative Substitution in Cyclopentadienylmetal Compounds[1]

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Abstract: The reactions of $Rh(\eta^5\text{-}C_9H_7)(CO)_2$, $Rh(\eta^5\text{-}C_9(CH_3)_7)(CO)_2$, $Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2$, and $[Rh(\eta^5\text{-}C_5H_4PPh_3)(CO)_2]^+$ with triphenylphosphine (PPh_3) take place readily to form monosubstituted products. These reactions proceed solely by a second-order process, first order in the metal complex and first order in PPh_3. The rates of reaction follow the order $Rh(\eta^5\text{-}C_9H_7)(CO)_2 > Rh(\eta^5\text{-}C_9(CH_3)_7)(CO)_2 > Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2 > [Rh(\eta^5\text{-}C_5H_4PPh_3)(CO)_2]^+$, and all are orders of magnitude greater than that of $Rh(\eta^5\text{-}C_5H_5)(CO)_2$. The reasons for this ordering are discussed in terms of the presumed transition states of these reactions, relative to the corresponding reaction of $Rh(\eta^5\text{-}C_5H_5)(CO)_2$.

In 1966 we reported[2] that the rates of reaction of $Rh(\eta^5\text{-}C_5H_5)(CO)_2$ with a variety of phosphine, phosphite, and isocyanide ligands are dependent on the concentration of both the rhodium complex and the incoming nucleophile. The associative nature of the substitution of this 18-electron compound was explained by transfer of an electron pair from rhodium to the cyclopentadienyl ligand, creating an empty orbital for nucleophilic attack. It seemed necessary at the time that some such process be involved, because it was known[3] that the pseudoisoelectronic $Fe(CO)_5$ undergoes CO substitution very slowly and by a dissociative process. Although our suggestion predated the Tolman[4] 16–18-electron rule, we recognized that formation of a 20-electron species, $Rh(\eta^5\text{-}C_5H_5)(CO)_2L$, was unfavored so that some process by which an 18-electron count at rhodium be maintained seemed appropriate. Since the fundamental difference between $Fe(CO)_5$ and the pseudoisoelectronic $Rh(\eta^5\text{-}C_5H_5)(CO)_2$ is the cyclopentadienyl ligand, it was felt that the cyclopentadienyl ligand allows an associative reaction at the 18-electron rhodium center by accepting an electron pair and creating a vacant low-energy metal orbital to accept a pair of electrons from the entering nucleophile.

Cramer and Seiwell[5] examined the kinetics of substitution for the analogous ethylene complex, $Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2$. Associative substitution was observed with certain nucleophiles, and they also felt that transfer of an electron pair from rhodium to the cyclpentadienyl ligand was essential in the substitution process. They

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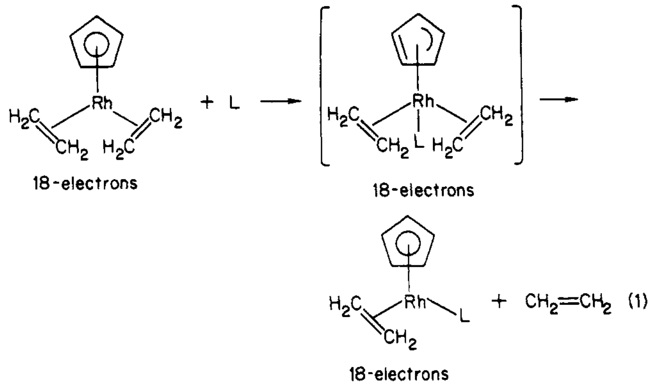
envisioned this process was shown in (1). This was the first proposal of an η^3 "slipped" cyclopentadienyl ligand in associative substitution reactions of transition-metal cyclopentadienyl compounds. Recently, Casey and co-workers[6] have observed η^5 to η^1 slippage of the cyclopentadienyl ligand in a variety of compounds when allowed to react with excess trimethylphosphine (PMe_3). One example[6c] is $Re(C_5\text{-}C_5H_5)(CO)_3$ which adds two PMe_3 ligands to give *fac*-$Re(\eta^1\text{-}C_5H_5)(CO)_3(PMe_3)_2$. The reaction presumably proceeds stepwise via $Re(\eta^3\text{-}C_5H_5)(CO)_3PMe_3$, although no evidence for this intermediate was observed.



Our interest in the associative reactions of organometallic compounds has led us to consider the η^5 to η^3 rearrangement mechanism in greater detail. Several ways may be envisioned to affect the rate of substitution. First is by addition of electron-donating or electron-withdrawing groups to the cyclpentadienyl ring. Electron-donating groups should slow down the rate of S_N2 substitution by making the ring more electron rich, thus less likely to accept an electron pair from the metal. We recently reported[7] that the electron rich pentamethylcyclopentadienyl ligand slows down the rate of CO substitution in $Rh(\eta^5\text{-}C_5(CH_3)_5)(CO)_2$ relative to $Rh(\eta^5\text{-}C_5H_5)(CO)_2$. The decrease in rate was due to electronic and steric factors, and it was not possible to separate them quantitatively. Cramer and Seiwell[5] also found that $Rh(\eta^5\text{-}C_5(CH_3)_5)(C_2H_4)_2$ reacts more slowly than $Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2$. Addition of an electron-withdrawing group to the cyclopentadienyl ligand makes the ring less electron rich, which means it should more readily accept an electron pair from the metal and accelerate S_N2 substitution. For example,[5] it is known that the strongly electron-withdrawing cyano group accelerates S_N2 substitution in $Rh(\eta^5\text{-}C_5H_4CN)(C_2H_4)_2$, relative to $Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2$.

Mawby and co-workers[8] have shown that indenyl compounds undergo substitution reactions more readily than do the analogous cyclopentadienyl compounds. This is true for dissociative as well as associative reactions. Mawby and Hart-Davis[8a] were the frist to propose an η^3-indenyl intermediate for the ligand-dependent methyl migration of $Mo(\eta^5\text{-}C_9H_7)(CO)_3CH_3$, and they suggested that the aromatized benzene of the η^3-indenyl ring would stabilize such an intermediate. Others[9] have used this to explain the greater lability of C_2H_4 in $Rh(\eta^5\text{-}C_9H_7)(C_2H_4)_2$ compared to $Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2$. We recently reported[1b] that $Rh(\eta^5\text{-}C_9H_7)(CO)_2$ reacts 3.8×10^8 times faster with PPh_3 than does $Rh(\eta^5\text{-}C_5H_5)(CO)_2$; we refer[1b] to this tremendous rate enhancement as the *indenyl ligand effect*.

One other method of increasing the rate of S_N2 substitution is to provide a positive charge on the complex; cationic carbonyls are more susceptible to nucleophile attack then are corresponding neutral compounds. An example[10] where this has been qualitatively observed is $[Mo(\eta^5\text{-}C_5H_5)(CO)(NO)_2]^+$ which replaces CO with PPh_3 under milder conditions than does the isoelectronic $Mo(\eta^5\text{-}C_5H_5)(CO)_2NO$.

All of these methods of altering the rate of S_N2 substitution may be applied to 18-electron dicarbonylrhodium species, allowing a quantitative comparison of these effects. Herein we report the kinetics of CO substitution by PPh_3 in the compounds $Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2$, $Rh(\eta^5\text{-}C_9H_7)(CO)_2$, $Rh(\eta^5\text{-}C_9(CH_3)_7)(CO)_2$, and $[Rh(C_5H_4PPh_3)(CO)_2]^+$. Since creation of a vacant coordination site is fundamental to catalytic processes, an understanding of how coordinatively saturated organometallic compounds react by associative mechanisms is relevant to synthetic and catalytic transformations.

Experimental Section

Compounds and Solvents. All experimental operations were carried out under an atmosphere of N_2. Hexanes were stored over H_2SO_4 and then distilled from Na/benzophenone. Toluene was distilled from Na and then bubbled with N_2 for 1 h when used for kinetic measurements. Tetrahydrofuran was distilled from Na/bvenzophenone, and dichloromethane was distilled from P_2O_5. Acetonitrile was distilled twice from P_2O_5, and methanol was distilled from Mg. Cyclohexane was distilled from Na.

Triphenylphosphine was recrystallized from ethanol before use in kinetic experiments. The compounds $[Rh(\eta^5\text{-}C_5H_4PPh_3)(CO)_2]BF_4$,[11] $[Rh(\eta^5\text{-}C_kH_4PPh_3)(CO)(PPh_3)]BF_4$,[11] and $Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2$[12] were prepared by methods described in the literature and were characterized by their IR and NMR spectra. Heptamethylindene was obtained as a generous gift from Professor David Bergbreiter of Texas A&M University. Indene (Aldrich) was reduced with NaH, and heptamethylidene was reduced with *n*-butyllithium, for use in synthetic reactions.

$Rh(\eta^5\text{-}C_9H_7)(CO)_2$. A solution of 0.5 g of $[Rh(CO)_2Cl]_2$ and 1.0 g of NaC_9H_7 (2.5-fold excess) in 25 mL of THF was stirred at room temperature for 12 h. The THF was removed in vacuo, 30 mL of hexane was added, and the solution was stirred vigorously. The solution was filtered to remove any solids and was bubbled with CO for 30 min to remove any $Rh_3(C_5\text{-}C_9H_7)_3(CO)_3$ which formed. Addition of CO rapidly changes the solution from green (trimer) to yellow (monomer). Solvent was removed in vacuo, and the solid was sublimed at 40 °C and 0.01 mmHg to afford 0.42 g (61%) as yellow needles: $\nu_{CO} = 2048, 1993\ cm^{-1}$ (hexane); $\lambda_{max} = 340$ nm (ϵ 5940) in toluene. The IR spectra agree with that previously reported.[7b]

$Rh(\eta^5\text{-}C_9H_7)(CO)PPh_3$. A solution of 0.120 g of $Rh(\eta^5\text{-}C_9H_7)(CO)_2$ in 12 mL of hexane was prepared, then 0.115 g of PPh_3 (1:1) was added by ampule transfer with constant stirring. A bright yellow precipitate immediately formed. The solution was stirred for 10 min and then filtered to afford 0.130 g of $Rh(\eta^5\text{-}C_9H_7)(CO)PPh_3$ (59%) as a bright yellow powder. Anal. Calcd: C, 66.15, H, 4.37. Found: C, 65.89; H, 4.40. $\nu_{CO} = 1967\ cm^{-1}$ (hexane); $\lambda_{max} = 362$ nm (ϵ 6630) in toluene.

$Rh(\eta^5\text{-}C_9(CH_3)_7)(CO)_2$. A solution of 1.0 g of $C_9(CH_3)_7H$ in 30 mL of THF was prepared and then 3 mL of 1.6 M *n*-BuLi/hexane (Aldrich, 1:1) was added, producing a deep yellow solution. After the solution was stirred for 1 h, a solution of 0.5 g of $[Rh(CO)_2Cl]_2$ in 10 mL of THF was added dropwise, and after this addition the mixture was completely stirred for 16 h at room temperature. The THF was removed in vacuo, 30 mL of hexane was added, and the mixture was stirred and filtered. A second portion of hexane (15 mL) was added to the residue and then filtered. The combined hexane solutions were bubbled with CO for 30 min to remove any trimeric impurities. Hexane was removed in vacuo and the solid was recrystallized from pentane at −72 °C to afford 0.384 g of $Rh(\eta^5\text{-}C_9(CH_3)_7)(CO)_2$ (41.7%) as a light brown solid. The compound appears to decompose upon sublimation. Anal. Calcd: C, 60.36, H, 5.92. Found: c, 60.87; H, 6.02. $\nu_{CO} = 2020, 1967\ cm^{-1}$ (hexane); $\lambda_{max} = 360$ nm (sh, ϵ 2750) in toluene.

$Rh(\eta^5\text{-}C_9(CH_3)_7)(CO)PPh_3$. A solution of 0.100 g of $Rh(\eta^5\text{-}C_9(CH_3)_7)(CO)_2$ in 5 mL of hexane was prepared and then 0.074 g of PPh_3 (1:1) was added by ampule transfer. The solution was allowed to stir for 30 min while a bright orange precipitate formed and then the precipitate was collected by filtration: collected 0.123 g of $Rh(\eta^5\text{-}C_9(CH_3)_7)$-

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Table I. Rate Constants and Activation Parameters for the Reaction $Rh(L)(CO)_2 + PPh_3 \rightarrow Rh(L)(CO)PPh_3 + CO$ in Toluene

compound	T, °C	k, $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$[Rh(\eta^5\text{-}C_5H_4PPh_3)(CO)_2]^{+\,a}$	25	2.54×10^{-2}	+13.3	−21.2
	16	1.20×10^{-2}		
	6	5.11×10^{-3}		
$Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2$	25	1.26	+12.0	−17.9
	37	2.58		
	49	6.14		
$Rh(\eta^5\text{-}C_9(CH_3)_7)(CO)_2$	21	44		
$Rh(\eta^5\text{-}C_9H_7)(CO)_2$	21	2.8×10^4		
$Rh(\eta^5\text{-}C_5H_5)(CO)_2{}^b$	40	3.1×10^{-4}	$+15^c$	-20^c

[a] In CH_2Cl_2. [b] Reference 2. [c] For PEt_2Ph, not PPh_3.

$(CO)PPh_3$ (74.4%) as orange crystals. Anal. Calcd: C, 69.30; H, 5.99. Found: C, 69.24, H, 6.23. $\nu_{CO} = 1953\ cm^{-1}$ (hexane); $\lambda_{max} = 380$ nm (sh, ϵ 5260) in toluene.

$Rh(\eta^5\text{-}C_5H_4NO_2)(CO)PPh_3$. A solution of 0.058 g of $Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2$ in 5 mL of hexane was prepared and then 0.056 g PPh_3 (1:1) was added by ampule transfer. The solution was stirred for 1 h during which a crimson precipitate formed. The precipitate was collected by filtration to give 0.077 g of $Rh(\eta^5\text{-}C_5H_4NO_2)(CO)PPh_3$ (71.1%) as a red powder. Anal. Calcd: C, 57.27; H, 3.81; N, 2.78. Found: C, 56.53; H, 4.04; N, 2.66. $\nu_{CO} = 1980\ cm^{-1}$ (hexane); $\lambda_{max} = 380$ nm (ϵ 1.28×10^4) in toluene.

Instrumentation. A Perkin-Elmer Model 283 spectrometer was used to record IR spectra, and a Perkin-Elmer Model 330 spectrophotometer was used to record UV–vis spectra. For kinetic measurements, the time drive mode was used. The reactions of $Rh(\eta^5\text{-}C_9H_7)(CO)_2$ and $Rh(\eta^5\text{-}C_9(CH_3)_7)(CO)_2$ with PPh_3 in toluene were monitored by using an Applied Photophysics Ltd. Model 1705 stopped-flow spectrophotometer adapted for air-sensitive work. We were not able to obtain satisfactory results at lower or elevated temperatures so that the activation parameters for these two compounds were not obtained. A JEOL-270X spectrometer was used to record NMR spectra. Compounds were stored in a Vacuum Atmospheres glovebox, and solutions were prepared by ampule transfer. A Neslab RTE-8 refrigerated circulating bath connected to a 1-cm-jacketed cell holder was used to thermostat reactions of $Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2$ and $[Rh(C^5\text{-}C_5H_4PPh_3)(CO)_2]^+$ with PPh_3.

Kinetic Measurement. All reactions were studied by near-UV spectrophotometry. Reactions of $Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2$ and $[Rh(C_5\text{-}C_5H_4PPh_3)(CO)_2]^+$ with PPh_3 were examined as follows: a solution of PPh_3 in an appropriate solvent was added to a 1-cm quartz cell adapted for air-sensitive work. The cell was placed in a thermostated cell holder and allowed to equilibrate. A solution of complex (50 mL) was then added to the cell and shaken. The compounds $Rh(\eta^5\text{-}C_9H_7)(CO)_2$ and $Rh(C_5\text{-}C_9(CH_3)_7(CO)_2$ were studied by using stopped-flow spectrophotometry. Rate constants were determined by monitoring the increase in absorption at λ_{max} of the appropriate PPh_3-substituted product as a function of time. These wavelengths are given with the preparation of these compounds; for $[Rh(\eta^5\text{-}C_5H_4PPh_3)(CO)(PPh_3)]^+$ $\lambda_{max} = 380$ nm. A plot of $\ln((A - A_\infty)/(A_0 - A_\infty))$ vs. time was linear for more than three half-lives, and k_{obsd} was determined from the slope of this line by the least-squares method. The correlation coefficient of the least-squares line ($R^2 > 0.996$) was very good. All kinetic experiments were carried out under pseudo-first-order conditions with at least a tenfold excess of nucleophile. All reactions proceed to completion to give the appropriate PPh_3-substituted product.

Results

The compounds $Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2$, $[Rh(\eta^5\text{-}C_5H_4PPh_3)(CO)_2]^+$, $Rh(\eta^5\text{-}C_9H_7)(CO)_2$, and $Rh(\eta^5\text{-}C_9(CH_3)_7)(CO)_2$ all react with PPh_3 as shown in (2). The rates

$$Rh(L)(CO)_2 + PPh_3 \rightarrow Rh(L)(CO)PPh_3 + CO \qquad (2)$$

$$L = C_5H_4NO_2^-,\ C_5H_4PPh_3,\ C_9H_7^-,\ C_9(CH_3)_7^-$$

of reaction are first order in complex and first order in PPh_3 for all compounds. Plots of k_{obsd} vs. $[PPh_3]$ are linear with a zero intercept, indicating no detectable dissociative substitution taking place for (2). Table I gives the rate constants and activation parameters. Activation parameters were not obtained for $L = C_9H_7^-$ and $C_9(CH_3)_7^-$ due to experimental limitations of our stopped-flow apparatus. Table II lists the CO stretching frequencies (ν_{CO}) and relative rates for this reaction compared to $L = C_5H_5^-$. The relative rates of this reaction are $C_9H_7^- > C_9(CH_3)_7^- > C_5H_4NO_2^- > C_5H_4PPh_3 > C_5H_5^-$. Results of a solvent dependency study for the substitution reaction of $L = C_5H_4NO_2^-$ are shown in Table III. There is a factor of ten increase in the rate of reaction going from tetrahydrofuran to methanol.

Table II. Relative Rates of CO Substitution of Some Dicarbonylrhodium Compounds and Their Carbonyl Stretching Frequencies

compound	k_{rel}	ν_{CO}, cm^{-1}
$Rh(\eta^5\text{-}C_9H_7)(CO)_2$	3.8×10^8	2048, 1993
$Rh(\eta^5\text{-}C_9(CH_3)_7)(CO)_2$	6.1×10^5	2021, 1965
$Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2$	1.2×10^4	2067, 2011
$[Rh(\eta^5\text{-}C_5H_4PPh_3)(CO)_2]^+$	1.1×10^2	2062, 2002^a
$Rh(\eta^5\text{-}C_5H_5)(CO)_2$	1	2051, 1985^b
$Rh(\eta^5\text{-}C_5(CH_3)_5)(CO)_2$	$2.2 \times 10^{-2\,c}$	2020, 1967

[a] In CH_3NO_2. [b] Reference 22. [c] For L = n-Bu_3.

Table III. Solvent Effect on the Rate of the Reaction $Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2 + PPh_3 \rightarrow Rh(\eta^5\text{-}C_5H_4NO_2)(CO)PPh_3 + CO$ at 25 °C

solvent	ϵ, $M^{-1}\ cm^{-1}$	k_1, $M^{-1}\ s^{-1}$
tetrahydrofuran	7.58	0.963
toluene	2.38	1.26
dichloromethane	8.93	2.81
cyclohexane	2.02	3.92
n-hexane	1.88	4.44
acetonitrile	38.8	9.58
methanol	32.7	10.4

Discussion

All four compounds studied, $[Rh(\eta^5\text{-}C_5H_4PPh_3)(CO)_2]^+$, $Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2$, $Rh(\eta^5\text{-}C_9(CH_3)_7)(CO)_2$, and $Rh(\eta^5\text{-}C_9H_7)(CO)_2$, undergo substitution of CO by PPh_3, with a rate which is directly dependent on the concentration of PPh_3. The activation parameters (Table I) for the substitution of CO by PPh_3 in $[Rh(\eta^5\text{-}C_5H_4PPh_3)(CO)_2]^p$ and in $Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2$ support the associative nature of the reaction, especially the negative values of $\Delta S^{\ddagger}$. Substitution of CO by PPh_3 in the compounds $[Rh(\eta^5 hC_5H_4PPh_3)(CO)_2]^+$, $Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2$, $Rh(\eta^5\text{-}C_9(CH_3)_7)(CO)_2$, and $Rh(\eta^5\text{-}C_9H_7)(CO)_2$ occurs at a faster rate than in the parent compound, $Rh(\eta^5\text{-}C_kH_5)(CO)_2$. The reasons for this rate enhancement are best understood when considering each compound individually.

As shown in Table II, $Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2$ reacts 1.2×10^4 times faster with PPh_3 in toluene at 25 °C then does $Rh(\eta^5\text{-}C_5H_5)(CO)_2$. Although there is no question that the nitro substituent is responsible for this increase in rate, there are several ways in which it may do so. According to the mechanism for S_N2 reactions of 18-electron cyclopentadienylmetal compounds shown in (1), any change in the ring is expected to influence the transition state to a much greater extent than the ground state. However, as shown in Table II, addition of the strongly electron-withdrawing nitro group to the cyclopentadienyl ring results in a shift of ν_{CO} to higher frequency, relative to $Rh(\eta^5\text{-}C_5H_5)(CO)_2$. This shift to higher frequency is attributed to the reduced nature of back-bonding between rhodium and carbon, making the CO bond closer to the triple bond in free CO. The nitro group is causing the ring to pull more electron density away from the metal in the ground state, suggesting that the nitro compound may also have a greater tendency to accept electron density from the metal in the transition state, relative to the parent cyclopentadienyl compound. These two effects may be illustrated by writing the two resonance structures for each species in the reaction as shown in (3).

Each structure has an importance in this reaction. Mechanistically, it is important to try to determine how much of a contribution the 16-electron fulvenic structure shown in (3b) makes to the ground state. It is known[13] that 16-electron species, such

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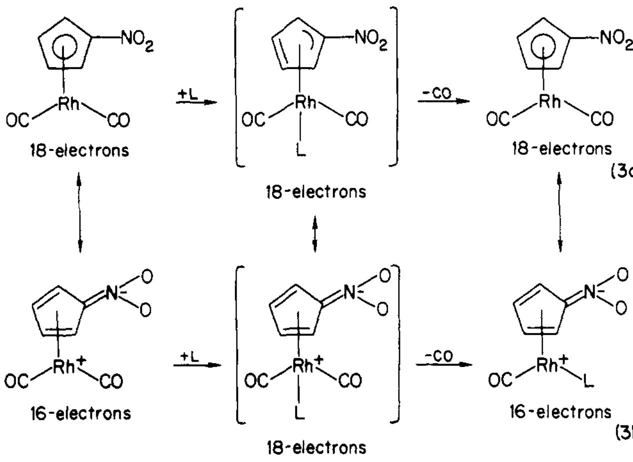
(13) (a) Basolo, F.; Chatt, J.; Gray, H. B.; Pearson, R. G.; Shaw, B. R. *J. Chem. Soc.* **1961**, *2207*. (b) Belluco, V.; Ettone, R.; Basolo, F.; Pearson, R. G.; Turco, A. *Inorg. Chem.* **1966**, *5*, 591.

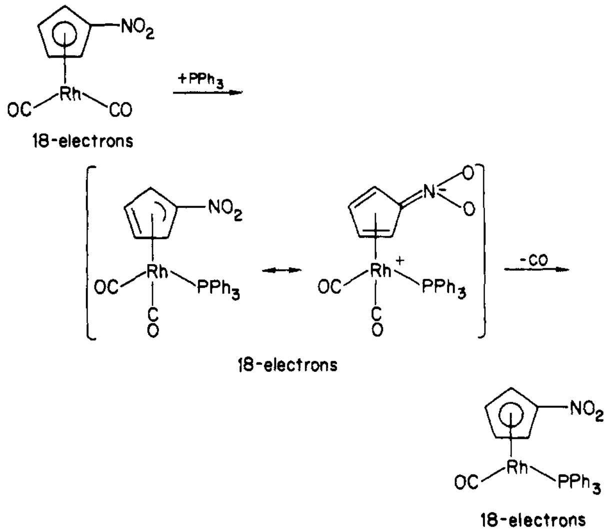


(3a)

(3b)

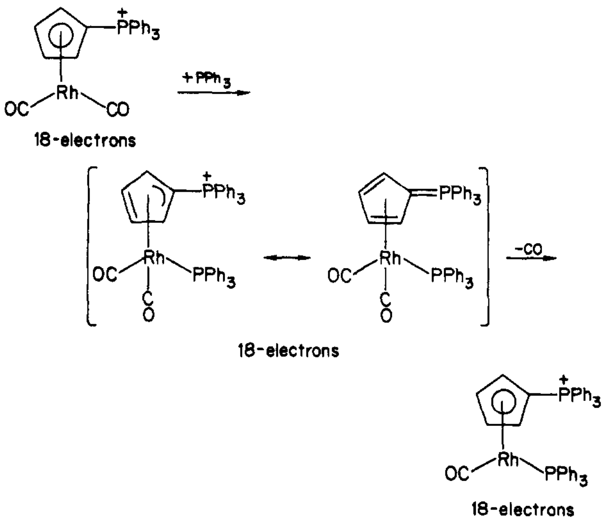
as Pt(II) square-planar compounds, undergo S_N2 substitution reactions readily, because the 16-electron complexes already have the vacant orbital necessary for S_N2 attack. Atwood and co-workers[12] have reported the crystal structure of $Rh(\eta^5-C_5H_4NO_2)(CO)_2$. Although there is a large degree of nonpolarity in the nitrocyclopentadienyl ligand, suggesting some contribution from the fulvenic representation in (3b), the Rh–C bond distances to the cyclopentadienyl ring and the C–C bond distances in the ring are more consistent with the cyclopentadienyl representation in (3a).

Neither reaction path, (3a) nor (3b) is expected to show a dependence on solvent polarity, since there is no change in the polarity of the transition state relative to the ground state. However, if the resonance structure of the transition state in (3b) makes an important contribution to reaction path 3a, then the rates of substitution are expected to increase with increasing polarity of the solvent. If instead the resonance structure of the transition state in (3a) makes an important contribution to reaction path 3b, then the rates of substitution should decrease with increasing polarity of solvent. Table III gives the results of the solvent dependence study on the substitution of CO by PPh_3 in $Rh(\eta^5-C_5H_4NO_2)(CO)_2$. A tenfold increase in the rate of substitution is observed in going from tetrahydrofuran to methanol as solvents. With the exception of *n*-hexane and cyclohexane, the rates of reaction increase with increasing solvent dielectric constants. This is consistent with reaction pathway (3a), having a contribution from the fulvenic resonance structure (path 3b) in the transition state. Although larger rate enhancements for increasing solvent polarity (40–70 times) are observed[14] for organic reactions in which developing charge separation is important in the transition state such as the reaction of amines with alkyl iodides, a tenfold increase suggests a large contribution from the charged separated fulvenic transition state for the reaction of $Rh(\eta^5-C_5H_4NO_2)(CO)_2$ with PPh_3. The rate enhancement of 1.2×10^4 upon addition of the nitro substituent relevant to hydrogen in the cyclopentadienyl ring is comparable to what is observed in nucleophilic aromatic substitution. An example[15] is 2,4-dinitrochlorobenzene which undergoes reaction with methoxide 6.73×10^5 times faster than does 2-nitrochlorobenzene in methanol. The rate enhancement is attributed to the cyclohexadiene resonance form available to 2,4-dinitrochlorobenzene which is not available to 2-nitrochlorobenzene. This is analogous to the proposed fulvenic transition state. Thus, on the basis of our present evidence, we prefer to write the mechanism for the substitution of CO by PPh_3 in $Rh(\eta^5-C_5H_4NO_2)(CO)_2$ as shown in (4). The principal effect of the nitro substituent on the rate of CO substitution in this Rh complex appears to be on the transition state, not the ground state, although it is known that the nitro group does affect the ground state.



(4)

Tresoldi, Recca, Finocchiaro, and Faraone[11] report the syntheses and characterizations of $[Rh(\eta^5-C_5H_4PPh_3)(CO)_2]PF_6$ and of $[Rh(\eta^5-C_5H_4PPh_3)CO)(CPPh_3)]PF_6$. In their communication they report the qualitative observation that $[Rh(\eta^5-C_5H_4PPh_3)(CO)_2]^+$ reacts with PPh_3 under milder conditions than does $Rh(\eta^5-C_5H_5)(CO)_2$. We have examined the kinetics of this reaction in dichloromethane (Table I), and in accord with the observation of Faraone and co-workers,[11] $[Rh(\eta^5-C_5H_4PPh_3)(CO)_2]^+$ undergoes substitution of CO by PPh_3 1.1×10^2 times faster than does $Rh(\eta^5-C_5H_5)(CO)_2$. This rate enhancement can be attributed to the cationic charge on the complex. Faraone and co-workers[11] have shown by ^{13}C NMR spectroscopy that the triphenylphosphonium cyclopentadienylide ligand is pentahapto, with the positive charge principally on the phosphorus atom. The triphenylphosphonium group has an electron-withdrawing effect on the ring, as reflected in the values of ν_{CO} for this compound; they are at higher frequency than those of $Rh(\eta^5-C_5H_5)(CO)_2$ (Table II). Since the rate enhancement is smaller than that observed for $Rh(\eta^5-C_5H_4NO_2)(CO)_2$, it is believed that the $C_5H_4PPh_3$ ring is not as electron withdrawing as is the $C_5H_4NO_2^-$ ring (vide infra). The $C_5H_4PPh_3$ also has an ylide resonance form which may contribute to the transition state, as is shown in (5).



(5)

The indenyl ligand has been shown by Mawby and co-workers[8] to accelerate both S_N1 and S_N2 substitutions of CO at metal centers. We recently reported[1b] that $Rh(\eta^5-C_9H_7)(CO)_2$ reacts 3.8×10^8 times faster with PPh_3 in toluene than does the analogous cyclopentadienyl compound, and we referred to this as the *indenyl ligand effect*. This tremendous rate enhancement merits further comment. As shown in Table II, $Rh(\eta^5-C_9H_7)(CO)_2$ and $Rh(\eta^5-C_5H_5)(CO)_2$ have almost identical values of ν_{CO}, indicating that the electronic environment at the metal is very similar. One

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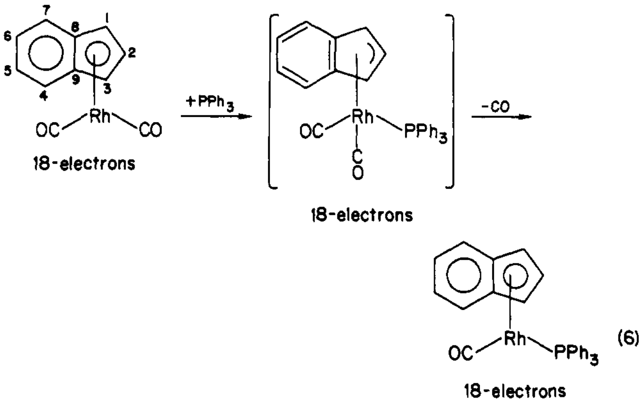
[14] (a) Menshutkin, N. *Z. Phys. Chem. Stoechiom. Verwandtschaftsl.* **1890**, *5*, 589. (b) Cox, H. E. *J. Chem. Soc.* **1921**, *119*, 142. (c) Hawkins, J. A. *Ibid.* **1922**, *121*, 1170.

[15] Miller, J.; Parker, A. J. *Aust. J. Chem.* **1958**, *11*, 302.

fundamental question is whether the idenyl ligand is trihapto or pentahapto, giving rise to a 16-electron or 18-electron metal compound, respectively. If the indenyl complex is a 16-electron species, comparison with Rh(η^5-C_5H_5)$(CO)_2$ is inappropriate. Köhler[16] has shown that ^{13}C NMR is an effective method for distinguishing between η^3 and η^5 indenyl ligands. The key to making this distinction is the resonance positions for C(8) and C(9) (quarternary carbons). In general, if these resonances occur at a higher field than the arene C–H resonances, they are bonded to the metal center. This is also true for fluorenylmetal compounds.[17] We observe the resonances for C(8) and C(9) at 118.3 ppm, relative to Me_4Si, which is in the metal-coordinated range. Nixon and Eshtiagh-Hosseini[9a] observed this resonance at 112.3 ppm for Rh(η^5-C_9H_7)$(C_2H_4)_2$ and concluded that the indenyl ligand is pentahapto, as do we. Since the indenyl and cyclopentadienyl compounds are similar, the tremendous difference in rate must be due to a difference in their transition states for substitution reactions. The mechanism of S_N2 reactions of indenylmetal compounds, first proposed by Mawby and Hart-Davis,[8a] is shown in (6). The complete aromatization of benzene in the transition state is said to be the reason for the large rate enhancement of indenyl over cyclopentadienyl in these substitution reactions. That rhodium is particularly effective in allowing an η^5-to-η^3 shift may reflect the ease with which rhodium forms allyl species. An example[18] is the facile isomerization of 1,3 and 1,4 dienes by Rh(I) which proceeds via allylic hydride species.



(6)

Further information on the indenyl substitution process can be gained by adding substitution groups to the five-membered ring. We have prepared the new heptamethylindenyl compound Rh(η^5-$C_9(CH_3)_7$)$(CO)_2$ by reaction of $Rh_2(CO)_4Cl_2$ with $LiC_9(CH_3)_7$ in THF at room temperature. The compound was characterized by IR, NMR, and UV–vis spectroscopy and elemental analyses. Unlike the indenyl analogue, it decomposes upon sublimation. The solid is stable at room temperature under N_2 for periods greater than 6–9 months. Methyl substitution makes the ring more electron rich; ν_{CO} shifts to lower frequency relative to Rh(η^5-C_9H_7)$(CO)_2$ (Table II). It is interesting to note that whereas Rh(η^5-C_9H_7)$(CO)_2$ and Rh(η^5-C_5H_5)$(CO)_2$ have almost identical ν_{CO}, so do Rh(η^5-$C_9(CH_3)_7$)$(CO)_2$ and Rh(η^5-$C_5(CH_3)_5$)$(CO)_2$. Methyl substitution of the indenyl ring results in a decreased rate of CO substitution; Rh(η^5-C_9H_7)$(CO)_2$ reacts 6.3 × 10^2 times faster with PPh_3 than does Rh(η^5-$C_9(CH_3)_7$)$(CO)_2$. When compared with Rh(η^5-C_5H_5)$(CO)_2$ the indenyl ring still dominates; Rh(η^5-$C_9(CH_3)_7$)$(CO)_2$ reacts 6.1 × 10^5 times faster with PPh_3 than does Rh(η^5-C_5H_5)$(CO)_2$. The heptamethylindenyl ligand is not as sterically demanding as is the pentamethylcyclopentadienyl ligand, since Rh(η^5-$C_9(CH_3)_7$)$(CO)_2$ reacts readily with PPh_3 while Rh(η^5-$C_5(CH_3)_5$)$(CO)_2$ does not react with PPh_3 even at higher (70 °C) temperatures.[7] Presumably PPh_3 cannot approach close enough to Rh in Rh(η^5-$C_5(CH_3)_5$)$(CO)_2$ for S_N2 substitution to occur. For this reason we attribute the decrease in rate going from indenyl to heptamethylindenyl as primarily electronic in nature, and this supports the mechanism shown in (6).

Conclusions

A growing body of work[1,2,5-8] has established a good deal of support for the η^5-to-η^3 slippage mechanism for associative substitution reactions of indenyl and cyclopentadienyl compounds. An η^3-cyclopentadienyl ring has been observed[19] during the matrix photolysis of Fe(η^5-C_5H_5)$(CO)_2CH_3$. Hüttner and co-workers[20] have isolated an η^3-cyclopentadienyl compound W(η^5-C_5H_5)(η^3-C_5H_5)$(CO)_2$, and the indenyl analogue was prepared by Nesmeyanov and co-workers.[21] We find that changes in the electronic nature of the cyclopentadienyl ring can increase or decrease the rates of CO substitution at the metal center. Electron-withdrawing substituents such as nitro or triphenylphosphonium increase the rate of CO substitution relative to cyclopentadienyl. The indenyl ligand effect shows a rate enhancement of 3.8 × 10^8 times for the indenyl ligand relative to cyclopentadienyl, but methylation of the ring reduces this rate enhancement to 6.1 × 10^5 times. Since Rh(η^5-$C_9(CH_3)_7$)$(CO)_2$ reacts readily with PPh_3 while Rh(η^5-$C_5(CH_3)_5(CO)_2$ does not react, the heptamethylindenyl ligand would appear to offer less steric hinderence at the metal center than does the pentamethylcyclopentadienyl ligand. The rates of CO substitution from the $Rh(CO)_2$ moiety may be written as indenyl > heptamethylindenyl > nitrocyclopentadienyl > triphenylphosphonium cyclopentadienylide > cyclopentadienyl > pentamethylcyclopentadienyl. This list covers a factor of 10^{10} in terms of the rate of CO substitution from these compounds. Such studies point the way to further rate enhancements of substitution reactions of organometallic complexes, which has to provide important information relevant to homogeneous catalysis and to syntheses of new organometallic compounds.

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Registry No. [Rh(η^5-$C_5H_4PPh_3$)$(CO)_2$]BF_4, 91842-68-1; [Rh(η^5-$C_5H_4NO_2$)$(CO)_2$], 75862-04-3; Rh(η^5-$C_9(CH_3)_7$)$(CO)_2$, 91842-65-8; Rh(η^5-C_9H_7)$(CO)_2$, 12153-10-5; [Rh(η^5-$C_5H_4PPh_3$)(CO)(PPh_3)]BF_4, 91842-69-2; Rh(η^5-$C_5H_4NO_2$)(CO)(PPh_3), 91842-67-0; Rh(η^5-$C_9(CH_3)_7$)(CO)(PPh_3), 91842-66-9; Rh(η^5-C_9H_7)(CO)(PPh_3), 89340-98-7; $[Rh(CO)_2Cl]_2$, 14523-22-9; NaC_9H_7, 23181-84-2; $C_9(CH_3)_7H$, 77242-77-4; THF, 109-99-9; toluene, 108-88-3; dichloromethane, 75-09-2; cyclohexane, 110-82-7; *n*-hexane, 110-54-3; acetonitrile, 75-05-8; methanol, 67-56-1.

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