Chemistry of [.eta.6-bis(tri-n-butylstannyl)benzene]chromium tricarbonyl complexes. Versatile intermediates in the preparation of substituted (.eta.6-arene)chromium tricarbonyl systems

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57.50; H, 4.22. Found: C, 57.84; H, 4.22.

Method B. 1-Chloro-2,4-pentadiene was added dropwise to a tetrahydrofuran solution of (η^5-C_9H_7)Mo$(CO)_3$Na (2.08 g, 6.65 mmol) at 0 °C and stirred for 3 h. The solution was evaporated to dryness and chromatographed through neutral alumina column using ether as the eluting solvent. A yellow band was developed, collected, and evaporated to dryness to give a yellow solid. Further recrystallization from ether gave yellow crystals (0.042 g, 0.12 mmol).

(H) Synthesis of (η^5-$C_{13}H_9$)Mo$(CO)_2$(η^3-C_5H_7) (9). Method A. Sodium fluorenide (0.50 g, 2.62 mmol) was added dropwise to **2** (1 g, 2.62 mmol) in 30 mL of tetrahydrofuran solution and stirred at 0 °C for 16 h. The solution was evaporated to dryness and chromatographed through a neutral alumina column using ether as the eluting solvent. A yellow band was developed, collected, and evaporated to dryness. The residues were heated under vacuum (4.0×10^{-4} Torr) at 60 °C until fluorene solids were completely removed. The residues were chromatographed through a neutral alumina column using ether as the solvent. A yellow band was collected concentrated and cooled to 0 °C to give yellow crystals (0.399 g, 1.04 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.57 (1 H, dd, H^1), 0.85 (1 H, dd, H^2), 1.51 (1 H, t, H^4), 3.17 (1 H, td, H^3), 4.69 (1 H, dd, H^6), 5.05 (1 H, td, H^5), 7.05 (2 H, m), 7.20 (2 H, m), 7.57 (1 H, d), 7.61 (1 H, d), 7.62 (1 H, d), 7.65 (1 H, d), J_{12} = 2.4 Hz, J_{13} = 10.2 Hz, J_{23} = 7.1 Hz, J_{34} = 10.4 Hz, J_{45} = 10.4 Hz, J_{56} = 16.4 Hz, J_{57} = 10.0 Hz, J_{67} = 1.3 Hz. Mass spectrum (12 eV, ^{98}Mo, 23.78%): *m/e* 386 (M^+), 358 (M^+ – CO), 336 (M^+ – 2CO). IR spectrum (CH_2Cl_2): ν(C=C) 1614 cm^{-1}; ν(CO) 1943 (s), 1864 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{16}MoO_2$: C, 62.51; H, 4.20. Found: C, 62.74; H, 4.34.

Method B. This complex can be also obtained from the reaction between (η^5-$C_{13}H_9$)Mo$(CO)_3$Na and 1-chloro-2,4-pentadiene in tetrahydrofuran at 0 °C. The yield is 2–0.5%.

(I) X-ray Diffraction Study of 2, 3, and 4. Data were collected at room temperature on a CAD4 diffractometer, using graphite-monochromated Mo Kα radiation. All data reduction and structure refinement were performed by using the NRCC-SDP-VAX package. Crystal data, details of data collection, and structure analysis are summarized in Table IV. Compound **2** has a noncentric space group and the one presented had the best *R* factor (R_f = 2.4%; R_w = 2.6%). The other enantiomorphic structures had higher *R* factor after refinement (R_F = 4.7%; R_w = 4.6%).

The structure of three compounds were solved by Patterson method. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were added at idealized positions and included in the structure factor calculations.

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Registry No. **1**, 117652-88-7; **2**, 117652-89-8; **3**, 117652-90-1; **4** (anti isomer), 117652-91-2; **4**·$CHCl_3$ (anti isomer), 117708-21-1; **4** (syn isomer), 117708-20-0; **5**, 117652-92-3; **6**, 117652-93-4; **8** (exo isomer), 117652-94-5; **8** (endo isomer), 117708-22-2; **9**, 117652-95-6; Mo$(CO)_6$, 13939-06-5; Mo$(CO)_3(CH_3CN)_3$, 15038-48-9; (η^5-CaH_7)Mo$(CO)_3$Na, 12088-81-2; $NaC_{13}H_9$, 3531-83-7; (η^5-$C_{13}H_9$)-Mo$(CO)_3$Na, 117652-96-7; 1-chloro-2,4-pentadiene, 40596-30-3; 1-bromo-2,4-pentadiene, 1001-93-0; indene, 95-13-6.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and complete bond distances and bond angles for **2**, **3**, and **4** (9 pages); listings of structure factor amplitdues for **2**, **3**, and **4** (85 pages). Ordering information is given on any current masthead page.

Chemistry of {η^6-Bis(tri-*n*-butylstannyl)benzene}chromium Tricarbonyl Complexes: Versatile Intermediates in the Preparation of Substituted (η^6-Arene)chromium Tricarbonyl Systems

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The {η^6-1,3-bis(tri-*n*-butylstannyl)benzene}- and {η^6-1,4-bis(tri-*n*-butylstannyl)benzene}chromium tricarbonyl complexes, prepared as stable yellow oils, react smoothly with *n*-BuLi at –78 °C in tetrahydrofuran (THF) to produce the (η^6-1,3-dilithiobenzene)- and (η^6-1,4-dilithiobenzene)Cr$(CO)_3$ complexes. The latter react with a variety of reagents to give good to excellent yields of some new (η^6-arene)Cr$(CO)_3$ complexes. The transmetalations were found to proceed most efficiently in THF; almost no reaction took place in ether. The Cr$(CO)_3$ complexation is capable of directing the transmetalation in {η^6-4,4′-bis(tri-*n*-butylstannyl)-biphenyl}Cr$(CO)_3$ regioselectively to the coordinated phenyl ring. The palladium-catalyzed cross-coupling of selected aryl halides, (η^6-C_6H_5Cl)Cr$(CO)_3$, and trimethyl(phenylethynyl)stannane was studied. The study indicated that the Cr$(CO)_3$ complexation significantly enhanced the rate of the cross-coupling reaction.

Introduction

(η^6-Arene)Cr$(CO)_3$ complexes have been studied extensively in a wide variety of applications ranging from their use as stoichiometric asymmetric reagents to models for ligand substitution reactions.[1] The widespread use of the complexes is in part due to their robust nature and often simple and high-yield syntheses. The Cr$(CO)_3$ complexation activates the arene ligand in nucleophilic substitution and deprotonaton reactions, and the Cr$(CO)_3$ unit can be easily removed from the arene ligand at the end of the synthetic sequence.

In general, the syntheses of (η^6-arene)Cr$(CO)_3$ complexes in which the arene contains electron-withdrawing groups usually proceed in low conversions and require a large excess of arene present.[2] In cases where the arene is a solid

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(1) Davis. R.; Kane-Maguire, L. A. P. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, pp 1001–54 and references cited therein.

(2) For examples see: (a) Fischer, E. O.; Öfele, K.; Essler, H.; Frohlich, W.; Mortensen, P.; Semmlinger, W. *Chem. Ber.* **1958**, *91*, 2763. (b) Strohmeier, W.; Hartmann, P. Z. *Naturforsch.*, *B* **1963**, *18*, 506. (c) Klopman, G.; Calderazzo, F. *Inorg. Chem.* **1967**, *6*, 977.

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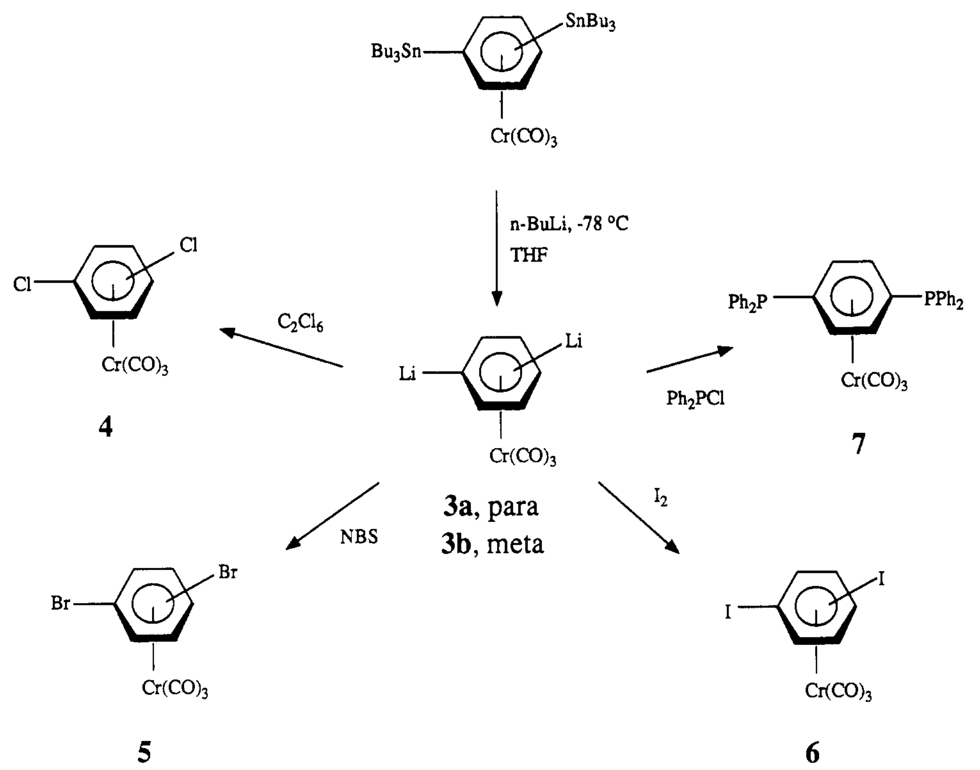
Scheme I

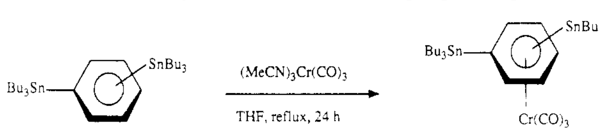


or a high boiling liquid, purification of the desired (η^6-arene)Cr(CO)$_3$ complex can be extremely difficult. An efficient route to complexes containing electron-withdrawing groups on the arene ligand was developed independently by Rausch[3] and Semmelhack[4] where the (η^6-C$_6$H$_5$Li)Cr(CO)$_3$ complex is generated and then used in reactions with various electrophiles. Metalation of ferrocene and other η^5-cyclopentadienyl transition-metal complexes has also provided valuable synthetic intermediates for the elaboration of η^5-cyclopentadienyl complexes.[5]

For the utilization (η^6-1,3-dihaloarene)- and (η^6-1,4-dihaloarene)Cr(CO)$_3$ complexes in a series of palladium-catalyzed polycondensation reactions,[6] we needed to develop efficient routes for their synthesis. The existing methods were not satisfactory, with only the preparation of (η^6-1,3-dichlorobenzene)Cr(CO)$_3$ an exception.[7] We have developed a route for the synthesis of {η^6-1,3-bis(functionalized)benzene}- and {η^6-1,4-bis(functionalized)benzene}Cr(CO)$_3$ complexes based on the (η^6-1,3-dilithiobenzene)- and (η^6-1,4-dilithiobenzene)Cr(CO)$_3$ complexes. The latter were prepared by the transmetalation[8] of the {η^6-1,3-bis(tri-*n*-butylstannyl)benzene}- and {η^6-1,4-bis(tri-*n*-butylstannyl)benzene}Cr(CO)$_3$ compounds with *n*-BuLi in THF at −78 °C and subsequently treated with a variety of electrophiles. The reactions proceed regiospecifically and in good to excellent yields.

Results and Discussion

Reaction of 1,4- or 1,3-bis(tributylstannyl)benzene with (MeCN)$_3$Cr(CO)$_3$ in THF produces **2a** (91%) and **2b** (75%) as yellow oils (eq 1). Attempts to induce crystallization of **2** have not been successful. The spectra of **2a** are similar to those of {η^6-1,4-bis(trimethylstannyl)benzene}Cr(CO)$_3$ (**8**) which has been prepared previously.[9]



(1)

2a, para
2b, meta

It was of interest to explore the palladium catalyzed cross-coupling[10] chemistry of complex **2a**. Treatment of

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(3) Rausch, M. D.; Gloth, R. E. *J. Organomet. Chem.* **1978**, *153*, 59.

(4) Semmelhack, M. F.; Bisaha, J.; Czarny, M. *J. Am. Chem. Soc.* **1979**, *101*, 768.

(5) Ferrocene metalation: Rosenblum, M. *Chemistry of the Iron Group Metallocenes*; Wiley: New York, 1965. Green, M. L. H. *Organometallic Compounds*; Chapman & Hill: London, 1968; Vol. 2. Slocum, D. W.; Engelmann, T. R.; Ernest, C.; Jennings, C. A.; Jones, W.; Koonsvitsky, B.; Lewis, J.; Shenkin, P. *J. Chem. Educ.* **1969**, *46*, 144. [1]Ferrocenophane transmetalations: Seyferth, D.; Withers, H. P., Jr. *Organometallics* **1982**, *1*, 1275. Withers, H. P., Jr.; Seyferth, D.; Fellmann, J. D.; Garrou, P. E.; Martin, S. *Ibid.* **1982**, *1*, 1283. Other cyclopentadienyl metalations: Dean, W. K.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1061. Werner, H.; Hofmann, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 464. Berryhill, S. R.; Sharenow, B. *J. Organomet. Chem* **1981**, *221*, 143. Orlova, T.; Setkina, V. N.; Sizoi, V. F.; Kursanov, D. N. *J. Organomet. Chem.* **1983**, *252*, 201. Orlova, T.; Setkina, V. N.; Kursanov, D. N. *J. Organomet. Chem.* **1984**, *267*, 309. Head, P. C.; Patton, A. T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1185. Wright, M. E.; Day, V. W. *J. Organomet. Chem.* **1987**, *329*, 43. Lynch, T. J.; Dominguez, R. *Organometallics*, in press.

(6) Wright, M. E. *Macromolecules*, submitted for publication. Wright, M. E. *Polym. Prepr.* **1988**, *29*, 294.

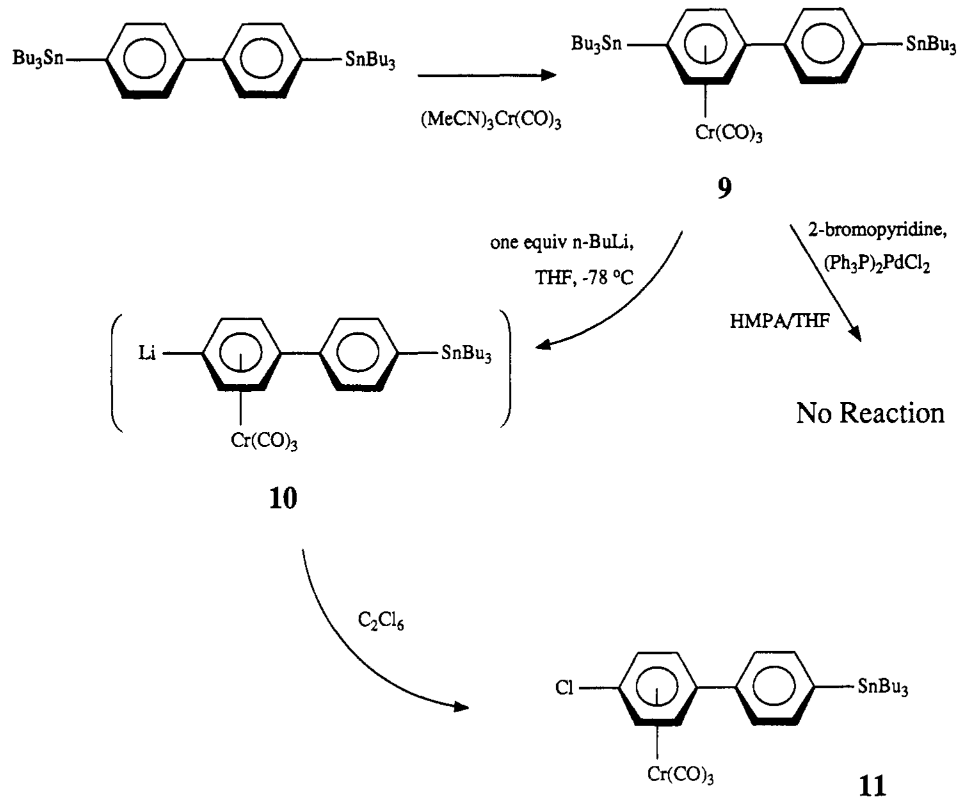
(7) Alemagna, A., Cremonesi, P.; Del Buttero, P.; Licandro, E.; Maiorana, S. *J. Org. Chem.* **1982**, *48*, 3114.

(8) Transmetalation reactions of tri-*n*-butylstannyl groups have been used extensively in organic synthesis since their discovery by Seyferth et al.: Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1961**, *83*, 3583. Seyferth, D.; Vaughn, L. G. *J. Am. Chem. Soc.* **1962**, *84*, 361; *J. Am. Chem. Soc.* **1964**, *86*, 883. For a more recent application of this reaction see: Wulff, W. D.; Peterson, G. A.; Bauta, W. E.; Chan, K.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem.* **1986**, *51*, 279 and references cited therein.

(9) Poeth, T. P.; Harrison, P. G.; Long, T. J.; Willeford, B. R.; Zuckerman, J. J. *Inorg. Chem.* **1971**, *10*, 522.

(10) For reviews concerning the palladium-catalyzed cross-coupling of organotin reagents see: Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771. Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *250*, 551. Kosugi, M.; Migita, T. *Yuki Gosei Kagaku Kyokaishi* **1980**, *38*, 1142.

Scheme II



2a with activated halides (e.g., 2-bromopyridine, benzoyl chloride, and iodobenzene) and a palladium(II) precatalyst showed little or no coupling reaction and almost complete recovery of **2a**. Reactions carried out at elevated temperatures led to decomposition of the tin reagent before significant coupling took place. Complex **8** also was found to be unreactive in the palladium-catalyzed cross-coupling reactions.

Complexes **2** react smoothly with 2.1 molar equiv of *n*-BuLi at −78 °C to afford the (η^6-1,4-dilithiobenzene)- and (η^6-1,3-dilithiobenzene)$Cr(CO)_3$ complexes (**3**). Typically, the THF solutions of **3** are homogeneous and light yellow in color, but if the concentration of **3** exceeds ~0.1 M, the dilithio complex **3** will precipitate in part. Compound **3** reacts with a variety of reagents to give the (η^6-1,4-disubstituted benzene)- and (η^6-1,3-disubstituted benzene)$Cr(CO)_3$ (**4–7**) complexes in good to excellent yields (Scheme I). The tetrabutylstannane byproduct is easily separated from the $Cr(CO)_3$ complexes by column chromatography on alumina eluting first with hexanes. Attempts to carry out the transmetalation reaction in ether gave only minor conversion to **3**, and **2** was recovered.

Complex **7** is particularly illustrative in showing how the use of the dilithio complex **3a** at −78 °C eliminates competing reactions such as ligand substitution at the metal center, which occur at higher reaction temperatures (e.g. carbonyl substitution by the phosphorus ligand).[11]

Since the {1,4-bis(trialkylstannyl)benzene}$Cr(CO)_3$ complexes are, for all practical purposes, inert in the palladium-catalyzed cross-coupling reaction, we prepared the biphenyl analogues. The latter should relieve some of the steric hindrance near each tin site. The preparation of complex **9** is straightforward and proceeds in good yield (Scheme II).

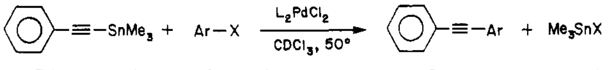
We found that **9** does not undergo the palladium-catalyzed cross-coupling reaction with 2-bromopyridine at elevated temperatures in HMPA/THF solution. Spectroscopic data indicated that neither of the two tributyltin sites were reactive. Compound **9** did react regioselectively with 1 equiv of *n*-BuLi (THF, 30 min, −78 °C) followed by treatment with hexachloroethane to afford complex **11**. Thus $Cr(CO)_3$ complexation activates the aryl–tin bond in the transmetalation reaction.

Table I. Relative Rates for the Palladium-Catalyzed Cross-Coupling of Selected Arene Halides and Phenyl(trimethylstannyl)acetylene at 50 °C (Eq 2)

arene	rel react rates L = PPh_3	 L_2 = $Fe(C_5H_4PPh_2)_2$
PhBr	0.2	
2-Brpy	1.0	
PhI	1.0[a]	0.6
{(η^6-PhCl)$Cr(CO)_3$}	15	1.2

[a] Relative reaction rates are calculated by using the first half-life time and arbitrarily setting iodobenzene as the reference reagent.

In view of our interest in utilizing (η^6-arene)$Cr(CO)_3$ complexes in palladium-catalyzed polycondensation reactions, we also explored the relative reactivity of complexed and "free" aryl halides in their palladium-catalyzed cross-coupling with trimethyl(phenylethynyl)stannane (eq 2).



(2)

The results of the relative rate study are summarized in Table I. The $Cr(CO)_3$ coordination clearly activates the aryl halide bond in the cross-coupling reaction. These data are consistent with the previous work by Milstein and Stille[12] in which it was shown that electron-withdrawing groups on the aryl halide accelerated the palladium-catalyzed cross-coupling reaction with organotin reagents. The analogy of the $Cr(CO)_3$ unit with a para nitro group holds

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(11) Bowden, J. A.; Colton, R. *Aust. J. Chem.* **1971**, *24*, 2471.

(12) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4992.

well in the present cross-coupling reaction with acetylenic tin reagents.[13]

A somewhat unexpected result is the relative slowness of the reaction in which the $\{(C_5H_4PPh_2)_2Fe\}PdCl_2$ precatalyst was used. Monitoring the reaction by ^1H NMR spectroscopy showed a leveling off of the reaction rate with time, regardless of the substrate. The difference in reactivity observed between the two palladium precatalysts is not understood.

Experimental Section

General Data. All manipulations of compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents.[14] Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian XL 300; ^{13}C NMR, Varian XL 300 (at 75.4 MHz); infrared, Perkin-Elmer 1750 FT-IR spectrometer. NMR chemical shifts are reported in δ vs $Me_4Si(^1H)$ and the $CDCl_3$ resonance (^{13}C, 77.00 ppm). The ^{31}P NMR spectra were referenced to external 85% H_3PO_4(aq) at δ 0.00 ppm. Chromium hexacarbonyl, tributyltin chloride, 4,4′-dibromobiphenyl, and *n*-BuLi (2.5 M in hexanes) were purchased from Aldrich Chemical Co. and used as received. The chlorodiphenylphosphine was distilled prior to use, and the hexachloroethane was dried in a benzene solution over CaH_2, filtered, and the solvent removed under reduced pressure. The palladium(II) precatalysts,[15] trimethyl(phenylethynyl)stannane,[16] 4,4′-bis(trimethylstannyl)biphenyl,[17] and 1,3- and 1,4-bis(tributylstannyl)benzene[18] were prepared by literature methods. Column chromatography utilized nonactivated neutral alumina (32–63) purchased from Universal Scientific. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

{η^6-1,4-Bis(tri-*n*-butylstannyl)benzene}chromium Tricarbonyl (2a). Chromium hexacarbonyl (2.00 g, 9.10 mmol) was converted to $(MeCN)_3Cr(CO)_3$ in refluxing MeCN and the solvent removed under reduced pressure. Then dioxane (50 mL) and 1,4-bis(tributylstannyl)benzene (5.00 g, 7.62 mmol) were added, and the mixture was heated at reflux for 48 h. The mixture was allowed to cool, then diluted with hexanes (50 mL), and filtered through a pad of alumina (5 × 3 cm). The alumina was washed with hexanes (75 mL), and the solvents were removed from the filtrate under reduced pressure to yield 6.0 g of crude product. The yellow oil was diluted with hexanes (5 mL) and subjected to column chromatography on alumina. Elution with hexanes was used until the yellow band reached the bottom of column, and then ethyl acetate/hexanes (1/4, v/v) was utilized to bring the remainder of the yellow band down the column. The yellow band was collected and the solvent removed under reduced pressure to give analytically pure **2a** as a yellow oil (5.5 g, 91%): ^1H NMR ($CDCl_3$) δ 5.19 (s, 4 H), 1.56 (m, 12 H), 1.35 (m, 12 H), 1.12 (m, 12 H), 0.92 (t, $J = 7$ Hz, 18 H); ^{13}C NMR ($CDCl_3$) δ 233.8 (CO), 102.2 (SnC_6H_4), 101.2 (phenyl), 29.0 (CH_2), 27.5 (CH_2), 13.8 (CH_3), 10.5 ($SnCH_2$); IR (CH_2Cl_2) ν_{CO} 1956, 1878 cm^{-1}. Anal. Calcd for $C_{33}H_{58}O_3CrSn_2$: C, 50.03; H, 7.38. Found: C, 50.50; H, 7.46.

{η^6-1,3-Bis(tri-*n*-butylstannyl)benzene}chromium Tricarbonyl (2b). Similar as above for **2a**, $(MeCN)_3Cr(CO)_3$ was prepared from $Cr(CO)_6$(5.0 g, 22.7 mmol) and reacted with 1,3-bis(tri-*n*-butylstannyl)benzene (13.1 g, 20.0 mmol) in dioxane at reflux for 48 h. The mixture was allowed to cool to ambient temperature, diluted with hexanes (100 mL), and then filtered through a pad of alumina. The alumina was washed with benzene (100 mL), and the solvents were removed under reduced pressure. The crude product was column chromatographed on alumina with hexanes/benzene (9/1, v/v) to give a fast moving yellow band which was collected and the solvent removed to afford pure **2b** (11.9 g, 75%) as a yellow oil: ^1H NMR ($CDCl_3$) δ 5.31 (d, J = 6 Hz, 2 H), 5.18 (s with satellites, 1 H), 5.02 t, $J = 6$ Hz, 1 H), 1.47 (m, 12 H), 1.26 (m, 12 H), 1.02 (apparent t, $J = 8$ Hz, 12 H), 0.83 (t, $J = 8$ Hz, 18 H); ^{13}C NMR ($CDCl_3$) δ 234.6 (CO), 109.7, 102.7, 100.5 (CH), 93.1 (phenyl–$SnBu_3$); IR (CH_2Cl_2) ν_{CO} 1957, 1880 cm^{-1}. Anal. Calcd for $C_{33}H_{58}O_3CrSn_2$: C, 50.03; H, 7.38. Found: C, 50.68; H, 7.52.

(η^6-1,3-Dilithiobenzene)- or (η^6-1,4-Dilithiobenzene)chromium Tricarbonyl (3). A chilled (−78 °C) THF (50 mL) solution containing **2** (5.40 g, 6.8 mmol) was treated with 2.1 equiv of *n*-BuLi (5.8 mL, 2.5 M in hexanes) and stirred for an additional 20 min. The pale yellow heterogeneous mixture is then treated with the appropriate electrophile at −78 °C (see below).

(η^6-1,4-Dichlorobenzene)chromium Tricarbonyl (4a). Complex **3** was generated from **2b** (4.88 g, 6.2 mmol) in THF (50 mL) by treatment with *n*-BuLi at −78 °C. A THF (10 mL) solution containing hexachloroethane (3.67 g, 15.5 mmol) was cannulated onto the heterogeneous mixture of **3** at −78 °C. The mixture was stirred at −78 °C for 15 min and then allowed to warm to ambient temperature over 2 h. The mixture was diluted with hexanes (50 mL) and filtered through Celite, and the filtrate was concentrated under reduced pressure. The crude product was subjected to column chromatography (2 × 25 cm) on alumina, eluting with hexanes/benzene (9/1, v/v). The first yellow band was collected, and the solvents were removed to afford pure **4a** (1.31 g, 75%; mp 86–87 °C (lit.[2b] mp 88 °C)).

(η^6-1,3-Dichlorobenzene)chromium Tricarbonyl (4b). Complex **4b** was prepared in 65% yield from **2b** by using an analogous procedure as for **4a**. Final purification was achieved by recrystallization by diffusing pentanes into a chloroform solution containing **4b** while at −25 °C. Spectroscopic data for **4b**: ^1H NMR ($CDCl_3$) δ 5.61 (t, $J = 1.5$ Hz, 1 H), 5.50 (t, $J = 6.4$ Hz, 1 H), 5.18 (dd, J = 1.5, 6.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 230.3 ($C{\equiv}O$), 113.3 (phenyl–Cl), 92.0, 90.1, 87.2 (phenyl CH's); IR ($CDCl_3$) ν_{CO} 1991, 1925 cm^{-1}; mp 120–122 °C (lit.[7] mp 122–124 °C).

(η^6-1,4-Dibromobenzene)chromium Tricarbonyl (5). A THF (50 mL) solution of **3a** (from 3.57 g of **2a**, 4.51 mmol) was prepared and treated with a THF (10 mL) solution of NBS (1.67 g, 9.4 mmol) at −78 °C. The mixture was stirred at −78 °C for 45 min and then allowed to warm to 0 °C over ~1 h. The mixture was diluted with hexanes (50 mL) and filtered through a pad of alumina. The alumina was washed with benzene (50 mL), and the solvents were removed from the filtrate under reduced pressure. The crude product was dissolved in benzene and subjected to column chromatography on alumina eluting with hexanes/benzene (9/1, v/v). The first yellow band was collected and the solvent removed to afford a yellow solid. Final purification of **5** was achieved by diffusion of pentane into a chloroform solution containing **5** at −25 °C to give yellow needles (1.18 g, 70%; mp 125–127 °C): ^1H NMR ($CDCl_3$) δ 5.30 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 231.5 (CO), 92.7 (CH), 88.4 (CBr); IR (CH_2Cl_2) ν_{CO} 1974, 1897 cm^{-1}. Anal. Calcd for $C_9H_4O_3Br_2Cr$: C, 29.06; H, 1.08. Found: C, 29.22; H, 1.10.

(η^6-1,4-Diiodobenzene)chromium Tricarbonyl (6a). A THF (30 mL) solution containing **3a** (from 2.00 g of **2a**, 2.5 mmol) maintained at −78 °C was treated with a THF (10 mL) solution of I_2 (1.34 g, 5.3 mmol) and stirred for an additional 30 min. The mixture was allowed to warm to ambient temperature, diluted with hexanes (50 mL), and then filtered through a pad of alumina. The alumina was rinsed with benzene (100 mL), and the solvents were removed under reduced pressure. The crude product was dissolved in benzene (5 mL) and subjected to column chromatography on alumina using gradient elution {hexanes/benzene (1/1, v/v) ⇒ benzene}. The first yellow band was collected and the solvent removed to afford pure **6a** as a yellow, crystalline material (0.80 g, 68%; mp 132–134 °C): ^1H NMR ($CDCl_3$) δ 5.50 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 231.0 ($C{\equiv}O$), 100.1 (CH), 58.2 (*C*—I); IR ($CDCl_3$) ν_{CO} 1985, 1920 cm^{-1}. Anal. Calcd for $C_9H_4CrI_2O_3$: C, 23.20; H, 0.86. Found: C, 23.45; H, 0.90.

(η^6-1,3-Diiodobenzene)chromium Tricarbonyl (6b). A THF solution (50 mL) containing **2b** (3.11 g, 3.93 mmol) at −78 °C was treated with *n*-BuLi (8.3 mmol). The mixture was stirred at for an additional 20 min and then treated with a THF (10 mL)

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(13) Nicholls, B.; Whiting, M. C. *J. Chem. Soc.* **1959**, 551.

(14) Gordon, A. J.; Ford, R. A. *The Chemists Companion*; Wiley: New York, 1972.

(15) King, A. O.; Negishi, E.; Villani, F. J.; Silveira, A. *J. Org. Chem.* **1978**, *43*, 358.

(16) Mitchell, T. N. *J. Organomet. Chem.* **1977**, *141*, 289. Cetinkaya, B.; Lappert, M. F.; McMeeking, J.; Palmer, D. E. *J. Chem. Soc., Dalton Trans.* **1973**, 1202.

(17) Curtis, M. D.; Allred, A. L. *J. Am. Chem. Soc.* **1965**, *87*, 2554.

(18) Meta isomer: Jaura, K. L.; Singla, S. N.; Sharma, K. K. *J. Indian Chem. Soc.* **1969**, *46*, 835. Para isomer: Jaura, K. L.; Hundal, H. S.; Handa, R. D. *Indian J. Chem.* **1967**, *5*, 211.

solution of I_2 (2.11 g, 8.3 mmol). The cooling bath was removed and the mixture allowed to warm to ambient temperature. The reaction mixture was diluted with hexanes (50 mL) and filtered through a pad of alumina. The alumina was washed with benzene (100 mL), and the solvents were removed from the filtrate to give crude **6b**. The crude product was dissolved in benzene (5 mL) and subjected to column chromatography on alumina utilizing gradient elution (hexanes ⇒ benzene). The initial yellow band was collected, and the solvents were removed to afford **6b** contaminated ~5% of (η^6-C_6H_5I)CrT. Final purification was achieved by recrystallization by diffusion of pentanes into a $CHCl_3$ solution containing the 95% purity **6b** (mp with decomposition 128–130 °C): ^{1}H NMR ($CDCl_3$) δ 5.95 (s, 1 H), 5.52 (d, J = 6.4 Hz, 2 H), 5.21 (t, J = 6.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 231.1, 105.3, 96.5, 93.6 (phenyl CH's), 63.0 (phenyl *C*-I); IR (CH_2Cl_2) ν_{CO} 1983, 1917 cm^{-1}. Anal. Calcd for $C_9H_4CrI_2O_3$: C, 23.20; H, 0.86. Found: C, 23.60; H, 0.72.

{η^6-1,4-Bis(diphenylphosphino)benzene}chromium Tricarbonyl (7). Complex **3** (from 2.5 g of **2a**) was treated with 2.1 equiv of chlorodiphenylphosphine (1.2 mL, 6.7 mmol) at −78 °C, and the mixture was allowed to warm to ambient temperature. The solvent was removed under reduced pressure to yield a yellow solid. The crude product was dissolved in benzene (10 mL) and subjected to column chromatography on alumina. Gradient elution starting with hexanes and going to benzene gave a yellow band which was collected; the solvent was removed under reduced pressure to yield 1.50 g (83%; mp 161–162 °C) of crystalline **7**: ^{1}H NMR ($CDCl_3$) δ 7.38 (br s, 20 H), 5.04 (apparent t, J = 3 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 231.6 C≡O), 134.7 (d, J = 12 Hz), 133.9 (d, J = 20 Hz), 129.6, 128.8 (d, J = 7 Hz), 104.3 (d, J = 19 Hz), 96.1 (dd, J = 4, 16 Hz); ^{31}P NMR ($CDCl_3$) δ 48.6; IR (CH_2Cl_2) ν_{CO} 1974, 1905 cm^{-1}. Recrystallized from $CDCl_3$ for elemental analysis. Anal. Calcd for $C_{33}H_{24}CrO_3P_2{\cdot}CDCl_3$: C, 58.09; H, 3.70; Cl, 15.13. Found: C, 58.18; H, 3.66; Cl, 15.06.

{η^6-4,4′-Bis(tributylstannyl)biphenyl}chromium Tricarbonyl (9). A *p*-dioxane (75 mL) solution containing ($CH_3CN)_3Cr(CO)_3$ (from 3.00 g $Cr(CO)_6$) and 4,4′-bis(tributylstannyl)biphenyl (9.95 g, 13.6 mmol) was heated at reflux for 20 h and then allowed to cool to ambient temperature. The solution was diluted with hexanes (75 mL) and filtered through a pad of alumina (2 × 5 cm), and the alumina pad was then washed with an additional 75 mL of hexanes. The solvents were removed under reduced pressure from the eluant to afford a yellow oil. The oil was diluted with hexanes (5 mL) and chromatographed (4 × 40 cm) on alumina using gradient elution {hexanes ⇒ hexanes/ethyl acetate, 19/1, v/v}; the yellow band was collected to afford pure **9** as a yellow oil (9.2 g, 78%): ^{1}H NMR ($CDCl_3$) δ 7.62–7.41 (m, 4 H), 5.58 (d, J = 6.5 Hz, 2 H), 5.48 (d, J = 6.5 Hz, 2 H), 1.60–1.50 (m, 12 H), 1.42–1.32 (m, 12 H), 1.17–1.04 (m, 12 H), 0.93 (t, J = 17.3 Hz, 9 H), 0.89 (t, J = 17.2 Hz, 9 H); ^{13}C NMR ($CDCl_3$) δ 233.4 (CO), 143.7, 136.6, 136.0, 126.3, 112.2, 101.3, 98.7, 91.9 (phenyl carbons), 29.1, 28.9, 27.5 (CH_2's), 13.8 (CH_3), 10.6, 9.8 ($SnCH_2$'s); IR (CH_2Cl_2) ν_{CO} 1961, 1886 cm^{-1}. Anal. Calcd for $C_{39}H_{62}CrO_3Sn_2$: C, 53.94; H, 7.20. Found: C, 54.60; H, 7.62.

{η^6-1-Chloro-4-(4′-(tributylstannyl)phenyl)benzene}chromium Tricarbonyl (11). A THF (25 mL) solution of **9** (1.90 g, 2.20 mmol) at −78 °C was treated with *n*-BuLi (2.4 M, 1.0 mL, 2.4 mmol) for 20 min. The yellow homogeneous mixture was treated with a THF (5 mL) solution of hexachloroethane (0.65 g, 2.7 mmol) in one portion. The mixture was maintained at −78 °C for 15 min and then allowed to warm to ambient temperature over about 1 h. The solvents were removed under reduced pressure to yield crude **11**. The crude product was diluted with benzene (3 mL) and subjected to column chromatography (3 cm × 30 cm) on alumina with gradient elution (hexanes ⇒ 50% benzene/hexanes). The first yellow band was collected, and the solvents were removed to give spectroscopically pure **11** as a yellow oil in 60% (0.80 g) yield: ^{1}H NMR ($CDCl_3$) δ 7.51 (d, J = 8 Hz, 2 H), 7.39 (d, J = 8.2 Hz, 2 H), 5.82 (d, J = 6.8 Hz, 2 H), 5.57 (d, J = 6.8 Hz, 2 H), 1.53 (m, 6 H), 1.35 (m, 6 H), 1.09 (m, 6 H), 0.92 (t, J = 7.6 Hz, 9 H); ^{13}C NMR ($CDCl_3$) δ 231.1 (C≡O), 143.9 (phenyl), 136.8 (phenyl CH), 134.8 (phenyl), 126.1 (phenyl CH), 111.7, 106.7 (η^6-phenyl), 92.5, 90.8 (η^6-phenyl CH's), 29.1, 27.4 (CH_2's), 13.7 (CH_3), 9.7 ($SnCH_2$); IR (CH_2Cl_2) ν_{CO} 1977, 1906 cm^{-1}.

Relative Rate Studies Using ^{1}H NMR Spectroscopy. Stock solutions of $C_6H_5C{\equiv}CSnMe_3$ and the dihalobenzene were prepared in $CDCl_3$ at 0.50 M. The catalyst solution (0.01 M) was prepared just before the experiment was run as the catalyst would precipitate out of solution after a few minutes. A 5-mm NMR tube was charged with 0.25 mL of each stock solution, capped, shaken to ensure homogeneity, and then placed in the NMR spectrometer with the probe already heated to 50.0 °C. The progress of the reaction was monitored by measuring the relative peak areas for the trimethyltin resonances for the trimethyl(phenylethynyl)stannane and the cross-coupling product trimethyltin halide.

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Registry No. **2a**, 115775-86-5; **2b**, 117939-65-8; **3a**, 115775-85-4; **3b**, 117939-66-9; **4a**, 86409-62-3; **4b**, 86409-61-2; **5**, 117939-67-0; **6a**, 117939-72-1; **6b**, 117939-69-2; **7**, 117939-70-5; **9**, 117939-71-6; **11**, 117939-72-7; ($MeCN)_3Cr(CO)_3$, 16800-46-7; 2-Brpy, 109-04-6; PhBr, 108-86-1; PhI, 591-50-4; (η^6-PhCl)Cr(CO)$_3$, 12082-03-0; L_2PhCl_2 (L_2 = $Fe(C_5H_4PPh_2)_2$), 72287-26-4; L_2PhCl_2 (L = PPh_3), 13965-03-2; 1,4-bis(tributylstannyl)benzene, 17151-51-8; 1,3-bis(tri-*n*-butylstannyl)benzene, 24344-61-4; 4,4′-bis(tributylstannyl)biphenyl, 117897-79-7; trimethyl(phenylethynyl)stannane, 1199-95-7.