Thermal Carbon Monoxide Exchange Reactions of (Arene)tricarbonylchromium Complexes

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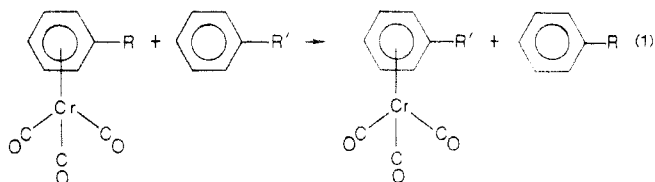
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Reactions of [13]CO-enriched (benzene)tricarbonylchromium with dilute mesitylene, in the presence of (benzene-d_6)Cr(CO)$_3$, reveal a carbon monoxide redistribution reaction between the two complexes. External CO does not enter into the redistribution process, and redistribution is $\sim$10 times faster than (arene)Cr(CO)$_3$ catalysis of arene exchange. A bis(carbonyl)-bridged dimer is postulated as the intermediate for both the internal [13]CO scrambling and the arene complex catalyzed arene-exchange reaction. Observed external CO exchange in reactions of [13]CO-enriched (arene)Cr(CO)$_3$ complexes under [12]CO is shown to be independent of arene exchange and is postulated to occur along the pathway to Cr(CO)$_6$.

Introduction

Early kinetic studies of Strohmeier[1] and more recent studies of Pauson[2] and of Willeford[3] have indicated that (arene)tricarbonylchromium complexes exchange arenes (eq 1) in the processes which appear to take three independent pathways involving the complex (C), the arene (A), and a catalyst (cat.). In our reexamination of this reaction we confirmed the k_1 term as well as the k_3 term for catalysts such as ketones and ethers.[4] However, the k_2 term was shown[5] to depend upon the total arene complex rather than to the second power of the reactant [k_3-(C)(total (arene)tricarbonylchromium complex) rather than C^2]. This result and further work have made it clear that the carbonyl complex acts as a nucleophilic catalyst, perhaps in a manner similar to catalyses by ketones. We thus suggested the catalytic intermediate I.[5] However,


$$-dC/dt = k_1(C)(A) + k_2(C)^2 + k_3(C)(cat.) \quad (2)$$

I
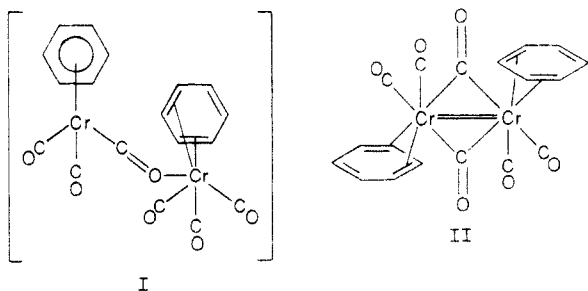
since many carbonyl-bridged dimetallic complexes are known[6] and many carbonyl-exchange processes have been

reported,[7,8] we have also considered bridged formulations such as II. We demonstrated earlier[4] that the tris [13]CO-labeled tricarbonyl group could be transferred intact in the presence of [12]CO, eliminating external CO exchange as an integral part of the k_1, k_2, or k_3 pathways (eq 3).
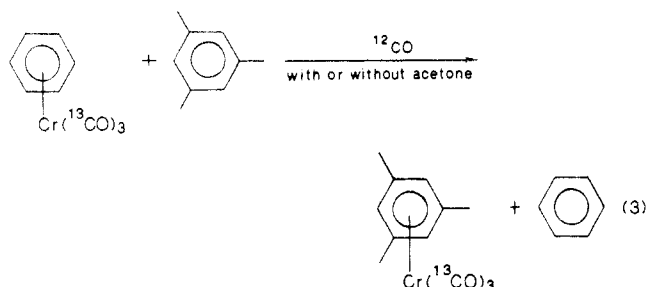
Since the exchange reaction can be carried out without external CO exchange,[4] it is possible to probe for the occurrence of II by searching for internal exchange (scrambling). This has been accomplished by a double-labeling experiment depicted in eq 4 (where CO refers to [12]CO). The intermediate of structure I would not lead to scrambling.
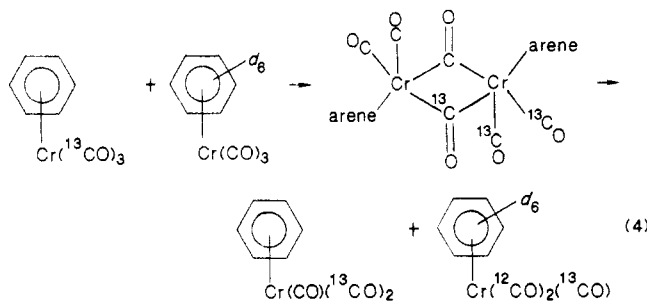
Experimental Section

General Data. Proton NMR spectra were recorded on both a Varian EM-390 90-MHz spectrometer and a fabricated ^{1}H NMR spectrometer equipped with a Nicolet 1180E computer operating at 360 MHz. Mass spectra were recorded on a VG-ZAB 1F high-resolution mass spectrometer using 20-eV ionizing energy and an accelerator voltage of 8000 eV, with a resolution of 2000.

(1) Strohmeier, W.; Mittnacht, H. *Z. Phys. Chem. (Munich)* 1961, 29, 339. Strohmeier, W.; Staricco, E. H. *Ibid.* 1963, 38, 315. Strohmeier, W.; Muller, R. *Ibid.* 1964, 40, 85.

(2) Mahaffy, C. A. L.; Pauson, P. L. *J. Chem. Res.. Synop.* 1979, 126; *J. Chem. Res., Minipr.* 1979, 752.

(3) Zimmerman, C. L.; Shaner, S. L.; Roth, S. A.; Willeford, B. R. *J. Chem. Res., Synop.* 1980, 108; *J. Chem. Res., Minipr.* 1980, 1289.

(4) (a) Traylor, T. G.; Stewart, K. J.; Goldberg, M. *J. J. Am. Chem. Soc.* 1984, 106, 4445. (b) Traylor, T. G.; Youngerman, E., unpublished data.

(5) Traylor, T. G.; Stewart, K. *Organometallics* 1984, 3, 325.

(6) Behrens, H.; Harder, N. *Chem. Ber.* 1964, 97, 426, 433. Behrens, H.; Anders, H. *Z. Naturforsch, B: Anorg. Chem., Org. Chem. Biochem., Biophys. Biol.* 1964, 19B, 767.

(7) Booth, B. L.; Else, M. J.; Fields, R.; Goldwhite, H.; Haszeldine, R. N. *J. Organomet. Chem.* 1968, 14, 417. Powell, J.; Shaw, B. L. *J. Chem. Soc. A* 1968, 211. Clark, R. J.; Brimm, E. O. *Inorg. Chem.* 1965, 4, 651. Garrou, P. E.; Hartwell, G. E. *Ibid.* 1976, 15, 646.

(8) Cotton, F. A.; Frenz, B. A.; Kruczynski, L. *J. Am. Chem. Soc.* 1973, 95, 951. Bullitt, J. G.; Cotton, F. A.; Marks, T. J. *Ibid.* 1970, 92, 2155. Bullitt, J. G.; Cotton, F. A.; Marks, T. J. *Inorg. Chem.* 1972, 11, 671. Cotton, F. A.; Kruczynski, L.; Shapiro, B. L. *J. Am. Chem. Soc.* 1972, 94, 6191. Cotton, F. A.; Adams, R. D. *Ibid.* 6193.

Carbon-13 NMR spectra were recorded on a Nicolet 200 spectrometer operating at 50.3 MHz. Infrared spectra were recorded on a Nicolet 7199 infrared spectrometer. FT-IR spectra of isolated complexes were recorded in 0.11-mm CaF_2 solution cells. Photolyses were done in a Rayonet ultraviolet photochemical reactor. Solvents and liquid reactants were handled by using either Precision Sampling Corp. pressure-lok syringes or Popper and Sons, Inc., Perfektum glass syringes. NMR tubes were 9-in. length and 5-mm o.d., Model 507-PP, from the Wilmad Glass Co.

Reagents and Materials. Deuterated solvents, cyclohexane-d_{12} (99.5% atom-d), benzene-d_6 (99.5% atom-d), and acetone-d_6 (99.5% atom-d) were used as purchased in sealed ampules from either Aldrich or Sigma. Other reactants or solvents were purified according to literature methods[9] and distilled. Carbon-13 carbon monoxide was 90% carbon-13 from Merck, Sharp and Dohme. Chromium complexes were synthesized by the method of Pauson.[10a] Measured properties are as follows. (Hexamethylbenzene)Cr(CO)₃: mp 230–232 °C; IR (CHCl₃, CaF₂) ν(CO) 1949, 1868 cm^{-1}; ^{1}H NMR (90 MHz, C₆H₆, Me₄Si) δ 1.8 (s, 18 H). (Benzene-d_6) Cr(CO)₃: mp 163–164 °C; IR (CHCl₃, NaCl) ν(CO) 1978, 1898 cm^{-1}; ^{1}H NMR (90 MHz, C₆H₆, Me₄Si) δ ~4.5 (br s); mass spectra, m/e (*I*) 222 (2), 221 (10), 220 (49), 219 (2), 164 (12), 137 (13), 136 (75), 53 (12), 52 (100).

[13]CO-Enriched (Benzene)tricarbonylchromium. (Benzene)tricarbonylchromium (0.15 g, 7 mmol) was weighed into a 50-mL round-bottom flask equipped with gas adapter, septum, and magnetic stirrer. Tetrahydrofuran (THF) (25 mL) was added and the flask placed on a vacuum line. The reaction mixture then was subjected to five freeze–pump–thaw cycles, and [13]CO was then introduced. The stopcock of the gas adapter was closed and the flask removed from the apparatus and placed into the UV photochemical reactor for 20 h. Degassing and [13]CO introduction were repeated, and the mixture was stirred and photolyzed for an additional 26 h. The solvent was evaporated and crude yellow solid sublimed to provide yellow crystals (0.85 g, 57% yield): mp 162–163 °C; IR (CHCl₃, CaF₂) ν(CO) 1962, 1950, 1928, 1875, 1858 cm^{-1}; ^{13}C NMR (50.3 MHz, C₆D₁₂–C₉H₁₂) δ 231.9, 91.3;[10b] mass spectra (EI, 20 eV), m/e (*I*) 217 (24), 216 (38), 215 (30), 214 (14), 187 (6), 159 (16), 130 (15), 78 (93), 52 (33).

(*endo*-Dibenzobicyclo[2.2.2]octadiene)Cr(CO)₃[11] was labeled with [13]CO in a similar manner: mp 197–198.5 °C; IR (CDCl₃, 0.11-mm CaF₂) ν(CO) 1952, 1939, 1922, 1867, 1845 cm^{-1}; ^{1}H NMR (90 MHz, C₆D₆) δ 7.3 (s, 4 H), 5.1 (m, 2 H), 4.6 (m, 2 H), 3.7 (s, 2 H), 1.4 (dd, 4 H); mass spectra (DI, 70 eV), m/e (% RA) 346 (3.3), 345 (8.3), 344 (10.1), 343 (5.7), 258 (100), 230 (56.5), 178 (85.3), 129 (37.7), 52 (79.6).

Carbon Monoxide Exchange. [13]CO-enriched (benzene)tricarbonylchromium (5–10 mg, 2.5–5 mmol) was introduced into an NMR tube. Mesitylene (0.2–0.5 mL) and cyclohexane or cyclohexane-d_{12} (0.3–0.5 mL) were added via syringe, and the NMR tube was placed on a vacuum line inside a fume hood. The reaction mixture was subjected to three to five freeze–pump–thaw cycles, and carbon monoxide was passed through the solution until saturation was achieved. The valve was closed, the solution frozen with liquid nitrogen, and the NMR tube sealed with a torch. The ratio of free CO to complexed CO varied from 2:1 to 4:1 depending upon the initial complex concentration. This procedure was used in all cases to put the reaction mixture under an atmosphere of CO.

The reaction tubes were heated for various lengths of time and usually were monitored in the ^{1}H NMR to evaluate the extent of arene exchange. After a certain extent of exchange, the tubes were opened and complexes isolated by HPLC on a Waters analytical-porasil column under the following conditions: pump speed, 3 mL/min; eluent, 98:2 hexanes–ethyl acetate; variable wavelength detector set at 325 nm. Free mesitylene eluted rapidly (1 min) followed by coordinated mesitylene (2 min) and finally benzene complex (3 min). Mass spectra were recorded by probe introduction at 20 eV EI and two per second scan time. Some

(9) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, 1966.

(10) (a) Pauson, P. L.; Mahaffy, C. A. L. *Inorg. Synth.* **1979**, *19*, 154. (b) Bodner, G. M.; Todd, O. J. *Inorg. Chem.* **1974**, *13*, 360.

(11) This compound was synthesized for another study: Goldberg, M. J., unpublished results, University of California, San Diego.

of the hexacarbonylchromium produced as a side reaction under the CO atmosphere usually was isolated by gently warming the solution in the sealed NMR tube to sublime the Cr(CO)₆ to the top of the tube. The tube was broken just above the solution, and the top portion of the NMR tube containing the Cr(CO)₆ was capped and stored in the freezer until the IR spectra could be recorded.

In the cross-labeling experiments, a mixture of [13]CO-enriched benzene complex and benzene-d_6 complex were used as starting material and reaction mixture were analyzed by GC–MS instead of preliminary separation by HPLC. The GC was a HP 5790 gas chromatograph interfaced directly to the mass spectrometer. The complexes were separated on an OV-101 25-m capillary column with the following retention times: benzene complex (4.9 min), mesitylene complex (5.4 min), and the hexamethylbenzene complex (7.1 min). Gas chromatography conditions: injection temperature, 200 °C, temperature program, 50 °C (1 min) to 220 °C (15 °C/min), He carrier gas at 25 cm³/s flow rate. Mass spectra was collected by using 20 eV EI over the mass range 40–500 at a one per second scan time.

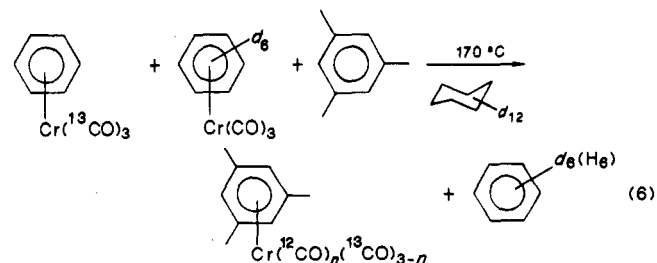The mass spectra results required correction for the presence of the four different isotopes of Cr: [50]Cr, 4%; [52]Cr, 84%; [53]Cr, 10%; [54]Cr, 2%. This is accomplished simply by writing an equation for each parent ion intensity in terms of the four unknowns N, M, B and T, which provides four equations and four unknowns. These are separated into two column matrices and a 4 × 4 "natural abundance of the isotopes" matrix. The values of the unknowns N, M, B and T then are calculated on a computer using a Gaussian elimination program. The data are corrected for the ^{13}C natural abundance (1.1%) in the aromatic ligands of the complexes. It is assumed in the correction that the cross terms, probability of two or more carbons of the ring being ^{13}C, are negligible.

Results

The process that prompted this study is the reaction (eq 5) which is bimolecular in the complex. (The complex

(5)
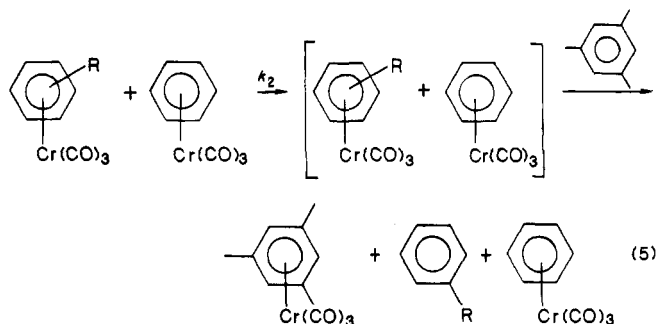
bearing R can be either the benzene or mesitylene complex.) Because k_2 is about 10 times k_1 (of reaction 2), this k_2 term can be made to carry most of the reaction at high complex and low mesitylene concentrations. Under the conditions used (0.72 M mesitylene and 0.1 M (benzene)tricarbonylchromium), the known rate constants[4] indicate that 71% of the reaction proceeds through this (k_2) process. The overall reaction is shown in eq 6, and Table

(6)

I shows the fractions of (arene)Cr([12]CO)₃ (N),(arene)Cr-([12]CO)₂([13]CO) (M), (arene)Cr([12]CO)([13]CO)₂ (B), and (arene)Cr([13]CO)₃ (T), corrected for natural abundance chromium and carbon isotopes for the original complex (ex-

periment 1) and the recovered complexes as well as the product (mesitylene)tricarbonylchromium complex (experiments 2-4). Reactions were carried out for various lengths of time and, in some cases, under an atmosphere of ^{12}CO (experiments 3 and 4).

A comparison of the distributions of variously labeled complexes with those of the starting complexes shows either complete or substantial scrambling even at very low amounts of arene exchange. In experiment 2 the exchange of mesitylene for benzene has proceeded only 30% while scrambling is complete. Experiments 3 and 4 show that very little external ^{12}CO is incorporated during the scrambling reactions.

The scrambling between (benzene)tricarbonylchromium (^{13}CO) and (hexamethylbenzene)tricarbonylchromium (^{12}CO) is seen to be complete in experiment 5. The hexamethylbenzene complex shows no arene exchange. These data are shown as percentages of ^{13}CO in the beginning or recovered complexes in Table II. This table also gives the percentage of external ^{12}CO incorporation in experiments 3 and 4. From these data the rates of internal scrambling and external CO incorporation can be calculated. Arene-exchange rates and external ^{12}CO exchange
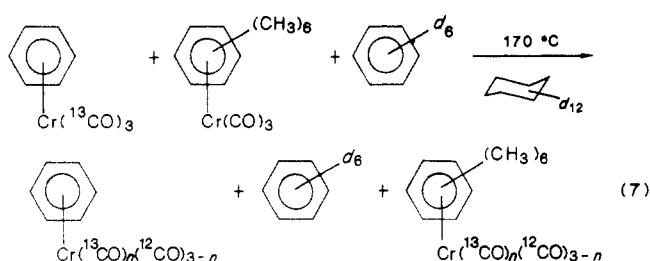
rates were compared by heating ^{13}CO-enriched (benzene)tricarbonylchromium under an atmosphere of carbon monoxide in cyclohexane containing mesitylene at concentrations ranging from zero to 11 M (see eq 3). In one case acetone was added. These data are summarized in Table III along with percentage of arene exchange determined by NMR.[4] This table indicates that substantial arene exchange occurs with little external CO incorporation. It is also clear that the formation of chromium hexacarbonyl parallels CO incorporation.

The last three entries in Table III are especially informative in showing that complete internal arene exchange occurs with almost no external CO exchange.

Discussion

The processes which we documented here and elsewhere[4a] are shown in Scheme I.

The rate constants for these processes are tabulated in Table IV and the appropriate rate constants shown in eq 8-13. The k_{10} values were previously determined by NMR kinetic methods.[4a] Although the other rate constants were obtained from various one-point rate determinations by mass spectra or product isolations, they are sufficiently accurate to be definitive in the following discussions.

We first address the relationship between external CO exchange (eq 8) and arene exchange (eq 10). Although the bimolecular rate constant for external CO exchange, $k_8 \simeq 3 \times 10^{-5}$ M^{-1} s^{-1}, is large, it seems to be independent of arene exchange. Thus, the presence of CO gas does not accelerate or retard arene exchange.[10] At high concentration of arene, the arene exchange proceeds to low conversion without external CO exchange. In addition, acetone catalyzes arene but not CO exchange (experiment 2 of Table IV). A clear demonstration of arene exchange without external CO exchange is the migration of the labeled $Cr(^{13}CO)_3$ moiety without incorporation of ^{12}CO

Scheme I
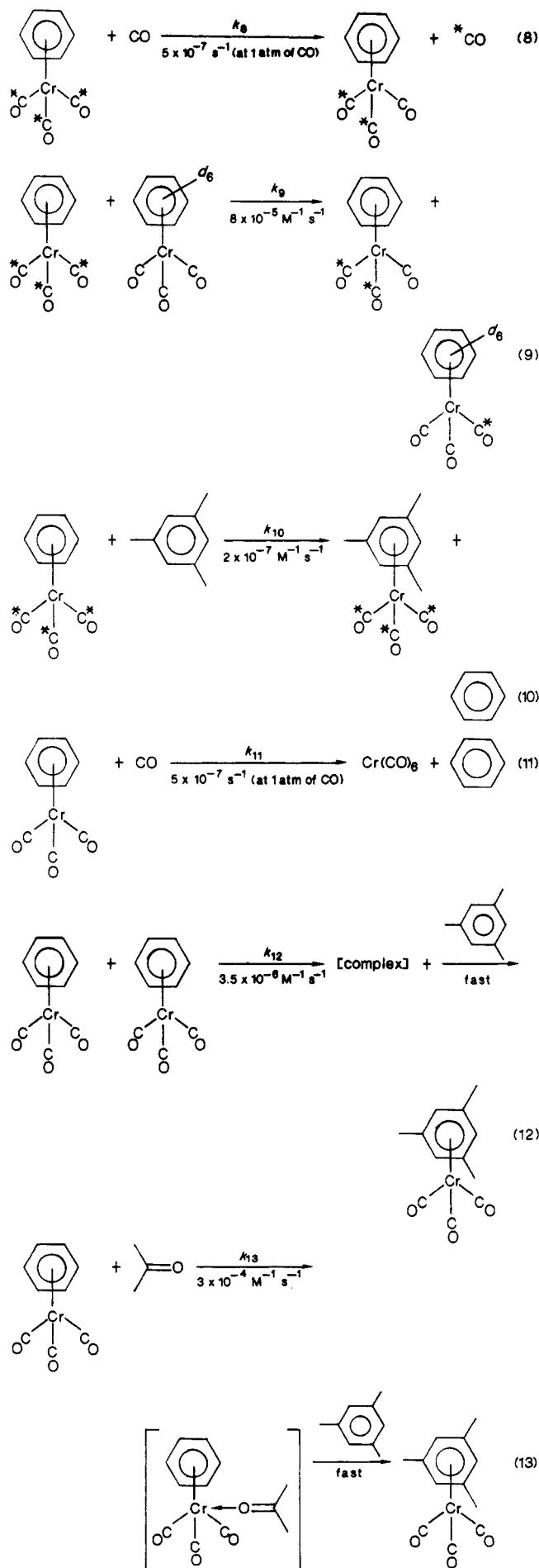
Table I. Fractions of Variously (^{13}CO) Labeled Complexes Recovered after the Reaction of 0.05 M ^{13}CO-Enriched (Benzene)tricarbonylchromium with 0.05 M (Benzene-d_6)tricarbonylchromium and 0.72 M Mesitylene in Cyclohexane-d_{12} at 170 °C for Various Lengths of Time, from Mass Spectral Data[a]

		BzCr(CO)$_3$				(Bz-d_6)Cr(CO)$_3$				MsCr(CO)$_3$			
expt	time, h	N	M	B	T	N	M	B	T	N	M	B	T
1	0	0.13	0.30	0.38	0.19	1.0	0	0	0	0	0	0	0
2	268	0.34	0.40	0.21	0.05	0.36	0.38	0.21	0.06	0.35	0.39	0.20	0.06
statistical[b]						0.34	0.44	0.19	0.03				
3[c]	30	0.25	0.36	0.27	0.11	0.58	0.27	0.11	0.03	0.40	0.30	0.21	0.08
4[c]	96	0.39	0.37	0.18	0.05	0.53	0.32	0.12	0.03	0.44	0.34	0.17	0.05

		BzCr(CO)$_3$				(Bz-d_6)Cr(CO)$_3$				HMBCr(CO)$_3$			
expt	time, h	N	M	B	T	N	M	B	T	N	M	B	T
5[d,e]	96	0.38	0.39	0.18	0.05	0.39	0.38	0.18	0.05	0.39	0.38	0.18	0.05

[a] N, M, B and T represent the fractions of the parent ions of the no label, mono label, bis label and tris label species of the complexes, respectively, after correction for Cr isotopes. [b] The statistical distribution was calculated by using binomial distribution for various % ^{13}CO assuming a mechanism for equilibration of all complexed CO. [c] Under an atmosphere of CO. [d] The reactants were 0.04 M (benzene)Cr-(^{13}CO)$_3$, 0.04 M (hexamethylbenzene)Cr(CO)$_3$, and 2.2 M benzene-d_6 in cyclohexane. [e] Last four column entries for this reaction are for hexamethylbenzene complex (see footnote c).

Table II. Summary of Percent ^{13}CO in Recovered Benzene, Benzene-d_6, and Mesitylene Complexes in the Cross-Labeling Experiments[a]

		% ^{13}CO			
expt	time, h	BzCr(CO)$_3$	(Bz-d_6)Cr(CO)$_3$	MsCr(CO)$_3$	% LL[b]
1	0	54.3			
2	268	32.0	32.0	32.3	
3	30	41.4	20.0	32.7	4
4	96	29.9	21.2	27.7	19
5	96	29.9	29.1	29.7[c]	

[a] This data represents a continuation of Table I, and one should refer there for important information. [b] % LL represents % ^{13}CO exchanged with external CO during cross-labeling experiments under an atmosphere of CO. [c] Value for recovered hexamethylbenzene complex.

Table III. External CO Exchange (or Label Loss) in the Recovered Complexes after Exchange Reactions of ^{13}CO-Enriched Complexes under an Atmosphere of ^{12}CO at 170 °C, Using Mass Spectral Analysis

				% external CO exchange			
expt	complex[a] concn, M	arene,[b] M	time, min	MsCr(CO)$_3$	BzCr(CO)$_3$	% arene exchange	% Cr(CO)$_6$
1	0.10	mesit, 7.2	2315	1.4	7.2	30	
2	0.05	mesit, 7.2[c]	2550	7.3	8.0	75	
3	0.10	mesit, 2.9	4968	9.5	14.4	50	
4	0.10	mesit, 7.2	6708	8.1	16.8	60	
5	0.05	mesit, 7.2	13560	23.5		77	
6	0.05	mesit, 7.2	14180	26.5	42.4	72	33
7	0.05	mesit, 0	13560		47.2		
8	0.05	mesit, 0	14180		56.5		60
9[d]	0.05	mesit, 0	13560		3.1		

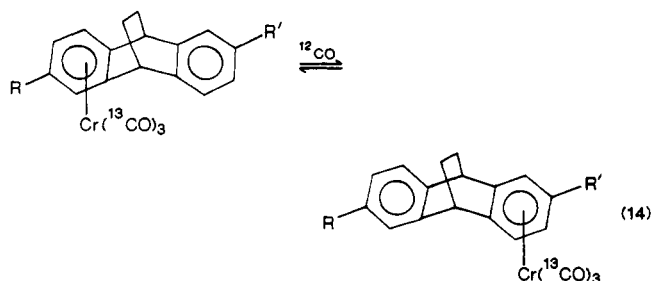|				% external CO exchange			
expt	complex[a] concn, M	arene,[b] M		(Bz-d_6)Cr(CO)$_3$	dibenzoCr(CO)$_3$	% arene exchange	% Cr(CO)$_6$
10	0.05	Bz-d_6, 11	45[e]		0.1		
11	0.05	Bz-d_6, 11	1254	3.1	1.0	37[f]	10
12	0.05	Bz-d_6[g], 11	530	2.6	0.7	33[f]	5

[a] (Benzene)tricarbonylchromium was used in experiments 1–9 and (*endo*-dibenzobicyclo[2.2.2]octadiene) Cr(CO)$_3$ was used in experiments 10–12. [b] Cyclohexane cosolvent. [c] 0.2 M acetone added. [d] No ^{12}CO. [e] Heated for time period corresponding to internal equilibration between rings of dibenzo complex in benzene-d_6 solvent (eq 14). The FT-IR spectra of the carbonyl region was unchanged by this treatment, no loss of tris ^{13}CO label. [f] External exchange to benzene-d_6. [g] 0.05 M acetone-d_6 added.

Table IV. Comparison of Calculated Second-Order Rate Constants for the Different Processes Occurring during Arene-Exchange Reactions of ^{13}CO-Enriched Benzene Complexes with Mesitylene at 170 °C

	mesitylene	$10^7 \, k$, M^{-1} s^{-1}					
expt	concn, M	k_8[a]	k_9	k_{10}[b]	k_{11}[a]	k_{12}	k_{13}
1	7.2	300			2	330	
2[c]	7.1	275					380[c]
3	0.7	250	800	2		37[d]	
4	0	480			560		

[a] Calculated by using ^{12}CO concentration equal to 1.8×10^{-2} M. Second-order behavior was not demonstrated. [b] Reference 4a. [c] 0.2 M acetone as catalyst. The complex catalysis term k_{14} is negligible. [d] Calculated by using data from Table II of ref 4a.

(experiments 10–12 of Table III) for internal and external arene exchange of ^{13}CO-enriched (*endo*-dibenzobicyclo[2.2.2]octadiene)tricarbonylchromium (eq 14). It appears


$$\text{(14)}$$

that external CO exchange is independent of the other processes, suggesting that the tetracarbonyl intermediate, besides losing CO, proceeds almost entirely to $Cr(CO)_6$ (eq 15).

(15)
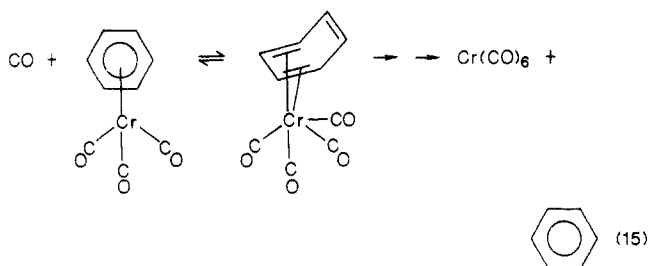
Therefore, external CO attack on the complex or intermediate need not be included in the arene-exchange mechanism. We have shown elsewhere that the rate of external CO exchange increases with increasing pressure of CO.[4b]

The principal discovery in this work is the rapid internal exchange (scrambling) of carbon monoxide under arene-exchange conditions (eq 9). It is equally important that this internal exchange operates independently of the external exchange (eq 8). The importance of internal CO exchange (scrambling) in these processes can be seen by comparing the relative rates for each of the five processes

Scheme II
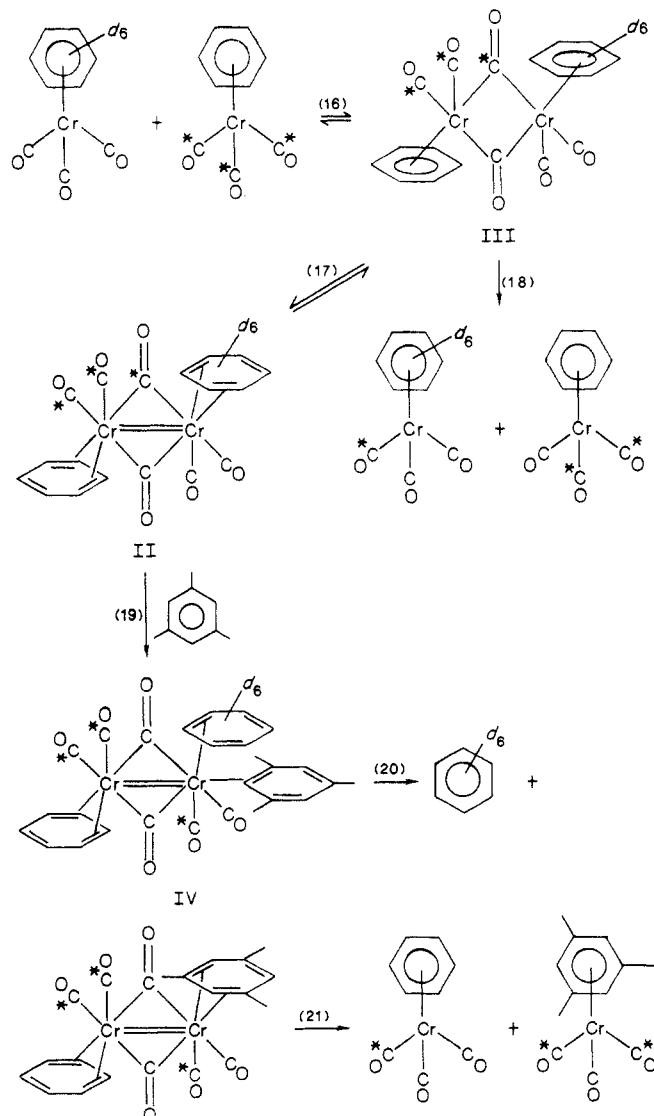
of eq 8–12 at 0.05 M complex in pure mesitylene (7.2 M). The calculated rates (in M s^{-1}) are as follows: internal CO exchange (eq 9), 2×10^{-7}; external CO exchange (eq 8), 2.5×10^{-8}; uncatalyzed arene exchange (eq 10), 1×10^{-8}; complex catalyzed arene exchange (12), 0.8×10^{-8}; chromium–hexacarbonyl formation (eq 11), 2.5×10^{-8}. Therefore even at the highest mesitylene concentration and low complex concentration, the CO scrambling is 10 times faster than total arene exchange, whereas arene exchange, external CO exchange, and formation of chromium hexacarbonyl have similar rates.

The simplest and most appealing mechanistic scheme for reactions 9 and 12, consistent with these results, is that shown (Scheme II). This scheme incorporates both the internal ^{13}CO exchange and the catalyzed arene exchange by using a common intermediate.
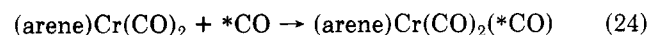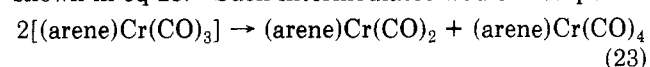
Either the bridge species II or III would satisfy the ^{13}CO exchange and both are 18-electron species on each chromium. However, the catalyzed arene exchange is accommodated somewhat more reasonably by II in which the arenes are η^4 and therefore much more subject to arene attack. This formulation resembles the ketone-catalyzed reaction which we discuss elsewhere.[4] There is evidence for the preequilibrium shown in eq 22. While it is possible

(22)
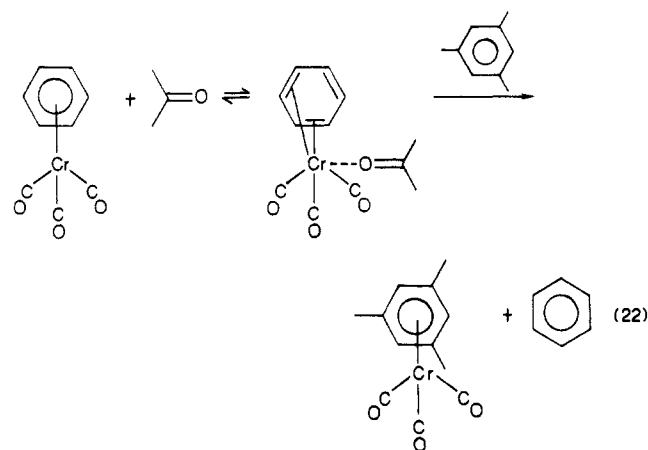
that the intermediate I could account for catalyzed arene exchange, it would have to collapse to some bridged species (e.g., II or III) to give ^{13}CO scrambling.

The fact that ^{13}CO exchange (eq 9) is 10–20 times faster than complex catalyzed arene exchange (eq 12) is nicely consistent with this scheme in which reaction 18 (the reversal of 16) proceeds ten times for each time the process represented by eq 17–21 occurs.

The occurrence of both reactions 9 and 12, without appreciable external CO exchange, clearly eliminates any possible CO transfer of the type suggested previously,[2] shown in eq 23. Such intermediates would incorporate

$$2[(arene)Cr(CO)_3] \rightarrow (arene)Cr(CO)_2 + (arene)Cr(CO)_4$$
(23)

$$(arene)Cr(CO)_2 + {}^*CO \rightarrow (arene)Cr(CO)_2({}^*CO)$$ (24)

external CO, and this process (24) is not observed to occur at rates which compare with exchange reactions (9) or (12). We therefore conclude that (arene)tricarbonylchromium catalyzed arene exchange (the k_2 process of eq 2) occurs through the intermediate IV.

Although no chromium dimers of the type shown in II or III are known,[12,13] there are other chromium dimers that

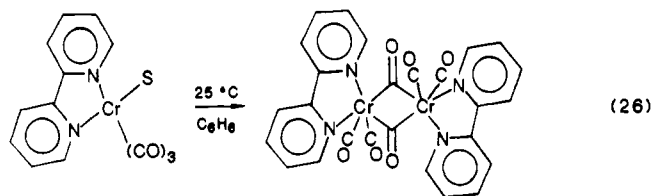(12) Fletcher, T. R.; Rosenfield, R. N. *J. Am. Chem. Soc.* **1985**, *107*, 2203.

(13) Domogatskaya, E. A.; Setkina, V. N.; Baranetskaya, N. K.; Trembovler, V. N.; Yavorskii, B. M.; Shteinshneider, A. Y.; Petrovskii, P. V. *J. Organomet. Chem.* **1982**, *248*, 161.

bear some similarity to both II and III. Knoll, Reiss, Schafer, and Klüfers[14] observed a bridged chromium dimer upon heating the monoacetonitrile complex as shown in eq 25. Behrens and co-workers have prepared the doubly

(25)
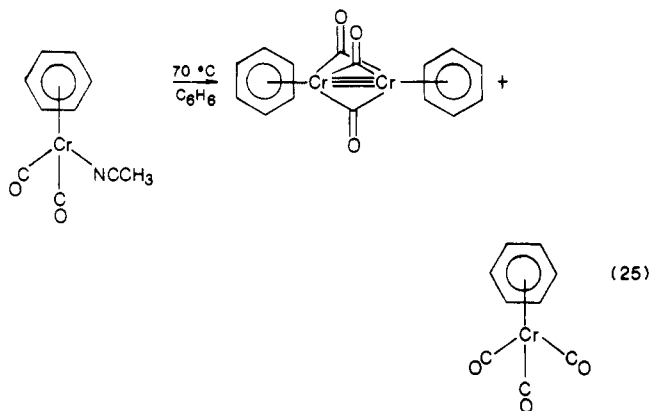
bridged species shown in eq 26 (M = Cr, Mo, W).[6] As written, the latter molecule is a 16-electron metal system.

(26)

Metal–metal bonding would saturate both metals. This suggests a mean of achieving the η^4 intermediates in the dimers which would result in the increased reactivity toward arene exchange.

Conclusion. We have discovered an internal scrambling of CO between (arene)tricarbonyl complexes. This process occurs at about 10 times the rate of the (arene)tricarbonylchromium-catalyzed arene-exchange reaction. These facts lead us to conclude that both scrambling and this catalyzed arene exchange proceed through bis(carbonyl)-bridged intermediates, as shown in eq 16–21.

(14) Knoll, L.; Reiss, K.; Schafer, J.; Klüfers, P. *J. Organomet. Chem.* 1980, 193, C40.

Reactivity of [HFe₃(CO)₁₁]⁻ toward Alkynes. 1. Case of Acetylene

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The [P(C₆H₅)₄][HFe₃(CO)₁₁] cluster (1) reacts at room temperature with acetylene leading to [P-(C₆H₅)₄][Fe₂(CO)₆(μ-CO)(μ-CHCH₂)] (2) and [P(C₆H₅)₄][Fe₃(CO)₁₀(μ₃-CCH₃)] (3) (yield 30 and 40%, respectively). In solution, 3 exists as two forms in equilibrium, [P(C₆H₅)₄][Fe₃(CO)₉(μ-CO)(μ₃-CCH₃)] (3a) and [P(C₆H₅)₄][Fe₃(CO)₉(μ₃-CO)(μ₃-CCH₃)] (3b), but in the solid state only 3b is present. In refluxing acetone, 3 generates [P(C₆H₅)₄][HFe₃(CO)₉(μ₃-η^2-CCH₂)] (4), which immediately reverts to 3 upon addition of carbon monoxide. The reactivity of 3 toward H⁺, C₂H₅⁺, and C(C₆H₅)₃⁺ has been studied. 3 reacts with H⁺ to give HFe₃(CO)₁₀(μ-CCH₃) (5), via the Fe₃(CO)₉(CCH₃)(COH) intermediate detected at low temperature. With C₂H₅⁺, Fe₃(CO)₉(μ₃-CCH₃)(μ₃-COC₂H₅) (6) has been formed and isolated while C(C₆H₅)₃⁺ leads to the formation of Fe₃(CO)₉(μ-CO)(μ₃-η^2-CCH₂) (7), which has also been produced from 5 in boiling methylcyclohexane. The reactivity of 3, 4, 5, and 6 toward hydrogen under pressure has also been tested. Formation of ethane (3) and ethylene (4) has been observed, and the most interesting result is obtained with 6 for which the main product obtained is C₂H₅OCH₂CH₂CH₃, i.e., the product resulting from the coupling and the hydrogenation of the two alkylidyne ligands.

Introduction

The reactivity of unsatured organic molecules with transition-metal clusters is now a well-developed area of investigation[1] and has been mainly studied with clusters of metals of the second and third period. Actually, most of the reactions observed with clusters of the first period are complicated by cluster fragmentation. Nevertheless, a weak metal–metal bond is potentially a propitious factor

of reactivity as metal–metal bond breaking is a way to create a vacant site.[2] It seemed interesting to find a transition-metal cluster of the first period stable enough to avoid or to limit fragmentation reaction but in which the metal–metal bond would be weak, in order to present a good reactivity. We have thought that the cluster [P-(C₆H₅)₄][HFe₃(CO)₁₁] (1), could achieve this challenge as we could expect that the occurrence of a nonlocalized negative charge could stabilize the metal core. Furthermore, the presence of a hydrido ligand was another potential of reactivity.

(1) (a) Deeming, A. J. *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: London, 1980; pp 391–469. (b) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* 1979, 25, 145–222. (c) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* 1983, 83, 203–239.

(2) Vahrenkamp, H. *Adv. Organomet. Chem.* 1983, 22, 169–208.