

ARENE-METAL COMPLEXES: PREPARATION AND REACTIONS OF h^6 -ARENE-Cr(CO)₂(DIPHOS) AND ANALOGS

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Summary

Reaction of 1,2-bis(triphenylphosphino)ethane (diphos) with h^6 -arenetricarbonylchromium(0) complexes results in replacement of one CO by diphos to give h^6 -arene(diphos)dicarbonylchromium(0) (e.g., complex 4) and μ -diphosbis(h^6 -arene)tetracarbonyldichromium(0). Comparison of rate of arene exchange for h^6 -benzenetricarbonylchromium, h^6 -benzene(triphenylphosphine)-dicarbonylchromium, and complex 4 showed that: (1) replacement of CO by a phosphine retards arene exchange and (2) the effect of diphos in stabilizing an h^4 -benzene ligand in complex 4 is not sufficient to allow rapid arene exchange. Nucleophilic substitution for hydrogen was observed for the first time in a phosphine-substituted arene-chromium complex.

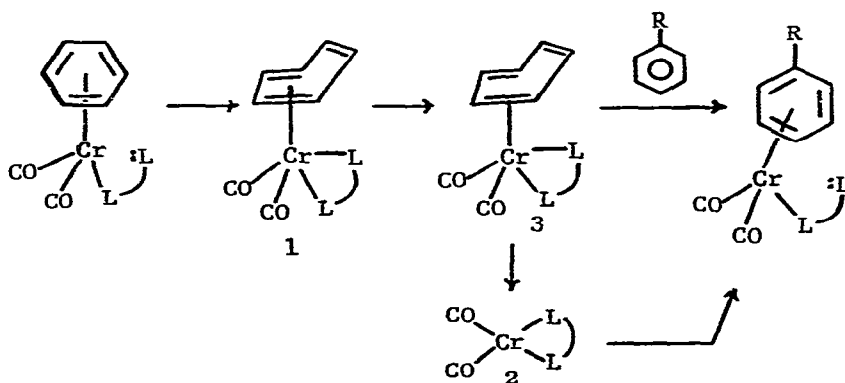
Introduction

The special reactivity of h^6 -arene ligands has been developed into useful organic synthesis methods [1,2]. With the exception of hydrogenation [2]. All of these processes are stoichiometric with respect to the activating metal–ligand units. We and others [3] have been working toward a catalytic process for aromatic substitution for halogen by carbon nucleophiles, a reaction which works well in a stoichiometric way with Cr(CO)₃ as the activating unit [1]. Implicit in any catalytic scheme is a favorable rate of arene ligand exchange, ideally at 25°C or below. In general, arene ligand exchange with Cr(CO)₃ requires temperatures in excess of 100°C, and is not efficient due to side reactions of the Cr(CO)₃ unit. We have pursued two solutions to this problem: (1) to construct a ligand system for chromium which will facilitate exchange and inhibit irreversible reactions of the chromium and (2) to find metal–ligand

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systems where arene exchange is rapid, and then to define conditions for efficient nucleophilic addition to the arene ligand. Here we report our initial efforts related to point (1).

We propose that arene ligand exchange in the h^6 -arene- CrL_3 system would be enhanced if one L unit could serve as a bidentate ligand, thereby reducing the barrier to formation of the h^4 -arene and h^2 -arene species (i.e., 1 and 3), and perhaps stabilizing a transient CrL_4 system (i.e., 2). This hypothesis is based on the assumption of a dissociative mechanism for arene exchange [4] and on the



observations that properly chosen donor molecules can enhance the rate of arene exchange in arene- $\text{Cr}(\text{CO})_3$ [3a–3c] and in arene- $\text{Mo}(\text{CO})_3$ [3d,4] complexes, presumably by forming a version of 1, 2 and/or 3. The extra ligand is expected to moderate the expected high reactivity of the coordinatively unsaturated intermediates (2, 3). It was proposed several years ago that available donor ligands (especially solvent) could induce dissociation of h^6 -arene ligands through tetra- and dihapto intermediates [5].

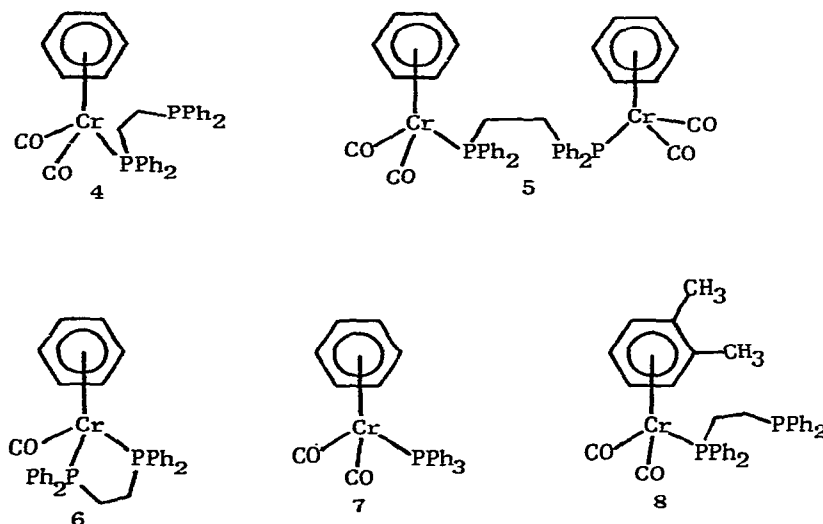
Results and discussion

Preparation of complexes

The first examples of h^6 -arene $\text{Cr}(\text{CO})_2\text{L}$, where L = monocoordinated diphos (e.g., 4) resulted from direct substitution with diphos and h^6 -arene $\text{Cr}(\text{CO})_3$. Optimum yields of 4 were obtained by irradiating an equimolar mixture of h^6 -benzene- $\text{Cr}(\text{CO})_3$ and diphos, ca. 0.01 M in benzene for 4 h at 50°C. Complex 4 was obtained in high purity (65% yield) by trituration of the crude mixture with ether; excess diphos and the dimeric complex, 5, are insoluble. Further purification attempts inevitably led to substantial losses. Complex 4 is more sensitive toward oxidative decomposition compared to h^6 -benzene- $\text{Cr}(\text{CO})_3$. The byproduct, 5, was obtained in high purity (54% yield) by irradiation of h^6 -benzene- $\text{Cr}(\text{CO})_3$ with diphos (0.4 mole-equiv). A small amount of unreacted diphos was removed by trituration with concentrated aqueous hydrochloric acid. Alternative structures such as 6 are ruled out primarily by IR and ^{31}P NMR data (see below). The formation of 6 is not expected, since attempts to replace a second CO ligand in arene- $\text{Cr}(\text{CO})_3$ with a donor ligand such as R_3P have failed [6,7]. However, related reactions with h^5 - $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ and diphos produce both a chelated product (analog of 6) and a diphos-bridged species

(analog of 5), but not the analog of 4 [8]. We failed to obtain 6 even on prolonged irradiation of 4.

The structures are assigned as follows. Both 4 and 5 show two CO stretching frequencies (Table 1) in the IR; the alternative structure 6 would be expected to give a single band, similar to $h^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})(\text{diphos})$ [8]. Phosphorus (^{31}P) NMR spectral data for 4 show singlets (proton decoupled) at δ 85.1 (complexed



phosphine) and -12.4 ppm (free phosphine), relative to external H_3PO_4 . For comparison, free ethyldiphenylphosphine [9] appears at $\delta -12.1$ ppm and the phosphorus of 7 is at δ 91.1 ppm [10]. The ^1H NMR spectrum shows two overlapping multiplets for the $-\text{CH}_2-$ units, centered at δ 2.44 and 2.22 ppm, and the benzene ligand appears as a narrow multiplet at δ 4.26 ppm. Osmometric molecular weight determination gave 575 (calcd. for $\text{C}_{34}\text{H}_{30}\text{CrO}_2\text{P}_2$ 584.5), while the peak of highest m/e in the mass spectrum is 556 (parent $-\text{CO}$). Satisfactory combustion analysis could not be obtained, probably due to difficulty in crystallization and chromatography of 4. The structure of 5 was

TABLE 1
INFRARED DATA FOR DIPHOS COMPLEXES

Complex	CO stretching absorption ^a	
	Nujol mull	CH_2Cl_2
$\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3$	1978, 1910	1967, 1891
$\text{C}_6\text{H}_5\text{Cr}(\text{CO})_2\text{PPh}_3$, 7	1892, 1832	1884, 1825
$\text{C}_6\text{H}_5\text{Cr}(\text{CO})_2\text{diphos}$, 4	1882, 1805	1884, 1806
$[\text{C}_6\text{H}_5\text{Cr}(\text{CO})_2]\text{diphos}$, 5	1889, 1816	1882, 1822
$\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{PPh}_3$	—	1934, 1862 ^b
$[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2]_2\text{diphos}$	—	1934, 1862 ^b
$\text{C}_5\text{H}_5\text{Mn}(\text{CO})\text{diphos}$	—	1818 ^b

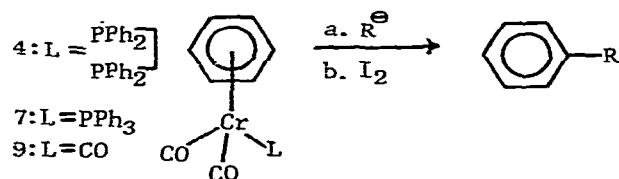
^a All bands are strong. ^b These data are from chloroform solution, reported in ref. 8.

established through parallel data, especially the ^{31}P NMR (singlet at δ 85.07 ppm, proton decoupled). ^1H NMR ($-\text{CH}_2-$ singlet at δ 2.20 ppm), and molecular weight data (osmometry, 707; mass spectral, 718. Calcd.: 718.70. Both 3 and 4 react with mild oxidizing agents to liberate 0.9–1.0 mol-equiv of benzene.

A similar synthesis procedure starting from h^6 -(*o*-xylene) $\text{Cr}(\text{CO})_3$ produced complex 8, characterised primarily by ^1H NMR.

Reactions of phosphine-substituted h^6 -arene complexes with carbon nucleophiles

In order to verify that replacement of a carbon monoxide ligand with phosphine does not prohibit addition to the arene ligand, reactions of 4 and 7 with two carbanions were carried out (Table 2). In each case, the addition/oxidation method was used to give overall substitution for hydrogen [11].



The results in Table 2 (especially the failure of the ester enolate, entry 5) suggest that the phosphine substitution lowers the electrophilic reactivity of the arene ligand, as expected [12], but does not prohibit the addition of simple carbon nucleophiles (entries 2–4).

Attempted arene exchange reactions

Reaction of a solution of 4 in toluene- d_8 (monitoring by ^1H NMR) for 20 h at 25°C or under irradiation for 3–4 h, produced no significant formation of free benzene nor diminution of the relative intensity of the benzene ligand signals compared to the aryl-H and $-\text{CH}_2-$ signals. Reaction of 4 with *o*-xylene (expected to be a more stable ligand than benzene [3a,c]) in benzene- d_6 also showed no significant formation of 8 after 52 h at 75°C . For careful comparison of thermal exchange rates, parallel experiments were carried out with complex 4, h^6 -benzene- $\text{Cr}(\text{CO})_3$, and complex 7 under the same conditions in benzene- d_6 solution, in sealed tubes. h^6 -Benzene- $\text{Cr}(\text{CO})_3$ shows 10% exchange after 3 h/ 135°C , 50% after an additional 3 h/ 150°C , and 100% after 18 h/ 150°C , consis-

TABLE 2
SUBSTITUTION FOR HYDROGEN IN COMPLEXES 4, 7, AND 9

Entry	Complex	Anion ^d	Product (yield, %)
1	9	$\text{LiC}(\text{CH}_3)_2\text{CN}$	$\text{PhC}(\text{CH}_3)_2\text{CN}$ (88) ^{a, c}
2	7	$\text{LiC}(\text{CH}_3)_2\text{CN}$	$\text{PhC}(\text{CH}_3)_2\text{CN}$ (63) ^a
3	7	$\text{LiC}(\text{CH}_3)_2\text{CN}$	$\text{PhC}(\text{CH}_3)_2\text{CN}$ (74) ^b
4	4	$\text{LiC}(\text{CH}_3)_2\text{CN}$	$\text{PhC}(\text{CN})_2\text{CN}$ (56)
5	7	$\text{LiCH}(\text{CH}_3)\text{CO}_2\text{R}$	$\text{PhCH}(\text{CH}_3)\text{CO}_2\text{R}$ (0)
6	9	$\text{LiCH}(\text{CH}_3)\text{CO}_2\text{R}$	$\text{PhCH}(\text{CH}_3)\text{CO}_2\text{R}$ (92) ^{b, c}

^a The solvent was THF. ^b The solvent was THF/HMPA. ^c See ref. 11. ^d All reactions were carried out at 0°C for 30 min followed by addition of excess iodine.

tent with previous studies [3]. With complex 4, no exchange (or any other spectral change) was observed up to 40 h/200°C! At 240°C, benzene begins to appear in the solution and the other spectral features deteriorate. Similarly, complex 7 underwent exchange more slowly than h^6 -benzene-Cr(CO)₃ (no exchange after 3 h/180°C; 15% exchange after 10 h/200°C), and a bit faster than 4. The slow (immeasurable) exchange of 4 is presumably due to the donor effect of the alkyldiphenylphosphine ligand (diphos), increasing the back-bonding to the arene ligand and strengthening the arene—Cr bond. This effect dwarfs any accelerating effect of the extra ligand in 4.

Summary and conclusions

h^6 -Arene-Cr(CO)₂L complexes can be prepared efficiently where L is monocoordinated diphos and the arene ligand can undergo addition by reactive carbanions. Presumably, substitution for halogen in an h^6 -haloarene analog would also proceed readily [12], although this point was not explicitly tested. However, the postulated effect of the “extra” donor ligand in 3, expected to assist the conversion of h^6 - to h^4 - and h^2 -arene intermediates, was insignificant compared to the effect of a donor phosphine in strengthening the arene—chromium bond.

Experimental

h^6 -Benzenetricarbonylchromium was prepared by standard procedures from benzene and hexacarbonylchromium; h^6 -(benzene)dicarbonyl(triphenylphosphine)chromium (7) was prepared according to a literature procedure [13]. Diphos was obtained from ICN Chemical Co. and used without further purification. All operations with organometallic complexes were carried out under argon, using Schlenk equipment and double manifold techniques [14]. Tetrahydrofuran, benzene, and toluene were purified by distillation from the sodium-benzophenone ketyl immediately before use. ¹H NMR spectra were obtained on a Perkin-Elmer Model 24B spectrometer at 60 MHz. ³¹P NMR spectra were obtained on a Varian Model XL-100 spectrometer at 40.5 MHz using external H₃PO₄ as a reference. Infrared spectra were obtained on a Perkin-Elmer Model 299 grating instrument.

Preparation of h^6 -benzene-1,2-bis(diphenylphosphino)ethanedicarbonylchromium (4)

A mixture of benzenetricarbonylchromium (214 mg, 1.00 mmol) and diphos (426 mg, 1.00 mmol) in benzene (40 ml) under argon in a Pyrex flask was irradiated by positioning a water-jacketed Hanovia 450-watt medium pressure lamp a few inches from the flask. The solution was irradiated for 3.5 h, the solvent was removed by rotary evaporation and the residue was stirred with 50 ml of ether. The combined ether solution was concentrated to yield orange crystals of 4, 370 mg, 63% yield, with no detectable impurities by ¹H NMR analysis. A sample (155 mg) was chromatographed on Florisil (10-cm column eluting with benzene/hexane (1/1) to produce a sample of 4 (55 mg) and much decomposition on the column; m.p. 160–165°C (turns yellow), 254–250°C (dec.). ³¹P NMR (CDCl₃, proton-decoupled): δ -12.429 (br s, uncomplexed P),

85.130 (br s, complexed P). ^1H NMR (CDCl_3): δ 7.78–7.26 (m, 20 H, aryl-P), 4.22 (m, 6 H, h^6 -benzene), 2.44 (m, 2 H, CH_2), 2.22 (m, 2 H, CH_2). ^1H NMR (C_6D_6): δ 7.85–7.12 (m, 20 H, aryl-P), 4.20 (m, 6 H, h^6 -benzene), 2.25 (m, 2 H, CH_2), 2.02 (m, 2 H, CH_2). IR (CH_2Cl_2): 1884s, 1806s cm^{-1} and IR (Nujol mull): 1882s, 1805s cm^{-1} . Osmometric (CHCl_3) mol. wt.: Calcd. for $\text{C}_{34}\text{H}_{30}\text{CrO}_2\text{P}_2$: 584.6. Found: 575. Mass spectrum: m/e 556 (13%), 449 (35%), 448 (83%), 205 (32%), 203 (43%). 78 (100%), 52 (76%).

Anal. Found: C, 68.19; H, 5.51; P, 10.59. $\text{C}_{34}\text{H}_{30}\text{CrO}_2\text{P}_2$ calcd.: C, 69.86; H, 5.17; P, 10.60%.

Preparation of μ -[1,2-bis(diphenylphosphino)ethane]tetracarbonyldibenzenedichromium, 5

A solution of h^6 -benzene- $\text{Cr}(\text{CO})_3$ (235 mg, 1.10 mmol) and diphos (213 mg, 0.50 mmol) in cyclohexane (20 ml) was irradiated as above for 10 h. A yellow solid separated (225 mg, 71% crude yield of 5). It was collected, washed with benzene and triturated sequentially with 20-ml portions of concentrated aqueous hydrochloric acid, water, ethyl alcohol, and hexane. The bright yellow product was dried at 0.01 Torr; 193 mg, 54% yield; m.p. 272°C , dec. ^{31}P NMR (CHCl_3 , proton decoupled): δ 85.07, singlet. ^1H NMR (CDCl_3): δ 7.17 (br s, 20 H, aryl-P), 4.51 (s, 12 H, h^6 -benzene), 2.20 (s, 4 H, $-\text{CH}_2-$). IR (CH_2Cl_2): 1883s and 1823s cm^{-1} . Osmometric (C_6H_6) mol. wt.: Calcd. for $\text{C}_{42}\text{H}_{36}\text{Cr}_2\text{O}_4\text{P}_2$: 718.70. Found: 707. Mass spectrum: m/e 718 (6%), 502 (34%), 450 (100%), 397 (58%), 262 (46%), 183 (58%), 78 (100%).

Oxidation of complexes 4 and 5 with excess iodine

In separate experiments, solutions of 4 (1.0 mmol) and 5 (1.0 mmol) in CDCl_3 containing 1.00 mmol equiv of *o*-xylene was treated with 2–3 mg-at of I_2 . After a few hours at 25°C , comparison of the ^1H NMR signal for *o*-xylene to the signal for benzene indicated a mole-ratio benzene/xylene of 0.90–1.0.

*Preparation of 1,2-bis(diphenylphosphino)ethanedicarbonyl- h^6 -(*o*-xylene)-chromium, 8*

A mixture of h^6 -(*o*-xylene)tricarbonylchromium [15] (242 mg, 1.00 mmol) and diphos (426 mg, 1.00 mmol) in benzene (80 ml) under argon was irradiated as before for 4.5 h. Removal of the solvent by rotary evaporation left a yellow solid which was >90% pure. Structure 8 was assigned based on ^1H NMR signals: δ 7.4–7.1 (m, 20 H, aryl-P), 4.4 (s, h^6 -arene-H), 2.14 (s, 6 H, aryl- CH_3), 2.20 (m, 2 H, $-\text{CH}_2-$), 2.00 (m, 2 H, $-\text{CH}_2-$). The sample could not be freed of small amounts of diphos.

Reaction of h^6 -benzenedicarbonyltriphenylphosphinechromium with 2-lithio-2-methylpropionitrile

To a solution of lithium diisopropylamide [16] (1.00 mmol) in 5 ml of THF at -78°C under argon was added 2-methylpropionitrile (91 μl , 69 mg, 1.00 mmol) dropwise. The mixture was allowed to warm to 0°C for 15 min, then returned to -78°C and a solution of complex 7 (448 mg, 1.0 mmol) in THF (7.0 ml) was added dropwise over a few minutes followed by HMPA, 3.0 ml. The solution became dark orange. After the mixture was warmed at 0°C

for 30 min, it was cooled to -78°C and a solution of iodine (0.76 g, 6 mg-at) in THF (6.0 ml) was added dropwise over a few minutes. The mixture was allowed to stir at 25°C for 3 h, then partitioned between aqueous sodium thiosulfate solution and ether. The ether layer was washed sequentially with 10% aqueous sodium bicarbonate, water, and saturated aqueous sodium chloride solutions. The ether solution was dried over anhydrous magnesium sulfate, concentrated by rotary evaporation, and the residue was purified by short path distillation ($100^{\circ}\text{C}/0.01$ Torr), 124 mg, 74% yield. It was identified as 2-methyl-2-phenylpropionitrile by comparison of GC retention time and ^1H NMR spectral data with a sample from alternative synthesis [1c].

Similarly, complex 7 (1.0 mmol) and 2-lithio-2-methylpropionitrile (1.0 mmol) were allowed to react in THF alone. Addition of iodine and isolation as before gave 2-methyl-2-phenylpropionitrile, 63% yield.

Similarly, complex 4 (180 mg, 0.31 mmol) and 2-lithio-2-methylpropionitrile (0.31 mmol) were mixed in THF at -78°C and allowed to stir at 0°C for 0.5 h. Addition of excess iodine (0.79 g, 3.1 mg-at) in THF (20 ml) gave, after 4 h at 25°C and isolation as above, 25 mg of 2-methyl-2-phenylpropionitrile (56% yield).

Similarly, an equimolar mixture of complex 7 and tert-butyl 2-lithiopropionate was allowed to react at 0°C for 0.5 h, treated with excess iodine, and the products isolated as before. The crude product was analyzed by GC and ^1H NMR, using a sample of tert-butyl 2-phenylpropionate for comparison. The yield of tert-butyl 2-phenylpropionate was $<2\%$.

Attempted exchange of o-xylene with complex 4

A mixture of h^6 -(benzene)tricarbonylchromium (21.4 mg, 0.1 mmol), diphos (42.6 mg, 0.1 mmol), *o*-xylene (0.1 ml, 0.6 mmol) and 0.3 ml of benzene- d_6 was sealed under argon in a 5-mm Pyrex NMR sample tube. Irradiation with a water-jacketed Hanovia 450-watt medium pressure lamp positioned a few cm from the sample produced a change in the ^1H NMR spectrum consistent with the formation of complex 4. The reaction was complete after 4 h. The ^1H NMR spectrum was monitored at intervals while heating the sample at 55°C for 18 h and 75°C for 52 h. Neither during the irradiation period nor during heating was a signal observed at δ 2.14 ppm, characteristic of the *o*-xylene complex, 8. Dur-

TABLE 3
FORMATION OF BENZENE FROM $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, 4 AND 7

Cumulative time (h)/temperature ($^{\circ}\text{C}$)	Free benzene (%)		
	$\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$	Complex 4	Complex 7
1/102	0	0	0
3/135	10	0	0
3/150	50	0	0
3/150	70	0	0
12/150	100	0	0
10/200	—	0	15
20/200	—	0	25
40/200	—	0	40

ing the heating period, no change was observed in the relative intensities and positions of signals attributed to 4 and to *o*-xylene.

Reactions of complex 4, complex 7, and h^6 -(benzene)tricarbonylchromium in benzene- d_6 at high temperature

Precisely parallel experiments were carried out with samples (ca. 0.1 mmol) of 4, 7, and h^6 -(benzene)tricarbonylchromium dissolved in 0.3–0.4 ml of C_6D_6 in a 5-mm NMR sample tube. The 1H NMR spectra were monitored for appearance of new absorptions (free benzene) and changes in relative intensities (h^6 -benzene relative to other signals in 4 and 7).

The 1H NMR spectrum of 4 in C_6H_6 after 40 h/200°C was identical in every respect with the spectrum before heating.

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