Heterobimetallic Indenyl Complexes. Kinetics and Mechanism of Substitution and Exchange Reactions of *trans*-[Cr(CO)$_3$-indenyl-Rh(CO)$_2$] with Olefins

Chiara Bonifaci, Giovanni Carta, Alberto Ceccon,* Alessandro Gambaro, and Saverio Santi

Dipartimento di Chimica Fisica, Università di Padova, Via Loredan 2, 35131 Padova, Italy

Alfonso Venzo

CNR, Centro di Studio sugli Stati Molecolari Radicalici ed Eccitati,
Via Loredan 2, 35131 Padova, Italy

Received October 2, 1995[⊗]

The *trans* coordination of the benzene ring of the indenyl-Rh(CO)$_2$ complex with tricarbonylchromium strongly enhances the rate of substitution of CO's with bidentate olefins, 1,5-cyclooctadiene (COD) and norbornadiene (NBD) ("extra-indenyl effect"). The activation parameters suggest an associative reaction pathway assumed to proceed via the intermediacy of a nonisolable low-hapticity species, η^1-indenyl-Rh(CO)$_2$(L$_2$). In addition, the rate of exchange of the Cr(CO)$_3$ group of the complexes *trans*-[Cr(CO)$_3$-indenyl-Rh(CO)$_2$], **3**, and *trans*-[Cr(CO)$_3$-indenyl-Rh(COD)], **3a**, and suitable acceptors (hexamethylbenzene and cycloheptatriene) is markedly increased with respect to that measured for the same reaction in the monometallic complex η-naphthalene-Cr(CO)$_3$ ("extra-naphthalene effect"). These mutual effects of the Cr(CO)$_3$ and RhL$_2$ units are transmitted through the 10 π electron indenyl framework, and the results obtained are in agreement with the existence of an haptomeric ground-state equilibrium between the two isomers *trans*-[Cr(CO)$_3$-μ,η^6:η^3-indenyl-RhL$_2$], **I**, and *trans*-[Cr(CO)$_3$-μ,η^4:η^5-indenyl-RhL$_2$], **II**.

Introduction

Kinetics and mechanism of ligand substitution reactions in the 18-electron cyclopentadienyl−M(CO)$_n$ systems have been carefully investigated during the last 2 decades. Substitution of carbon monoxide by phosphorus-donor nucleophiles has been studied in great details as early as 1966 by Schuster-Woldan and Basolo;[1] they investigated the reaction of η^5-CpRh(CO)$_2$ with several phosphine and phosphite ligands and proposed an S$_N$2 mechanism. The associative nature of the reaction was attributed to the ability of Cp to accept an electron pair from the metal, generating a coordinative vacancy which favors the nucleophilic attack of the incoming ligand. Evidence for an associative pathway is not confined to the CpRh(CO)$_2$ complex. In fact, a number of papers reported similar results in analogous cyclopentadienyl and related complexes of cobalt,[2] molybdenum,[3] and manganese.[4] An accurate study of the substituent effect in Cp- and indenyl-Rh(CO)$_2$ complexes was also described.[5]

The peculiar feature of the proposed substitution mechanism is the rate-determining formation of an η^3 intermediate by addition of the incoming ligand to rhodium. Because of the reorganization of the Cp ring π-electron cloud from an aromatic structure to an allyl−ene one, the metal can bind to the allyl frame mantaining an 18-electron configuration. Such a reaction pathway justifies the much higher reactivity observed for the indenyl complexes compared to the Cp complexes ("indenyl effect"),[6a] which has been ascribed to the stabilization of the transition state due to the aromatization of the fused benzene ring.[6]

The recent spectroscopic detection of the η^1-indenyl-Ir(COD)(CO)$_2$ intermediate in the substitution of COD by CO in η^5-indenyl-Ir(COD)[7] and the formation of η^1-species in the substitution reaction of phosphine ligands by CO in η^5-indenyl-Re(CO)$_3$[8] lead strong support to the importance of intermediates of low hapticity on the pathway of these substitution reactions. Nevertheless, attempts to obtain direct definitive evidence for an η^3-indenyl-RhL$_3$ intermediates failed, even though the η^3-indenyl-Ir(PR$_3$)$_3$,[9a] [η^3-indenyl-Fe(CO)$_3$]$^-$,[9b] and (η^3-indenyl,η^5-indenyl)V(CO)$_2$[9c] species are known.

It is commonly accepted that nucleophilic attack by unsaturated molecules at transition metal centers rep-

---

*To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts*, February 1, 1996.

(1) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1675.

(2) (a) Rerek, M. E.; Basolo, F. *Organometallics* **1983**, *2*, 372. (b) Moreno, C.; Macazaga, M. J.; Delgado, S. *Organometallics* **1991**, *10*, 1124.

(3) Hart-Davis, A. J.; Mawby, R. J. *J. Chem. Soc.* A **1969**, 2403.

(4) Ji, L. N.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740.

(5) (a) Cheong, M.; Basolo, F. *Organometallics* **1988**, *7*, 2041. (b) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908. (c) Kakkar, A. K.; Taylor, N. J.; Marder, T. B.; Shen, J. K.; Hallinan, N.; Basolo, F. *Inorg. Chim. Acta* **1992**, *198*−*200*, 219.

(6) (a) Rerek, M. E.; Ji, L. N.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208. (b) Wescott, S. A.; Kakkar, A. K.; Stringer, S.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, *394*, 777.

(7) Bellomo, S.; Ceccon, A.; Gambaro, A.; Santi, S.; Venzo, A. *J. Organomet. Chem.* **1993**, *453*, C4−C6.

(8) Bang, H.; Lynch, T. J.; Basolo, F. *Organometallics* **1992**, *11*, 40.

(9) (a) Merola, J. S.; Kacmarcik, R. T.; Van Engen, D. *Organometallics* **1992**, *11*, 40. (b) Forschner, T. C.; Cutler, A. R.; Kullnig, R. K. *Organometallics* **1987**, *6*, 889. Amhed, H.; Brown, D. A.; Fitzpatrick, N. J.; Glass, W. K. *J. Organomet. Chem.* **1991**, *418*, C14. (c) Kowalesky, R. M.; Rheingold, A. L.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1986**, *108*, 2460.

0276-7333/96/2315-1630$12.00/0

resents the crucial step in many isomerization and polymerization processes. In particular, indenyl-ML_2 complexes were shown to be efficient catalysts in the alkyne *cyclo*trimerization to produce substituted benzenes[10] and in the *cyclo*cotrimerization of alkynes and nitriles to give pyridine derivatives.[11] It is likely that the first step of the catalytic cycle consists in the substitution of one of the ancillary ligands by an alkyne molecule, and kinetic studies on the substitution reaction of CO by olefins at metal would provide useful informations about the mechanism of these processes. In spite of this, we are not aware of any reports dealing with this topic.

In continuation of our studies on the mutual effects of two metal units coordinated to the same bridging ligand, we have recently reported that *trans* coordination of the benzene ring of indenyl-RhL_2 complexes with the tricarbonylchromium group strongly enhances their chemical reactivity and, in particular, the catalytic activity in the cyclotrimerization of alkynes.[12] This effect may be related to a faster substitution of the ancillary ligands by the incoming alkyne molecule.

We report here the results of a kinetic study on the substitution of CO by two olefins, *viz.*, COD and NBD, at rhodium in *trans*-[$Cr(CO)_3$-indenyl-$Rh(CO)_2$] and argue that the presence of the second inorganic unit strongly increases the reaction rate. Moreover, since the mobility of $Cr(CO)_3$ is influenced by the presence of the $Rh(CO)_2$ unit, some results concerning the exchange reaction of $Cr(CO)_3$ between two indenyl complexes and cycloheptatriene, CHT, will be discussed as well.

Results and Discussion

In order to measure the effect of the $Cr(CO)_3$ group on the reactivity of the rhodium center we chose two monometallic complexes, indenyl-$Rh(CO)_2$, **1**, and 5-NO_2-indenyl-$Rh(CO)_2$, **2**, as reference compounds. The presence of NO_2 allows the evaluation of the extent of transmission of the polar effect from a strong electron-withdrawing group to the reaction center.[13]

Treatment of indenyl-Rh(COD) and 5-NO_2-indenyl-Rh(COD) with a blanket of CO at 25 °C in CH_2Cl_2 as solvent gave the corresponding indenyl-$Rh(CO)_2$ compounds **1** and **2** in a few minutes in quantitative yield.[14] In contrast, when *trans*-[$Cr(CO)_3$-indenyl-Rh(COD)], **3a**, was treated with CO under the same conditions, the reagent did not disappear completely, and an equilibrium was established in a ratio [reagent]/[product] $\approx$ 2. Pure *trans*-[$Cr(CO)_3$-indenyl-$Rh(CO)_2$], **3**, was obtained by bubbling CO through a CH_2Cl_2 solution of the COD derivative for *ca.* 1 h in order to shift the equilibrium by removal of the free COD.

As a suitable substrate for the estimation of the importance of polar effects of the $Cr(CO)_3$ group as transmitted to a rhodium center through a σ-connected cyclopentadienyl frame, we synthetized the [$Cr(CO)_3$-phenyl]-Cp-$Rh(CO)_2$ complex, **4**. This compound could not be obtained from the corresponding COD complex by an exchange reaction. In fact, in this case the substitution of COD by CO takes place only under forced conditions (p(CO) = 5 bar, T = 50 °C) and in very low yield (*ca.* 5%). However, the complex could be obtained in good yield by metalation of [$Cr(CO)_3$-phenyl]cyclopentadiene with KH in the presence of 18-crown-6 ether in THF followed by reaction with $[Rh(\mu\text{-}Cl)(CO)_2]_2$.

All complexes were obtained as microcrystalline orange-brown powders indefinitely stable in solid state. Complex **3** showed appreciable decomposition when dissolved in coordinating solvents. Physical and spectroscopic characteristics of **1**−**3** have been previously reported,[12a] and those of **4** are given in the Experimental Section.

Kinetics of Substitution of CO Groups at Rhodium. The substitution reaction of CO groups by olefins in cyclopentadienyl-$Rh(CO)_2$ complexes does not occur at all under mild conditions. Similarly, complex **4** in CH_2Cl_2 solution was shown to be inert even in the presence of a very large excess of COD at room temperature. Since the particular geometric arrangement in the bimetallic complex **4** ensures that the electron-withdrawing effect transmitted from chromium to the reaction center is mainly inductive in nature, the failure of complex **4** to undergo substitution shows that this effect seems to be unimportant.

In contrast, substitution of CO by olefins in indenyl-$Rh(CO)_2$ complexes occurs readily at room temperature to give the substitution product quantitatively. The kinetics of substitution by COD and NBD in mono- and bimetallic indenyl-$Rh(CO)_2$ complexes **1**−**3** was studied at several temperatures in different solvents. Under all experimental conditions investigated no low-hapticity η^1 or η^3 intermediates could be detected.

The progress of the reaction was followed by monitoring the decrease in intensity of a suitable absorption band of the reagent in the UV−vis region as a function of time (see Experimental Section). All the experiments were carried out under *pseudo*-first-order conditions, the molar ratio olefin/complex ranging from *ca.* 200 to 10 000, and the complex concentration being fixed at 10^{-4} M. Good first-order plots were obtained up to high conversion (80−90%) of the reagent. The *pseudo*-first-order rate contants, k_{obs}, depend linearly on the concentration of the olefin; the values of the intercepts are very close to zero indicating that the contribution of a dissociative pathway to the substitution process, if any, must be negligible (*cf.* Figure 1). Thus, the overall substitution is a bimolecular process represented by the second-order rate constant k_2, *i.e.*, the slope of the plot k_{obs} *vs* olefin concentration.

Measurements of the rate constants for the reaction with COD were carried out for the complexes **1**−**3** under identical conditions. Satisfactory plots were obtained in CH_2Cl_2 at 25 °C; k_2 values of 1.8×10^{-4}, 1.0×10^{-3}, and 3.7×10^{-1} M^{-1} s^{-1} were found for the three complexes, respectively.

Some qualitative observations on the effect of different electron-withdrawing substituents on the reactivity

---

[10] (a) Borrini, A.; Diversi, P.; Ingrosso, G.; Luccherini, A.; Serra, G. *J. Mol. Catal.* **1985**, *30*, 181. (b) Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 648.

[11] (a) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248. (b) Cioni, P.; Diversi, P.; Ingrosso, G.; Luccherini, A.; Ronca, P. *J. Mol. Catal.* **1987**, *40*, 337.

[12] (a) Ceccon, A.; Gambaro, A.; Santi, S.; Venzo, A. *J. Mol. Catal.* **1991**, *69*, L1−L6. (b) Bonifaci, C.; Ceccon, A.; Gambaro, A.; Ganis, P.; Mantovani, L.; Santi, S.; Venzo, A. *J. Organomet. Chem.* **1994**, *475*, 267.

[13] Ceccon, A.; Catelani, A. *J. Organomet. Chem.* **1974**, *72*, 79 and references therein.

[14] Kakkar, A. K.; Jones, S. F.; Taylor, N. J.; Collins, S.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1454.

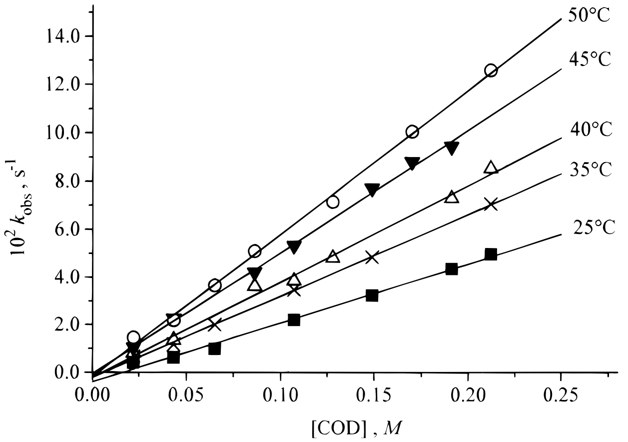


Figure 1. Plot of k_{obs} (s^{-1}) *versus* [COD] (M) for the reaction *trans*-[$Cr(CO)_3$-indenyl-$Rh(CO)_2$] + COD → *trans*-[$Cr(CO)_3$-indenyl-Rh(COD)] + 2 CO in cyclohexane.

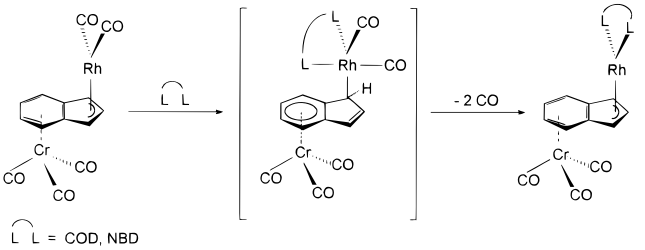
of rhodium in indenyl complexes have been discussed in a previous communication[12a] and are confirmed by the results reported here. In fact, the presence of a nitro group bonded to the indenyl six-membered ring increases the k_2 value *ca.* 5 times, a rather small effect if compared with that of *ca.* 2000 produced by the $Cr(CO)_3$ group. This huge difference cannot be attributed solely to the electron-withdrawing power of $Cr(CO)_3$ since its Hammet σ value is very close to that of the NO_2 group.[13] As discussed elsewere,[15] the simultaneous *trans* coordination of two inorganic 12-electron units to the same 10 π electron indenyl ligand sets up an electronic structure where both metals disclose an overall coordinative unsaturation. Such an interpretation made it possible to explain variations in ^1H, ^{13}C, and ^{103}Rh parameters observed on comparing the NMR spectra of several mono- and bimetallic indenyl complexes. In particular, the significant downfield shift experienced by the ^{103}Rh resonances induced by the presence of *trans*-$Cr(CO)_3$ indicates an appreciable polarization of the π-electron cloud away from rhodium and justifies the remarkable increase in its reactivity toward nucleophiles.

A more detailed kinetic study of the reaction of *trans*-[$Cr(CO)_3$-indenyl-$Rh(CO)_2$], **3**, with COD and NBD was performed in cyclohexane and 1,2-dichloroethane at different temperatures. The *pseudo*-first-order rate constants, k_{obs}, determined for the different runs are reported in Tables 1 and 2. As an example, the plots k_{obs} against [COD] obtained at different temperatures in cyclohexane are shown in Figure 1. The second-order rate constant, k_2, and the activation parameters obtained from Eyring plots are collected in Table 3.

The magnitude of the activation parameters supports the S_N2 nature of the substitution process. The $\Delta H^{\neq}$ values span from a maximum of 43.5 kJ mol^{-1} for NBD in cyclohexane to 25.9 kJ mol^{-1} for COD in the same solvent. For the bimolecular attack by phosphine ligands at rhodium in $CpRh(CO)_2$, $\Delta H^{\ddagger}$ values range from 54 to 75 kJ mol^{-1} dependent on the nature of the phosphorous ligand and almost independent of solvent.[1] Similar $\Delta H^{\ddagger}$'s were found for the analogous reaction of $(C_5H_4COOMe)Co(CO)_2$.[2b]

The low activation enthalpies found for the substitution of CO by olefins in **3** are in accord with a transition state characterized by significant Rh–olefin bond formation. If an intermediate were formed by addition of one molecule of COD or NBD, it should be an η^1-indenyl-RhL_4 species, where the olefin occupies two of the five coordinative positions of a trigonal bipyramid. As a matter of fact, a stable η^1 intermediate was detected on carbonylation of the indenyl-Ir(COD) complex[7] and characterized by NMR spectroscopy; it was formed quantitatively from the reagent on addition of two molecules of CO. Therefore, if the transition state had a structure close to that of the intermediate, the motion of the activated complex would be highly restricted relative to that of the reagent resulting in a large decrease in activation entropy. This is what has been found with both olefins, the $\Delta S^{\ddagger}$ values ranging between −129.2 J K^{-1} mol^{-1} for NBD and −170.1 J K^{-1} mol^{-1} for COD.

Quite instructive is the comparison between the activation parameters of the two olefins, COD and NBD, in the two solvents. The relative values of k_2 indicate that the attack by COD at the rhodium core is *ca.* five times faster than that of NBD; this is a consequence of its lower $\Delta H^{\ddagger}$, which largely overcomes the effect of the more negative entropy of activation. The negative values of $\Delta S^{\ddagger}$ arising from the restriction of motion on going from the free olefin to the activated complex must be greater for the more flexible COD than for the rigid NBD, as has been found. Moreover, the difference in activation entropy can be explained by a transition state in which the two double bonds are simultaneously coordinated to the metal but cannot be justified by considering as the rate-determining step the attack by only one of the double bonds followed by rapid addition of the other. The most plausible explanation is that the rate-determining addition of bidentate olefins produces an η^1 species, from which the loss of two CO's with restoration of an η^5 coordination occurs in a subsequent fast step:



The bipyramidal trigonal structure for the η^1 intermediate is suggested on analogy with that of the closely related intermediate spectroscopically observed in the reaction of the monometallic indenyl-Ir(COD) with CO.[7]

In this connection, the results obtained for the carbonylation of *trans*-[$Cr(CO)_3$-indenyl-Rh(COD)] and of its analogue *trans*-[$Cr(CO)_3$-indenyl-Ir(COD)], carried out at low temperature, are instructive. At −30 °C the iridium complex adds CO affording the stable pentacoordinate η^1-[$Cr(CO)_3$-indenyl]-$Ir(CO)_2$(COD).[16] Under the same conditions, no low-hapticity species could be detected for the rhodium complex, **3** being the only compound observed and isolated in this system. On the

---

[15] Ceccon, A.; Elsevier, C. J.; Ernsting, J. M.; Gambaro, A.; Santi, S.; Venzo, A. *Inorg. Chim. Acta* **1993**, *204*, 15.

[16] Bonifaci, C.; Ceccon, A.; Gambaro, A.; Manoli, F.; Santi, S.; Venzo, A. *Abstracts of the XVIth International Conference on Organometallic Chemistry*, Brighton, England, July 10–15, 1994; The Chemical Society: London, 1994; OA.9.

Table 1. *Pseudo*-First-Order Rate Constant values, 10^2k_{obs} (s^{-1}), for the Reaction of *trans*-[$Cr(CO)_3$-indenyl-$Rh(CO)_2$], 3, with COD in 1,2-Dichloroethane and Cyclohexane[a]

	solvent 1,2-dichloroethane					solvent cyclohexane				
[COD] (M)	20 °C	25 °C	30 °C	35 °C	40 °C	25 °C	35 °C	40 °C	45 °C	50 °C
0.022	0.76			1.16	1.35	0.42	0.67	0.82	1.05	1.46
0.043	1.30	1.24	1.70	1.78	2.44	0.63	1.17	1.35	2.25	2.18
0.065		1.68	2.03		3.41	0.99	2.00			3.67
0.086	2.06	2.33			4.42			3.62	4.21	5.10
0.107	2.49	2.91		3.63	5.76	2.20	3.48	3.85	5.32	
0.128	3.17	3.37	4.21	4.87	6.33			4.81		7.14
0.149			5.11	5.34	7.34	3.24	4.85		7.71	
0.170			5.61	6.71	8.43				8.80	10.06
0.191		4.45	6.21	6.93		4.36		7.29	9.43	
0.212		5.26				4.98	7.07	8.53		12.60

[a] *T*, ±0.1 °C; k_{obs}, ±5%.

Table 2. *Pseudo*-First-Order Rate Constant Values, 10^3k_{obs} (s^{-1}), for the Reaction of *trans*-[$Cr(CO)_3$-indenyl-$Rh(CO)_2$], 3, with NBD in 1,2-Dichloroethane and Cyclohexane[a]

	solvent 1,2-dichloroethane						solvent cyclohexane				
[NBD] (M)	20 °C	25 °C	30 °C	35 °C	41 °C	46 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.012					1.91						
0.025	1.22	1.69	1.86		4.41	5.42	1.44		1.84		
0.049	2.12	3.99	3.82	6.31	7.68	8.60	2.18	2.38	2.74	3.87	4.20
0.074	3.50	4.93	5.86	7.35	11.24	14.11		3.39	4.09		
0.098	4.23	5.74	7.78	10.38		19.03	3.66			6.64	8.30
0.122	5.82	9.06	8.93	13.68	20.05	22.47	4.02	6.45	7.90		10.80
0.146		10.66	11.29	14.74		26.07	5.43	8.31	9.85		
0.170				16.63		31.47		9.03	10.92	13.95	
0.194										15.66	
0.217						38.39			14.19		22.30
0.241	10.43	14.69	19.41	24.34			8.46	11.58	16.80		22.90

[a] *T*, ±0.1 °C; k_{obs}, ±5%.

Table 3. Second-Order Rate Constants and Activation Parameters for the Reaction of *trans*-[$Cr(CO)_3$-indenyl-$Rh(CO)_2$], 3, with COD and NBD in 1,2-Dichloroethane (A) and in Cyclohexane (B)

		COD			NBD		
solvent	*T* (°C)[a]	10^2k_2 (M^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	10^2k_2 (M^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
A	20	21.5 ± 1.3	28.0 ± 3.3	−161.8 ± 12.1	4.3 ± 0.1	40.5 ± 2.9	−132.1 ± 9.6
	25	22.9 ± 1.0			6.1 ± 0.5		
	30	32.0 ± 1.3			8.0 ± 0.2		
	35	35.5 ± 1.9			9.5 ± 0.4		
	40	47.4 ± 1.1					
	41				16.2 ± 0.6		
	46				17.5 ± 0.4		
B	25	24.8 ± 1.0	25.9 ± 1.7	−170.1 ± 4.6		43.5 ± 3.8	−129.2 ± 12.5
	30				3.3 ± 0.2		
	35	34.1 ± 0.5			5.0 ± 0.4		
	40	40.1 ± 1.5			6.9 ± 0.2		
	45	50.8 ± 1.1			8.5 ± 0.6		
	50	59.6 ± 1.5			10.4 ± 0.6		

[a] *T*, ±0.1 °C.

basis of these facts, the conclusion can be drawn that the potential η^1-indenyl intermediates of rhodium tend to lose two ligands to restore the η^5 coordination mode with the five-membered ring much faster than the iridium analogues. To the best of our knowledge, η^1- and η^3-cyclopentadienyl and -indenyl complexes of rhodium have never been detected experimentally, and their existence has been invoked in order to explain the kinetic data.[5]

Exchange of $Cr(CO)_3$. In order to extend the study of the mutual effect of two metal units *trans* coordinated to the same bridging ligand, we investigated the exchange of $Cr(CO)_3$ between the complexes *trans*-[$Cr(CO)_3$-indenyl-$Rh(CO)_2$], **3**, and *trans*-[$Cr(CO)_3$-indenyl-Rh(COD)], **3a**, and suitable acceptors. The results were compared with those obtained for monometallic η^6-arene-$Cr(CO)_3$ complexes. In preliminary experiments we obtained qualitative information by testing the reactivity of **3** and **3a**, η-naphthalene-$Cr(CO)_3$, **5**, and η^6-indene-$Cr(CO)_3$ toward hexamethylbenzene in decalin at 150 °C. The exchange, monitored by the disappearance of the reagents and the formation of η^6-$C_6Me_6Cr(CO)_3$ by TLC, was found to be complete within 10 min for **3** and **3a** and within *ca*. 4 h for η^6-naphthalene-$Cr(CO)_3$, whereas no reaction was observed for η^6-indene-$Cr(CO)_3$ even after 15 h. Therefore, the lability of the $Cr(CO)_3$-arene bond decreases in the order

$$\text{indene} \ll \text{naphthalene} < \text{bimetallic complexes } \mathbf{3} \text{ and } \mathbf{3a}$$

This trend was confirmed by kinetic measurements carried out by reacting **5** and **3a** with a large excess of a good $Cr(CO)_3$ scavenger such as cycloheptatriene (CHT) to give η^6-CHT-$Cr(CO)_3$, **6**, under mild conditions, *viz.*, 30 °C in methylene chloride solution. The choice of cycloheptatriene as a scavenger was determined by

Table 4. *Pseudo*-First-Order Rate Constants for the $Cr(CO)_3$ Exchange Reaction between *trans*-[$Cr(CO)_3$-indenyl-Rh(COD)], 3a, and Cycloheptatriene (CHT)[a]

[CHT] (M)	10^4k_{obs} (s^{-1})[b]	10^4k_{obs} (s^{-1})[c]	10^4k_{obs} (s^{-1})[d]	10^4k_{obs} (s^{-1})[e]
0.031	1.62			1.95
0.092	3.58			2.95
0.153	7.94	5.19	1.86	4.06
0.301	11.1	10.1	3.58	7.65
0.445	18.8			
0.584	22.5	15.5	6.04	14.0
0.764	28.1			
0.850	30.4		8.9	
1.223	43.7			29.0

[a] T = (30 ± 0.1) °C, k_{obs}, ±5%, solvent CH_2Cl_2. [b] [**3a**] = 1.0 × 10^{-4} M. [c] [**3a**] = 1.0 × 10^{-4} M, and [**6**] = 1.0 × 10^{-4} M was added to the reaction mixture. [d] [**3a**] = 1.0 × 10^{-4} M, and [**6**] = 3.0 × 10^{-4} M was added to the reaction mixture. [e] [**3a**] = 2.0 × 10^{-4} M.

Table 5. *Pseudo*-First-Order Rate Constants, k_{obs}, for the $Cr(CO)_3$ Exchange Reaction between η-naphthalene-$Cr(CO)_3$, 5, and Cycloheptatriene (CHT)[a]

[CHT] (M)	10^5k_{obs} (s^{-1})[b]	10^5k_{obs} (s^{-1})[c]
0.153	6.76	12.4
0.850	12.1	17.8
1.529	16.1	20.0

[a] T = (30 ± 0.1) °C, k_{obs}, ±5%, solvent CH_2Cl_2. [b] [**5**] = 3.09 × 10^{-4} M. [c] [**5**] = 1.0 × 10^{-4} M, and [**6**] = 1.0 × 10^{-4} M was added to the reaction mixture.

Table 6. Rate Constants of the Exchange Reaction of the $Cr(CO)_3$ Group in η-naphthalene-$Cr(CO)_3$, 5, and *trans*-[$Cr(CO)_3$-indenyl-Rh(COD)], 3a, with Cycloheptatriene (CHT)[a]

complex	[complex] (M)	[**6**] (M)[b]	10^5k_2 (M^{-1} s^{-1})	10^5k_1 (s^{-1})
5	3.09 × 10^{-4}		6.8 ± 0.5	5.9 ± 0.5
5	3.09 × 10^{-4}	3.09 × 10^{-4}	7.2 ± 0.5	11.4 ± 0.4
3a	1.00 × 10^{-4}		350 ± 10	14 ± 6
3a	2.00 × 10^{-4}		230 ± 30	8.3 ± 1.6
3a	1.00 × 10^{-4}	1.00 × 10^{-4}	240 ± 70	17 ± 3
3a	1.00 × 10^{-4}	3.09 × 10^{-4}	99 ± 30	4.2 ± 1.9

[a] T = (30 ± 0.1) °C, solvent CH_2Cl_2. [b] [**6**] is the concentration of (η^6-CHT)$Cr(CO)_3$ added to the reaction mixture.

its high reactivity toward $Cr(CO)_3$ allowing one to obtain kinetic data under experimental conditions similar to those used for CO substitution at rhodium. The progress of the reaction was monitored by measuring the decrease of an absorption band of the reagent in the UV−vis region (see Experimental Section), and the reaction rates were shown to obey a first order law up to high conversion. The kinetic data are collected in Tables 4−6, and plots of k_{obs} as a function of [CHT] are shown in Figures 2−4.

Examination of the results shows that the first-order contribution to the overall rate is much more significant in the case of the naphthalene complex, **5**, than in the case of the bimetallic complex **3a**. However, we were not able to establish whether the intercept value in the plots of k_{obs} against [CHT], representing the dissociative term, are related to the first-order formation of **6** or to a competitive decomposition of the reagent. Therefore, the evaluation of the rate of $Cr(CO)_3$ exchange has been done by taking into account only the associative bimolecular process measured by the k_2 value. From the k_2's of **3a** and **5** it results that the bimetallic complex exchanges $Cr(CO)_3$ *ca.* 47 times faster than naphthalene-$Cr(CO)_3$.

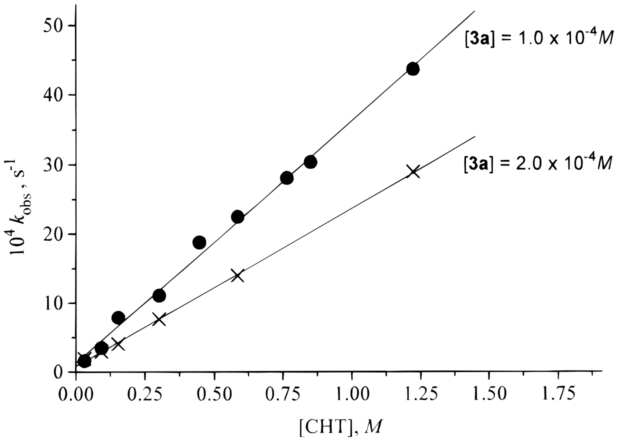


Figure 2. Plot of k_{obs} (s^{-1}) *versus* [CHT] (M) for the reaction *trans*-[$Cr(CO)_3$-indenyl-Rh(COD)] + CHT → (CHT)-$Cr(CO)_3$ + indenyl-Rh(COD) in CH_2Cl_2, with T = (30 ± 0.1) °C.

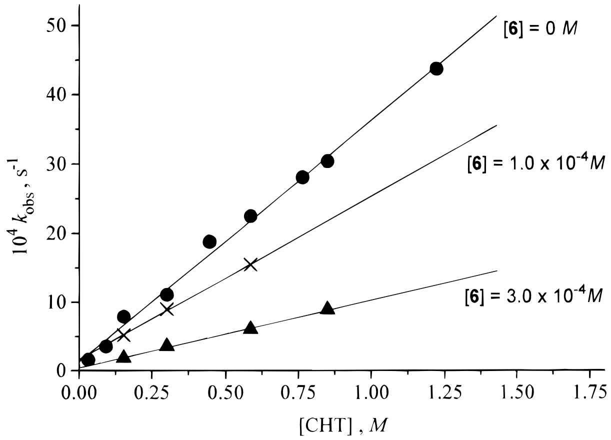


Figure 3. Plot of k_{obs} (s^{-1}) *versus* [CHT] (M) for the reaction *trans*-[$Cr(CO)_3$-indenyl-Rh(COD)] + CHT → (CHT)-$Cr(CO)_3$ + indenyl-Rh(COD) in CH_2Cl_2, with T = (30 ± 0.1) °C and [**3a**] = 1.0 × 10^{-4} M.

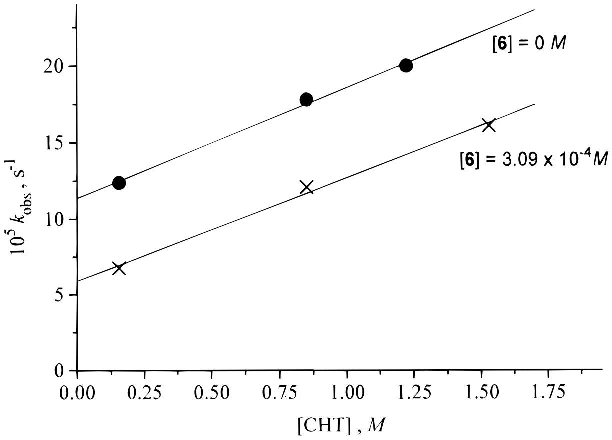
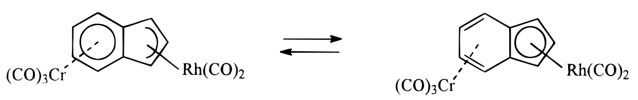


Figure 4. Plot of k_{obs} (s^{-1}) *versus* [CHT] (M) for the reaction η-naphthalene-$Cr(CO)_3$ + CHT → (CHT)$Cr(CO)_3$ + naphthalene in CH_2Cl_2, with T = (30 ± 0.1) °C and [**5**] = 3.09 × 10^{-4} M.

The intervention of lower hapticity intermediates in metal-exchange reactions of η^6-arene-$Cr(CO)_3$ complexes has been discussed by several authors, and the importance of an η^4-arene-$Cr(CO)_3$ species in the first step of the mechanism was generally accepted.[17] In particular, the high reactivity shown by naphthalene-$Cr(CO)_3$, which places this complex at the top of a list of arene complexes assembled according to the ease of $Cr(CO)_3$ displacement by phosphines, was attributed to the relative stability of an η^4-naphthalene-$Cr(CO)_3$ intermediate. The $\eta^6 \rightarrow \eta^4$ metal slippage is induced by the initial approach of the incoming ligand and it is energetically favored by the aromatization of the fused benzene ring ("naphthalene effect").[18] Since the indenyl bimetallic complexes here investigated are about 2 orders of magnitude more reactive than **5** ("extranaphthalene effect"), the reaction intermediate where chromium is η^4 coordinated to the indenyl ligand must be even more stable.

The indenyl effect itself was explained [6] by invoking a stabilization of an η^3 intermediate due to the rearomatization of the fused benzene ring, where the $\eta^5 \rightarrow \eta^3$ metal slippage is induced by the initial approach of the incoming ligand.

An alternative model which explains the kinetic results obtained for the bimetallic complexes both in the $Cr(CO)_3$ exchange process as well as those in the ligand substitution at rhodium requires the existence of an equilibrium between the two hapto isomers **I** and **II** in the ground state:



$\eta^6 : \eta^3$ **I** $\eta^4 : \eta^5$ **II**

This equilibrium arises by the simultaneous coordination of the two metals to the same bridging ligand that influences both rhodium−Cp and chromium−benzene bonding modes. It represents a suitable description of the coordinative unsaturation which can justify the increased reactivity of both metal centers toward the incoming nucleophile and the spectroscopic properties in solution.[12a,15] In particular, the hapto isomer **II** depicts a favorable situation for a fast exchange of $Cr(CO)_3$.[19]

The changes in rate constants observed at different initial concentrations of the reagent **3a** or those induced by addition of the reaction product, **6**, to the starting reaction mixtures support the establishment of a preliminary equilibrium between **I** and **II**. It was reported, in fact, that the exchange reaction of $Cr(CO)_3$ is often catalyzed by donors, such as ketones or acetonitrile,[20] or by the carbonyl groups bonded to the reagent itself or to the product.[21] Our results indicate that an opposite situation is operating for the bimetallic complex **3a**. Examination of the data reported in Table 6 shows that both the increased concentration of reagent **3a** or the addition of product **6** to the initial reaction mixture produces a measurable decrease of k_2; in contrast, for complex **5**, as already reported by Kündig *et al.*,[18] only a negligible effect on k_2 was found. The behavior of **3a** can be attributed to the stabilization of the ground state rather than that of the transition state, induced by carbonyls. In fact, the carbonyl ligands of the tricarbonylchromium group may compete for the unsaturated hapto isomer **II**, and the resulting saturation of the vacancies at chromium may slow down the attack by the external cycloheptatriene.

Experimental Section

NMR spectra were measured on a Bruker AM400 spectrometer operating in the FT mode at 400.133 and 100.614 MHz for ^1H and ^{13}C, respectively. Chemical shifts are given from Me_4Si as the internal standard. The ^{13}C peak assignment was based on selective proton-decoupling experiments and partially relaxed spectra. The proton assignements were accomplished by $^1H\{^1H\}$ NOE measurements: the usual procedure for gated experiments was modified,[22] and the selected multiplet was saturated by a 10 s cyclic perturbation of all lines with a 42 dB attenuation of a nominal 0.2 W decoupling power.

IR spectra were run as CH_2Cl_2 solutions (optical length 0.2 mm, CaF_2 windows) on a Perkin-Elmer 580B spectrophotometer equipped with a Perkin-Elmer 3600 data acquisition system. UV−visible measurements were performed on a Perkin-Elmer LAMBDA-2 spectrophotometer. The 70 eV EI mass spectra were recorded on a VG MicroMass-16 spectrometer.

All reactions were carried out in oxygen-free solution, under a blanket of purified argon. Solvents were purified according to standard procedures,[23] distilled and purged with argon before use. Hexamethylbenzene (Aldrich) was crystallized from ethanol. Commercial grade COD, NBD, and cycloheptatriene (Fluka) were twice distilled and deoxygenated before use. Commercial cycloheptatriene-$Cr(CO)_3$ (Aldrich) was crystallized from heptane. Syntheses and characterization of indenyl-$Rh(CO)_2$, **1**, 5-NO_2-indenyl-$Rh(CO)_2$, **2**, and $Cr(CO)_3$-indenyl-$Rh(CO)_2$, **3**, were previously reported.[12a]

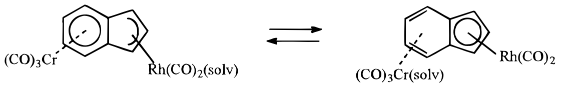
[Cr(CO)$_3$-phenyl]-cyclopentadienyl-Rh(COD)]. [$Cr(CO)_3$-phenyl]-cyclopentadiene[24] was converted into its anion by treatment of the THF solution with an excess of KH in the presence of 18-crown-6 ether at room temperature under argon.[25] The anion solution was added at room temperature to an equivalent amount of $[Rh(\mu\text{-}Cl)(COD)]_2$ in THF. After 1 h the solution was cooled to −40 °C, the solvent pumped off, and the residue washed with cyclohexane and crystallized from diethyl ether−hexane to give a light brown powder. Yield: 82%. Mp: 165−166 °C dec. Anal. Calcd for $C_{22}H_{21}CrO_3Rh$: C, 54.11; H, 4.33. Found: C, 54.02; H, 4.46. MS (*m/z*): 488 (M^+, 47.6%), 432 ($M^+ - 2(CO)$, 1.9), 404 ($M^+ - 3(CO)$, 100), 352 ($M^+ -$ [Cr, 3(CO)], 31.7), 244 ($M^+ -$ [Cr, 3(CO), COD], 28.9), 103 (Rh^+, 2.4) and 52 (Cr^+, 2.3). Spectroscopic data: IR ν_{max} (THF) 1963 vs, and 1886 vs cm^{-1} ($C\equiv O$); ^1H NMR (acetone-d_6) $\delta = 5.50$ (m, 4H, $H_{o,o'}$ and $H_{m,m'}$), 5.45 (m, 2H, $H_{2,5}$), 5.27 (m, 2H, $H_{3,4}$), 5.24 (m, 1H, H_p), 4.22 (m, 4H, =CH COD

---

[17] Zhang, S.; Shen, J. K.; Basolo, F.; Ju, T. D.; Lang, R. F.; Kiss, G.; Hoff, C. D. *Organometallics* **1994**, *13*, 3692 and references therein.

[18] Kündig, E. P.; Perret, C.; Spichiger, S. *J. Organomet. Chem.* **1985**, *286*, 183.

[19] One of the reviewers suggested an alternative view involving the solvent, which is consistent with the kinetic data and would result in the following equilibria:



The coordinative unsaturation of the metal(s) would justify the intervention of noncoordinating solvents which would be only weakly bound and easily removable by the attack of the incoming ligand. However, the neglegible solvent effect (see Table 3) suggests that specific interactions between solvent molecules and the metals, if any, must be scarcely important.

[20] (a) Strohmeier, W.; Mittnacht, H. *Z. Phys. Chem.* **1961**, *29*, 339. (b) Strohmeier, W.; Staricco, E. H. *Ibid.* **1963**, *38*, 315. (c) Strohmeier, W.; Muller, R. *Ibid.* **1964**, *40*, 85. (d) Mahaffy, C. A.; Pauson, P. L. *J. Chem. Res. (S)*, **1979**, 126. (e) Zimmerman, C. L. ; Shaner, S. L.; Roth, S. A.; Willeford, B. R. *Ibid.* **1980**, 108.

[21] Traylor, T. G.; Stewart, K. *Organometallics* **1984**, *3*, 325.

[22] Kinns, M.; Sanders, J. K. M. *J. Magn. Reson.* **1984**, *56*, 518.

[23] Perrin, D. D.; Armageo, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, England, 1988.

[24] Ceccon, A.; Gambaro, A.; Gottardi, F.; Manoli, F.; Venzo, A. *J. Organomet. Chem.* **1989**, *363*, 91.

[25] Ceccon, A.; Gambaro, A.; Gottardi, F.; Santi, S.; Venzo, A.; Lucchini, V. *J. Organomet. Chem.* **1989**, *379*, 67.

protons), and 1.9−1.7 (m, 8H, CH_2 COD protons); ^{13}C NMR (acetone-d_6) $\delta = 234.13$ (C≡O), 107.67 (C_j), 100.91 ($^1J(^{103}Rh-^{13}C) = 1.9$ Hz, C_1), 94.53 ($C_{m,m'}$), 90.68 (C_p), 89.82 ($C_{o,o'}$), 88.55 ($^1J(^{103}Rh-^{13}C) = 3.5$ Hz, $C_{3,5}$), 85.08 ($^1J(^{103}Rh-^{13}C) = 3.3$, $C_{2,4}$), 66.63 ($^1J(^{103}Rh-^{13}C) = 14.1$ Hz, =*C*H COD carbons) and 32.52 (CH_2 COD carbons).

[Cr(CO)$_3$-phenyl]cyclopentadienyl-Rh(CO)$_2$, 4. This complex was obtained as a yellow powder (from cyclohexane−THF) in 74% yield by reacting [Cr(CO)$_3$-phenyl]−cyclopentadienylpotassium with [Rh(μ-Cl)(CO)$_2$]$_2$ as described above. Mp: 113−115 °C dec. Anal. Calcd for $C_{16}H_9CrO_5Rh$: C, 44.06; H, 2.08. Found: C, 44.12; H, 2.19. MS (*m*/*z*): 436 (M^+, 32.8%), 380 ($M^+ - 2$(CO), 17.6), 352 ($M^+ - 3$(CO), 59.3), 324 ($M^+ - 4$(CO), 92.4), 296 ($M^+ - 5$(CO), 100), 244 ($M^+ -$ [Cr, 5(CO)], 35.5), 103 (Rh^+, 3.4) and 52 (Cr^+, 35.9). Spectroscopic data: IR: ν_{max} (THF): 2042 s, 1975 s, 1963 vs and 1890 vs cm^{-1} (C≡O); ^1H NMR (acetone-d_6) $\delta = 6.18$ (m, 2H, $H_{2,5}$), 6.02 (m, 2H, $H_{o,o}'$), 5.73 (m, 4H, $H_{m,m}'$ and $H_{3,4}$), and 5.57 (m, 1H, H_p); ^{13}C NMR (acetone-d_6) $\delta = 234.55$ (Cr−*C*≡O), 191.88 ($^1J(^{103}Rh-^{13}C) = 84.1$ Hz, Rh−*C*≡O), 111.02 (C_j), 109.34 ($^1J(^{103}Rh-^{13}C) = 2.0$ Hz, C_1), 94.96 ($C_{m,m}'$), 93.32 (C_p), 92.20 ($C_{o,o}'$), 90.16 ($^1J(^{103}Rh-^{13}C) = 3.1$ Hz, $C_{3,5}$), 86.64 ($^1J(^{103}Rh-^{13}C) = 3.1$ Hz, $C_{2,4}$).

Carbonylation of [Cr(CO)$_3$-phenyl]cyclopentadienyl-Rh(COD)]. A CO-saturated 0.1 M solution of [Cr(CO)$_3$-phenyl]cyclopentadienyl-Rh(COD) in CH_2Cl_2 (30 mL) was charged into a CO-filled stainless steel pressure vessel. The CO pressure was then increased to 5 bar and the temperature to 50 °C for 15 h. The resulting mixture contained 5% of **4** and 95% of the reactant (by NMR integration).

Kinetics of Ligand Exchange Reactions. The cuvette (10 mm optical path) containing a 10^{-4} M solution of the complex in the appropriate solvent was placed in the thermostated cell holder of the UV spectrophotometer. After thermal equilibration, the appropriate amount of pure COD or NBD, kept at the same temperature as the complex solution, was added and the absorbance at the appropiate wavelength ($\lambda =$ 343, 337, and 352 nm for **1**−**3**, respectively) recorded as a function of time.

Cr(CO)$_3$ Exchange Reactions with Hexamethylbenzene. Suitable amounts of complex and of hexamethylbenzene (in order to realize a 3×10^{-2} and 1.5 M solution, respectively) were added to 1.0 mL of decaline freshly distilled from sodium and kept oxygen free under an argon atmosphere in a 5 mL reaction vessel. The mixture was heated using an oil bath kept at 150 °C and time sampled by TLC.

Kinetics of the Cr(CO)$_3$ Exchange Reactions with Cycloheptatriene, CHT. A cuvette (10 mm optical path) containing the solution of the complex in CH_2Cl_2 was placed in the thermostated cell holder of the UV spectrophotometer kept at 30 °C. After thermal equilibration, the appropriate amount of pure CHT, kept at the same temperature as the complex solution, was added and the absorbance at $\lambda = 440$ nm recorded as a function of time. The concentrations of the substrates and of added reaction product, [**6**], are reported in Table 6. Because of the low stability of these solutions, the values of the first order constants, k_{obs}, were calculated from the initial rates.

Acknowledgment. This work was supported in part by the CNR, Rome, through its “Centro di Studio sugli Stati Molecolari Radicalici ed Eccitati” and through its Progetto Finalizzato “Chimica Fine II”. We are indebted to Dr. L. Birladeanu, Harvard University, for stimulating discussions.

Supporting Information Available: Plots of k_{obs} versus diene for the reactions *trans*-[Cr(CO)$_3$-indenyl-Rh(CO)$_2$] + COD in CH_2ClCH_2Cl and *trans*-[Cr(CO)$_3$-indenyl-Rh(CO)$_2$] + NBD in CH_2ClCH_2Cl and cyclohexane (4 pages). Ordering information is given on any current masthead page.

OM950775U