J|A|C|S
ARTICLES
Published on Web 05/06/2005

Accelerated Arene Ligand Exchange in the (Arene)$Cr(CO)_2L$ Series

M. F. Semmelhack,* Anatoly Chlenov, and Douglas M. Ho

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Received December 4, 2004; E-mail: mfshack@princeton.edu

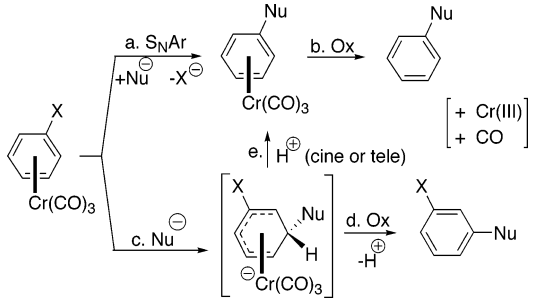
Abstract: Arene ligand exchange in the (η^6-arene)$Cr(CO)_2L$ series can be accelerated if the ligand L is an electronically unsymmetrical bidentate ligand. The system evaluated here employs derivatives of tris(pyrrolyl)-phosphine as L. A series of 2-L′-substituted pyrroles was prepared, where the substituents include: L′ = −SMe, $-CH_2SMe$, −SPh, $-CH_2SPh$, $-SCF_3$, −S-tBu, $-CO_2Me$, $-CONMe_2$, −2-pyridinyl, and $-PPh_2$. Reaction with $ClP(pyrrolyl)_2$ gave a new series of phosphines, (2-L′-pyrrolyl)$(pyrrolyl)_2$P. Each of these phosphines was converted to (arene)$Cr(CO)_2$[P(2-L′-pyrrolyl)$(pyrrolyl)_2$P) complexes. The substituents L′ are proposed to provide temporary coordination to the Cr and to lower the barrier to arene exchange. The series was evaluated where the arene in the complex (departing) is benzene, fluorobenzene, toluene, *o*-xylene, *m*-xylene, or *p*-xylene and the incoming arene is C_6D_6, chlorobenzene-d_5, anisole-d_8, fluorobenzene-d_5, toluene-d_8, *o*-xylene-d_{10}, *m*-xylene-d_{10}, *p*-xylene-d_{10}, or mesitylene-d_{12}. Most of the new complexes showed a significant increase in the rate of arene exchange due to the side chain unit L′. The strongest effects were seen with the examples where X = $-CO_2Me$, $-CONMe_2$, and −(2-pyridinyl), allowing exchange with a half lifetime as low as 8 h/22 °C.

Introduction

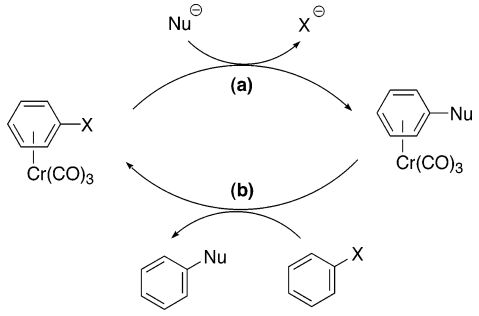
Complexation of an arene with transition metals activates the arene toward nucleophile addition, deprotonation of the ring, and formation of the benzylic cations, anions, and radicals.[1,2] The arene−$Cr(CO)_3$ series allows particularly general substitution sequences via nucleophile addition/elimination (S_NAr, path a/b) addition/oxidation (path c/d) and indirect substitution (path c/e/b; Scheme 1). Each of these reaction pathways has seen application as synthesis methodology on a research scale. However, the utility is limited by the need for stoichiometric amounts of the metal−ligand unit.[3,4]

A particularly simple catalytic cycle can be written for the S_NAr process (Scheme 2); the addition/substitution step is followed by spontaneous exchange of the arene ligands,

Scheme 1. General Conversions with $Cr(CO)_3$ Activation



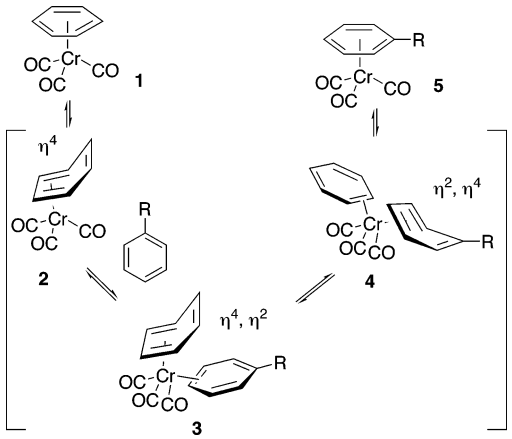
Scheme 2. Proposed Catalysis of the S_NAr Process



regenerating the reactant arene and freeing the product arene from the metal. Efficient catalysis, however, will require that the arene exchange step be compatible with the conditions of the S_NAr step and that arene exchange be highly efficient (high catalyst turnover). Here, we detail our efforts to influence the rate and efficiency of arene exchange by ligand effects.

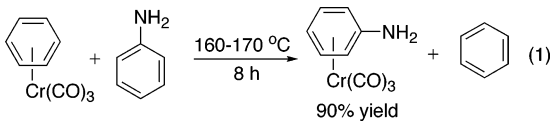
(1) Merlic, C. A.; Hietbrink, B. N.; Houk, K. N. *J. Org. Chem.* **2001**, *66*, 6738−6744.
(2) (a) Semmelhack, M. F.; Chlenov, A. Aromatic Nucleophilic Substitution. In *New Aspects of Transition Metal Arene Complexes*; Kundig, E. P., Ed.; Springer-Verlag, Berlin, 2004; p 43. (b) Rose-Munch, F.; Rose, E. Arenetricarbonylchromium Complexes: Ipso, Cine, Tele Nucleophilic Aromatic Substitution. In *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley-VCH Verlag: 2002; p 368.
(3) A Cp*Rh(III) system allows catalytic substitution of a limited number of fluoroarenes with alkoxide nucleophiles. See: (a) Goryunov, L. I.; Litvak, V. V.; Shteingarts, V. D. *Zh. Org. Khim.* **1988**, *24*, 401−405. (b) Goryunov, L. I.; Litvak, V. V.; Shteingarts, V. D. *Zh. Org. Khim.* **1987**, *28*, 1230−1237. (c) Litvak, V. V.; Goryunov, L. I.; Shteingarts, V. D. *Izv. SOAN SSSR. Ser. Khim. Nauk* **1985**, 132−134. (d) Goryunov, L. I.; Terent'eva, Y. A.; Litvak, V. V.; Shteingarts, V. D. *Zh. Org. Khim.* **1990**, *26*, 1058. (e) Houghton, R. P.; Voyle, M.; Price, R. *J. Chem. Soc., Perkin Trans. 1* **1984**, 925−931.
(4) In the only example of catalysis in the $Cr(CO)_3$ series, arene π complexation was used to accelerate Pd(0)-catalyzed coupling reactions with aryl chlorides: Brase, S. *Tetrahedron Lett.* **1999**, *40*, 6757−6759.

Scheme 3. Associative Mechanism of Arene Ligand Exchange



Background

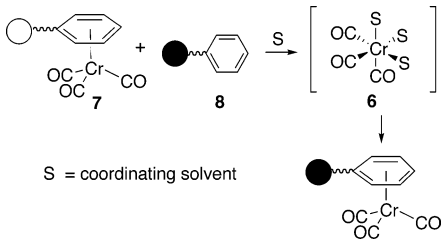
Mechanism Considerations. Arene exchange in the (arene)-$Cr(CO)_3$ series has been studied for 40 years.[5,6] Typically, high activation barriers are observed, and side reactions, such as chromium oligomerization via carbonyl bridging, are often faster and irreversible. Arene exchange reactions are typically run at 140−180 °C in the presence of a large excess of the incoming arene. Conversions are good when the incoming arene is more electron rich than the leaving arene, as in the case of (benzene)-$Cr(CO)_3$ and aniline to give the aniline complex (eq 1).[7]



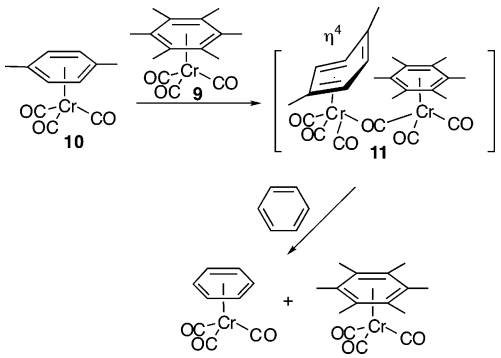
The first proposed mechanism involved complete dissociation of the $Cr(CO)_3$ unit followed by an S_N2-like attack on the arene ligand of another (arene)$Cr(CO)_3$ complex; the central observation favoring this picture was the second-order rate dependence on the (arene)$Cr(CO)_3$ concentration.[5,6] Additional experiments were incompatible with this mechanism, and it was soon replaced by a stepwise "unzipping" mechanism (Scheme 3).[8−10] In the first (rate-determining) step, one of the arene double bonds detaches from **1** to generate a coordinatively unsaturated η^4 intermediate, **2**. In a subsequent fast step, the incoming arene coordinates in η^2 fashion (in **3**). The leaving arene further detaches, while the incoming arene fills the liberated coordination site to give first the η^4, η^2 intermediate, **4**, and finally the η^6 product, **5**.

Details of the mechanism in Scheme 3 are still unclear since intermediates **2**, **3**, and **4** have not been observed spectroscopically. On the basis of Huckel molecular orbital (MO) calculations, direct attack of an arene on the chromium complex is improbable due to high electron density on the chromium center.[11] It was therefore proposed that predissociation of the

Scheme 4. Three-Phase Test for Exchange



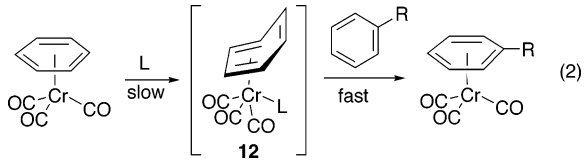
Scheme 5. AreneExchange Assisted by Interaction with a Second Arene Complex



arene is followed by attack on the resulting unsaturated η^4 species **2**. An alternative mechanism begins with a complete dissociation of the (arene)$Cr(CO)_3$ complex (to give intermediate **6** in Scheme 4) followed by fast coordination of the incoming arene. This was probed with a "three-phase test", where a bead-to-bead migration of the $Cr(CO)_3$ unit was detected at 170 °C in the presence of polar additives such as cyclohexanone or THF but not in their absence (cyclohexane solvent).[8]

Donor Ligand Effect on Arene Exchange. A key observation was that added (arene′)$Cr(CO)_3$ complex (**9** in Scheme 5) catalyzes arene exchange of another (arene)$Cr(CO)_3$ complex (**10**) without undergoing exchange itself.[9,10] This effect was attributed to coordination of the carbonyl ligand (in **11**) to lower the barrier to the $\eta^6 \rightarrow \eta^4$ conversion of the arene ligand.

Other donor molecules such as THF and cyclohexanone also catalyze arene exchange.[12,13] The relative catalytic ability of donor additives is: cyclohexanone/1400; benzonitrile/600; 1,5-cyclooctadiene/200; triglyme/200; THF/30; and complex **9**/30.[8] When cyclohexanone was used as an additive, the rate of arene exchange was proportional to the concentration of the starting arene complex and cyclohexanone, and independent of the concentration of the incoming arene.[8,13] These observations are consistent with slow displacement of one of the arene double bonds by the donor molecule to give **12** followed by a fast coordination of the incoming arene (eq 2). Arene exchange is detectable at temperatures as low as 80 °C [for (benzene)-$Cr(CO)_3$ as a substrate and hexamethylbenzene as an incoming arene in cyclohexanone], although typical experiments were still performed at 140 °C to ensure a complete reaction.[13]



Structure/Reactivity Relationship in Arene Exchange. When the temperature is sufficient for arene exchange to

(5) Strohmeier, W.; Mittnacht, H. *Z. Phys. Chem.* **1961**, *29*, 339−346.
(6) Strohmeier, W.; Staricco, E. H. *Z. Phys. Chem.* **1963**, *38*, 315−325.
(7) Natta, G.; Ercoli, R.; Calderazzo, F.; Santambrogio, E. *Chim. Ind.* **1958**, *40*, 1003−1007.
(8) Traylor, T. G.; Stewart, K. J.; Goldberg, M. J. *J. Am. Chem. Soc*. **1984**, *106*, 4445−4454.
(9) Traylor, T. G.; Stewart, K. J.; Goldberg, M. J. *Organometallics* **1986**, *5*, 2062−2067.
(10) Traylor, T. G.; Stewart, K. *Organometallics* **1984**, *3*, 325−327.
(11) Howell, J. A. S.; Ashford, N. F.; Dixon, D. T.; Kola, J. C.; Albright, T. A.; Kang, S. K. *Organometallics* **1991**, *10*, 1852−1864.

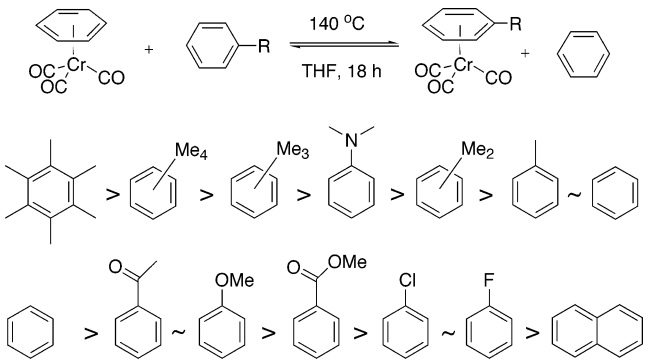


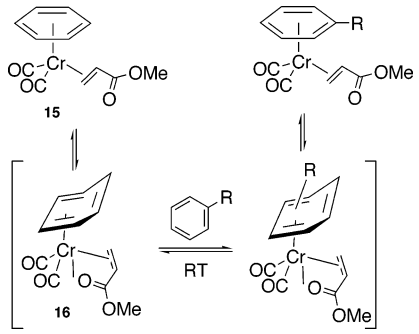
Figure 1. Relative stability of (arene)$Cr(CO)_3$ complexes.

proceed, the equilibrium constant determines the extent of the exchange reaction. From a study of the equilibrium constants for both the forward and reverse reactions,[8] the stability order presented in Figure 1 was determined. This order is consistent with the arene-chromium bond energies measured by microcalorimetry.[14−16] An interesting point is the absence of a destabilizing steric effect of the methyl groups on the thermodynamic stability of the (alkylbenzene)$Cr(CO)_3$ complexes. The stability order parallels the number of the methyl groups and is fairly independent of their relative position on the aromatic ring.

Notable is the low position of fluorobenzene in the series. This data point is important for our goal of designing a viable catalytic system as it implies that arene exchange must proceed thermodynamically uphill from a more stable arene−chromium complex to a less stable one in regenerating the activated fluoroarene (Scheme 2, step b). A somewhat unfavorable equilibrium can be tolerated in a catalytic process since the resulting fluoroarene complex will be consumed irreversibly in the addition/elimination step. The equilibrium constants for arene exchange are not very large in absolute magnitude, and the equilibrium can be shifted in the desired direction if a large excess of the incoming arene is employed.[12] Specifically, (fluorobenzene)$Cr(CO)_3$ can be obtained in over 70% yield from (benzene)$Cr(CO)_3$ using a large excess of fluorobenzene after 21 h at 150 °C in THF as a solvent.[12]

Kinetic factors that govern relative *rates* of arene exchange are much less studied. The effect of methyl substitution on the leaving arene was evaluated in the reaction of various (arene)-$Cr(CO)_3$ complexes with hexamethylbenzene in cyclohexanone.[13] Exchange rates were consistent with the more thermodynamically stable (mesitylene)$Cr(CO)_3$ complex reacting at a slower rate than those of *p*-xylene or benzene. The temperature dependence of the rates, however, showed that the enthalpy of activation was lowest for the mesitylene complex, leading to the conclusion that the rate difference was due to entropic factors.[13] In the case of fluoroarene substrates, ground-state destabilization of the starting material was invoked.[17] Again consistent with thermodynamic stability, the less stable (1,4-difluorobenzene)$Cr(CO)_3$ complex exchanges faster than

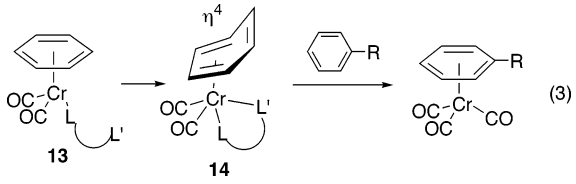
Scheme 6. Fast Exchange with Methyl Acrylate[23]



the fluorobenzene or benzene complex, with mesitylene as the incoming arene and no added donor catalyst.[17]

While the examples above of accelerated arene exchange based on substrate changes show significant effects, a generally useful S_NAr process would require that the catalytic efficiency be relatively independent of arene structure. An attractive approach to arene labilization is via modification of one of the spectator ligands (CO in this case). Replacement of a CO in an (arene)$Cr(CO)_3$ complex with a phosphine donor ligand (such as triphenyl- or trialkylphosphine) results in increased arene−chromium bond strength presumably due to increased back donation to the arene from the metal.[18,19,20,21] The increased arene−metal bond strength leads to a drastic inhibition of the arene exchange reaction. In addition to the retarding electronic effect of the phosphine donor ligand, a steric effect was also suggested to play a negative role.[22]

Temporary Coordination of a Ligand Side Chain to Accelerate Arene Exchange. We proposed[19] to replace one of the CO ligands with a bidentate ligand that would have a side chain group (L′ in **13**) able to coordinate temporarily to the chromium center (**14**, eq 3) and serve as the donor catalyst. The ligand chosen in the initial work (diphos) was not successful; it retarded the arene exchange, probably due to the electron donating power of the phosphine which increased the arene metal bond strength in the complex **13**.



A spectacular rate enhancement attributed to the same concept involves methyl methacrylate as the new ligand (Scheme 6).[23] Arene exchange with a series of alkylbenzenes was observed at 25 °C. The carbonyl group of the acrylate is suggested to provide the temporary "push" and reduce the barrier to exchange, potentially an example of the principle presented in

(12) Mahaffy, C. A. L.; Pauson, P. L. *J. Chem. Res., Synop.* **1979**, 126−127.
(13) Zimmerman, C. L.; Shaner, S. L.; Roth, S. A.; Willeford, B. R. *J. Chem. Res., Synop.* **1980**, 108.
(14) Mukerjee, S. L.; Lang, R. F.; Ju, T.; Kiss, G.; Hoff, C. D. *Inorg. Chem.* **1992**, *31*, 4885−4889.
(15) Brown, D. L. S.; Connor, J. A.; Demain, C. P.; Leung, M. L.; Martinho-Simoes, J. A.; Skinner, H. A.; Moattar, M. T. Z. *J. Organomet. Chem.* **1977**, *142*, 321−335.
(16) Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M. L.; Paz-Andrade, I. M.; Skinner, H. A. *J. Organomet. Chem.* **1975**, *97*, 221−228.
(17) Jagirdar, B. R.; Klabunde, K.J. *J. Coord. Chem.* **1995**, *34*, 31−43.
(18) Choi, H. W.; Sollberger, M. S. *J. Organomet. Chem.* **1983**, *243*, C39−C41.
(19) Semmelhack, M. F.; Seufert, W.; Keller, L. *J. Organomet. Chem.* **1982**, *226*, 183−190.
(20) Dabard, R.; Jaouen, G.; Simonneaux, G.; Cais, M.; Kohn, D. H.; Lapid, A.; Tatarsky, D. *J. Organomet. Chem.* **1980**, *184*, 91−101.
(21) Cais, M.; Kaftory, M.; Kohn, D. H.; Tatarsky, D. *J. Organomet. Chem.* **1980**, *184*, 103−112.
(22) Butler, I. S.; Ismail, A. A. *Inorg. Chem.* **1986**, *25*, 3910−3914.
(23) (a) Kundig, E. P.; Kondratenko, M.; Romanens, P. *Angew. Chem., Int. Ed.* **1998**, *37*, 3146−3148. (b) Kundig, E. P.; Robvieux, F.; Kondratenko, M. Synthesis, **2002**, 2053−2056.

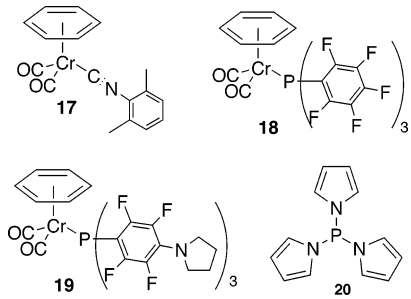


Figure 2. Possible replacements for CO.

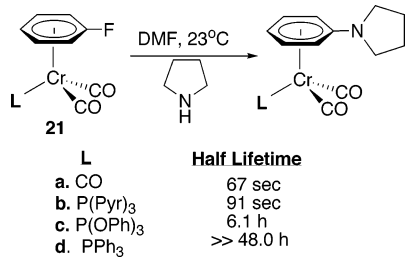


Figure 3. Relative reactivity toward the S_NAr reaction.

eq 3. An application in the catalysis of cycloaddition reactions via arene exchange has appeared.[23b]

Results and Discussion

S_NAr Reactivity Considerations in Ligand Design. The observations summarized above for the $Cr(CO)_3$ series and related studies with other metals not reviewed here support the hypothesis represented in eq 3. The ideal chelating ligand, L−L′, would allow rapid S_NAr reactions of fluoro- or chloroarenes and compatible conditions for arene ligand exchange without significant irreversible side reactions of the catalyst.

The S_NAr reactivity of the arene complexes is quite sensitive to the nature of the other ligands, with CO being a very strong activator. Ligands of varying electronic properties were considered, with an emphasis on electron-withdrawing ability. Obvious candidates are isonitriles,[24] (perfluoroalkyl)phosphines, (perfluoroaryl)phosphines, and tris(pyrrole)phosphines (Figure 2).[25] The isonitrile complex (**17**) was prepared,[26] showed significant instability under the typical S_NAr conditions (pyrrolidine nucleophile, DMF solvent), and was not pursued. Tris-(perfluoroalkyl)phosphine ligands present some interesting possibilities, and synthesis challenges[27] are under study. The tris(perfluorophenyl)phosphine complex **18** was readily prepared and characterized, but when exposed to pyrrolidine, a fast reaction occurred via substitution at the para position of the perfluorophenyl group (to give **19**).[28]

A simple reaction of (fluorobenzene)$Cr(CO)_3$ with pyrrolidine in DMF at 23 °C (the parent compound, **21a**, Figure 3) shows a half lifetime of 67 s. Replacement of CO with PPh_3 resulted in a much less reactive complex (Figure 3, **21a** vs **21d**).[29] The triphenyl phosphite analogue (**21c**) slows the process by a factor of ca. 330.[29] Tris(pyrrole)phosphine [$P(Pyr)_3$, **20**] was recognized by Molloy as having useful properties as a replacement for CO.[25] Unlike simple aminophosphines, $P(Pyr)_3$ is relatively stable toward cleavage of the N−P bond (recrystallizes from MeOH), relatively nonnucleophilic (no reaction with MeI), and is strongly electron withdrawing, comparable to CO.[25] It is easily prepared from pyrrole and PCl_3. In a calibration test, the $P(Pyr)_3$ ligand promoted rapid substitution for fluoride (Figure 3, **21b**) with a half lifetime of 91 s, only 1.4 times slower than the parent fluorobenzene−$Cr(CO)_3$ complex.[29]

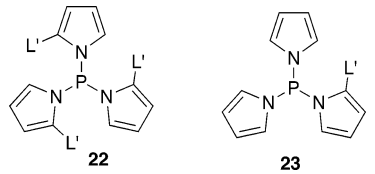


Figure 4. Pyrrolyl-based phosphine with donor side chains.

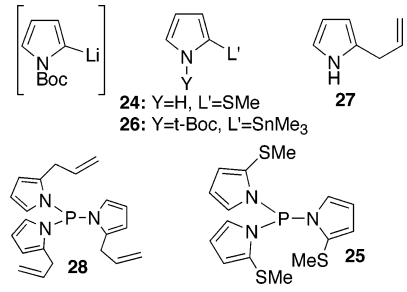


Figure 5. Tris(2-subs)pyrrolylphosphines.

Tris(pyrrole)phosphine as the Basis for Ligand Design in Accelerated Arene Exchange.[30] (a) Preparation of the Complexes. The role of temporary coordination via a side-chain donor group was explored using the tris(pyrrole)phosphine structure **20** as a starting point and positioning a donor group at the 2-position of the pyrrole (in **22** and **23**, Figure 4). The series with three substituted pyrroles (**22**) allowed a simple synthesis from PCl_3 and was tested first.

Treatment of N-tBoc pyrrole with LiTMP followed by quenching the 2-lithio intermediate with dimethyl disulfide and then deprotection gave 2-thiomethylpyrrole (**24**)[31,32] in about 40% yield on a moderate scale, Figure 5. A mixture of **24**, NaH, and PCl_3 produced phosphine **25** in 62% yield as a colorless solid with mp 76−77 °C. Similarly, the N-Boc-2-lithiopyrrole was trapped with Me_3SnCl to give the 2-stannyl derivative, **26**. Pd(0)-catalyzed cross coupling with allyl bromide followed by deprotection gave 2-allylpyrrole, **27**.[33] The tris(2-allyl)pyrrolylphosphine **28** was obtained in 41% yield as a colorless oil.

Following the general protocol[34] for replacing one CO from (arene)$Cr(CO)_3$ complexes with a donor ligand, the (arene)-

(24) For an example of S_NAr reactivity of fluorobenzene(arylisonitrile) dicarbonylchromium, see: Maiorana, S.; Baldoli, C.; Licandro, E.; Casiraghi, L.; de Magistris, E.; Paio, A.; Provera, S.; Seneci, P. *Tetrahedron Lett*. **2000**, *41*, 7271−7275.
(25) Moloy, K. G.; Petersen, J. L. *J. Am. Chem. Soc*. **1995**, *117*, 7696−7710.
(26) Unpublished work at Princeton.
(27) For discussion and examples, see: Ernst, M. F.; Roddick, D. M. *Inorg. Chem*. **1989**, *28*, 1624−1632.
(28) It is known that even the free tris(perfluorophenyl)phosphine undergoes S_NAr reactions at the para position with ease: Hannah, H. R.; Miller, J. M. *Can. J. Chem*. **1978**, *57*, 1011−1017.
(29) Semmelhack, M. F.; Hilt, G.; Colley, J. H. *Tetrahedron Lett*. **1998**, *39*, 7683−7686.
(30) A preliminary account of this work has appeared: Semmelhack, M. F.; Chlenov, A.; Wu, L.; Ho, D. M. *J. Am. Chem. Soc.* **2001**, *123*, 8438−8439.
(31) Prepared by a different method: Nedolya, N. A.; Brandsma, L.; Verkruijsse, H. D.; Trofimov, B. A. *Tetrahedron Lett*. **1997**, *38*, 7247−7248.
(32) We thank Dr. Lingyun Wu for the initial preparation of this compound, based on a general method for metalation/trapping/deprotection of N-boc-pyrrole: Gharpure, M.; Stoller, A.; Bellamy, F.; Firnau, G.; Snieckus, V. *Synthesis* **1991**, 1079−1082.
(33) Direct allylation of pyrrole is reported, but the yields are low and the product is a mixture of the 2- and 3-substitution product: Papadopoulos, E. P.; VanderWerf, C. A. *Heterocycles* **1982**, *19*, 343.

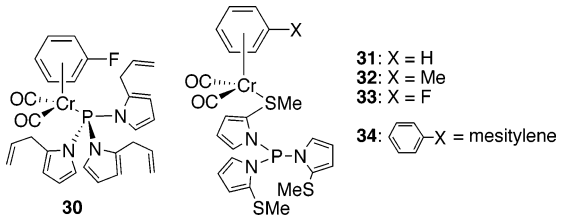


Figure 6. Complexes from the tris(2-subs)pyrrolylphosphines.

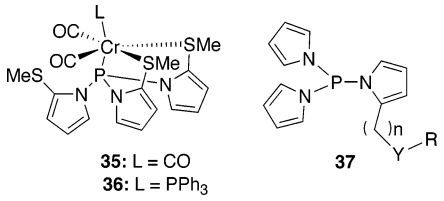
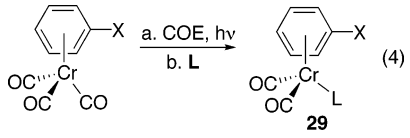


Figure 7. Chelate complexes and generic target ligand.

$Cr(CO)_3$ was irradiated in the presence of cyclooctene (COE) to give a reactive intermediate, (arene)$Cr(CO)_2$(COE). Then a thermal reaction at 23 °C produced the ligand substitution product, **29** (eq 4).

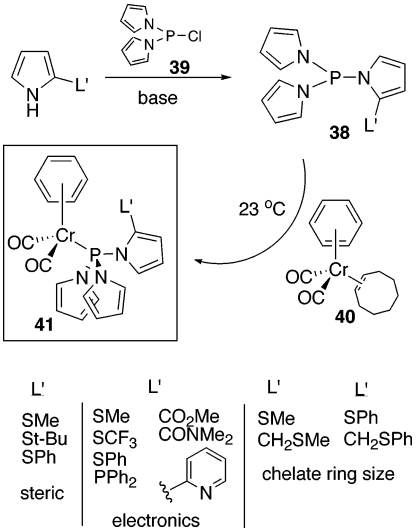


(4)

With tris(2-allylpyrrolyl)phosphine and (fluorobenzene)Cr-$(CO)_3$, the product **30** was obtained in 53% yield after chromatography on silica gel (Figure 6). The ^{1}H NMR spectrum showed evidence of restricted rotation at 23 °C but simplified at 70 °C. When heated at 70 °C in C_6H_6, no change was observed in the ^{1}H NMR spectrum after several days. At higher temperatures, slow decomposition occurred with no evidence of arene exchange.

With tris(2-methylthiopyrrolyl)phosphine and a series of (arene)$Cr(CO)_3$ precursors, somewhat labile complexes were obtained under the standard conditions for complexation. The major component in each case was tentatively characterized as the S-bound versions, **31**−**34**, Figure 6. The primary evidence is the dominant peak in the ^{31}P NMR spectrum at δ 21.9 ppm, characteristic of uncomplexed P (the P-bound complex is expected to show a peak at δ 170 ppm). In the ^{13}C NMR spectra, the Me group of the free phosphine ligand appears at δ 21.9 ppm, while in the complexes, one Me group appears 12 ppm further downfield. While this was not the intended mode of coordination, it does include a side-chain donor atom and satisfies the design principle. Heating of the fluorobenzene analogue (**33**) in mesitylene at 60 °C led to rapid loss of the fluorobenzene ligand and formation of the chelated version, **35**, in 23% yield (Figure 7). The extra CO ligand presumably arose from some decomposition of the complex. If the same reaction is carried out in the presence of triphenylphosphine, the analogous complex, **36**, was obtained and characterized by X-ray diffraction studies (Supporting Information). The instability of this series of complexes and easy loss of the fluorobenzene ligand was taken as an impetus to refine the ligand design. We

Scheme 7. Preparation of the Complexes **41**



imagined that, with only one side chain donor ligand as in **37**, any steric inhibition to phosphorus coordination would be less and the possibility of a stable chelated intermediate such as **35** would be removed.

A series of phosphine ligands with one functionalized pyrrole group as in **37** would allow systematic evaluation of the effects of side chain length and the coordinating group **Y**. Coordination via the side-chain group **Y** should be easily reversible so as to allow the incoming arene to compete successfully for the Cr and generate the arene-exchanged product. Several parameters were varied: **Y** can be soft (e.g., sulfur) or hard (e.g., nitrogen or oxygen) and isolated or part of an extended π system to allow back donation from the metal. The side chain (R in **37**) can have a secondary influence by modifying both steric and electronic properties of L′.

The target ligands, represented by **38**, were synthesized according to the general strategy shown in Scheme 7. Chlorodipyrrolylphosphine (**39**) was obtained in good yield from PCl_3 and two equivs of pyrrole with triethylamine as a base. Then, replacement of the chloride with a substituted pyrrole gave the general phosphine, **38**. Gentle thermal reaction of **38** with the COE complex **40** produced complex **41**.

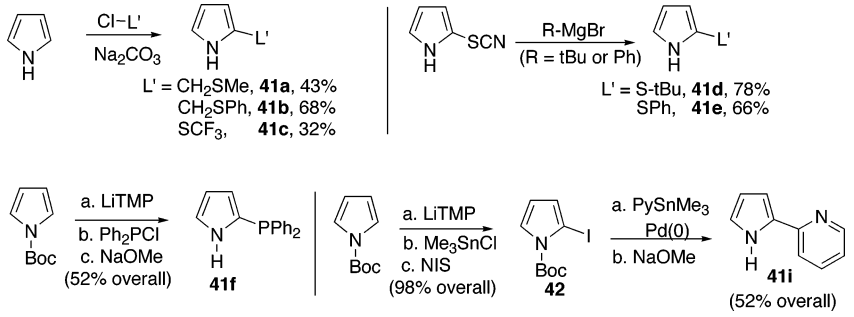
Sulfur was the first donor atom to be studied, partly because of the encouraging result with the tris(2-methylthiopyrrolyl)-phosphine ligand (**25**). Several varieties of the sulfur-containing side chains L′, which differed in coordinating ability, were envisioned (Scheme 7). Steric effects were evaluated in the series methylthio vs *tert*-butylthio vs phenylthio. Electronic effects should manifest themselves when comparing methylthio with (trifluoromethyl)thio and with phenylthio. The effect of the size of the chelate ring in an intermediate such as **14** (eq 3) was studied by comparing methylthio with methylthiomethyl and phenylthio with phenylthiomethyl. The hardness (polarizability) of the donating atom could also be varied by replacing sulfur with a phosphorus (L′ = PPh_2), nitrogen (L′ = 2-pyridyl), or oxygen (L′ = CO_2Me or C(O)NMe_2) group.

Several methods were available for the synthesis of the substituted pyrroles (Scheme 8). Electrophilic aromatic substitution on pyrrole[33,35] was used to make the methylthiomethyl-

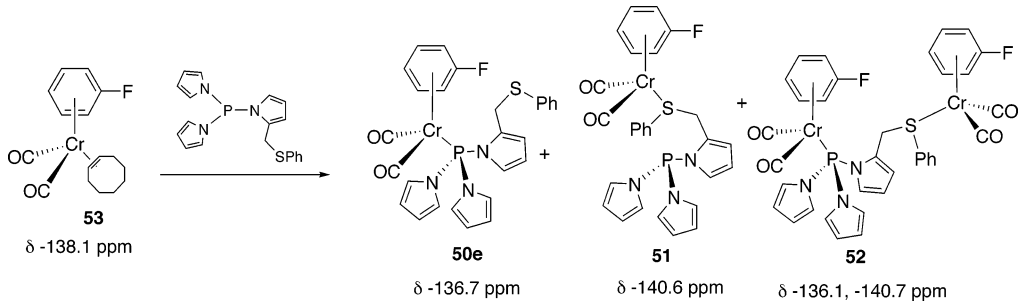
(34) Butler, I. S.; English, A. M.; Plowman, K. R. *Inorg. Synth*. **1982**, *21*, 1−6.

(35) Torisawa, Y.; Satoh, A.; Ikegami, S. *Tetrahedron Lett*. **1988**, *29*, 1729−1732.

Scheme 8. Preparation of 2-Substituted Pyrroles



Scheme 9. Complications from Side-Chain Coordination



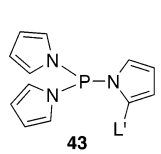
(**41a**), phenylthiomethyl- (**41b**),[36,37] and trifluoromethylthiopyrroles (**41c**).[38] Addition of tBuMgBr and PhMgBr to 2-thiocyanatopyrrole gave 2-*tert*-butylthiopyrrole (**41d**) and 2-phenylthiopyrrole (**41e**), respectively.[38] The 2-lithiation procedure on the N-boc-pyrrole followed by reaction with PPh_2Cl and deprotection gave the 2-phosphine derivative **41f** in 56% yield as a colorless oil.[39] Two acyl derivatives, methyl pyrrole-2-carboxylate (**41g**)[40] and the *N*,*N*-dimethyl amide (**41h**) of pyrrole-2-carboxylic acid, were prepared from the carboxylic acid following literature procedures.[41] Palladium coupling was chosen to synthesize 2-(2′-pyridino)pyrrole after several attempts to reproduce literature syntheses were unsuccessful.[42−44] N-Boc-pyrrole was converted to the 2-trimethylstannyl derivative[45] in excellent yield via a lithiation/electrophile trapping sequence. Iodination then yielded protected 2-iodopyrrole (**42**),[46,47] which was coupled with 2-trimethylstannylpyridine[48] using Pd(0) catalysis.[49] After deprotection, 2-pyridinopyrrole (**41i**) was obtained in better than 50% yield overall.

The synthesis of the trispyrrole phosphines **43** was achieved with DMAP as base at 65 °C in THF with Pyr_2PCl in the typical case, although the yields were slightly improved by using NaH in certain cases (Figure 8).

Benzene complexes of type **44** were all obtained in good yields from (benzene)tricarbonylchromium(0) by the general procedure described in eq 4. The structures and yields are given in Figure 9. Complexes **44a**−**e** and **44g** are moderately stable yellow solids. They were routinely purified by column chromatography on silica gel without special precautions. Recrystallization from ether/hexanes gave pure samples. When pure, complexes **44a**−**e,g** can be stored under Ar for a long time. Complexes **44f,h**−**j** are orange and relatively less stable. Column chromatography led to significant decomposition, and recrystallization had to be performed rigorously under Ar. Complex **44i** was only a minor product in the standard preparation and was not studied.

Typically, minor products were observed during complexation. In the case of the (2-methylthiomethyl)pyrrole and the (2-phenylthiomethyl)pyrrole cases (**44d**, and **44e**), two minor products were assigned to an isomer with the side-chain ligand instead of the phosphorus attached to Cr (**45**, **46**) and a dimeric structure, where the bidentate phosphine bridges between two (benzene)$Cr(CO)_2$ units (**47**, **48**). The composition of the mixtures changed with time. For example, when the product mixture from the (2-phenylthiomethyl)pyrrole case was allowed to stand at 23 °C overnight, the minor products slowly decreased in abundance, and the major isomer (P-bound) increased. With the (2-methylthiomethyl)pyrrole phosphine ligand, heating at 60 °C was necessary to initiate equilibration, and, again, the desired complex became essentially the only product. An extreme case of "wrong" complexation arose from the (2-diphenylphosphine)pyrrolylphosphine ligand (**43i**). In this case, a 4:1 mixture was obtained where the major product was isolated and fully characterized as the side-bound isomer, **49**. From NMR spectral data on the mixture, the minor isomer was assigned as the desired phosphine (**44i**). The ratio did not change when the mixture was allowed to stir for 3 h at 70 °C. The

(36) Barcock, R. A.; Moorcroft, N. A.; Storr, R. C.; Young, J. H.; Fuller, L. S. *Tetrahedron Lett*. **1993**, *34*, 1187−1190.
(37) Campiani, G.; Nacci, V.; Bechelli, S.; Ciani, S. M.; Garofalo, A.; Fiorini, I.; Wikstrom, H.; de Boer, P.; Liao, Y.; Tepper, P. G.; Cagnotto, A.; Mennini, T. *J. Med. Chem*. **1998**, *41*, 3763−3772.
(38) Haas, A.; Niemann, U. *Chem. Ber*. **1977**, *110*, 67−77.
(39) The pyrrole phosphine **41f** is known, from a different procedure: Allen, D. W.; Charlton, J. R.; Hutley, B. G. *Phosphorus* **1976** *6*, 191−194.
(40) Fischer, E.; van Slyke, D. D. *Chem. Ber*. **1911**, *44*, 3166−3171.
(41) Couch, P. W.; Games, D. E.; Jackson, A. H. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2492−2501.
(42) Seki, K.; Ohkura, K.; Terashima, M.; Kanaoka, Y. *Heterocycles* **1984**, *22*, 2347−2350.
(43) Corriu, R. J. P.; Huynh, V.; Iqbal, J.; Moreau, J. J. E.; Vernhet, C. *Tetrahedron* **1992**, *48*, 6231−6244.
(44) Savoia, D.; Concialini, V.; Roffia, S.; Tarsi, L. *J. Org. Chem*. **1991**, *56*, 1822−1827.
(45) Martina, S.; Enkelmann, V.; Wegner, G.; Schluter, A.-D. *Synthesis* **1991**, 613−615.
(46) Chen, W.; Cava, M. P. *Tetrahedron Lett*. **1987**, *28*, 6025−6026.
(47) Groenendaal, L.; Van Loo, M. E.; Vekemans, J. A. J. M.; Meijer, E. W. *Synth. Comm*. **1995**, *25*, 1589−1600.
(48) Anderson, D. G.; Webster, D. E. *J. Chem. Soc. B* **1968**, 765.
(49) Fan, Y.-H.; Haseltine, J. *J. Heterocyclic Chem*. **1999**, *36*, 869−872.



43

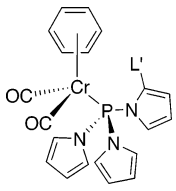
base = DMAP

a: L' = SMe (75 %)
b: L' = SCF_3 (46%)
c: L' = SPh (82%)
d: L' = CH_2SMe (37%)
e: L' = CH_2SPh (75%)
f: L' = $C(O)NMe_2$ (79%)

base = NaH

g: L' = S-*t*-Bu (93%)
h: L' = CO_2Me (64%)
i: L' = PPh_2 (50%)
j: L' = 2-Py (99%)

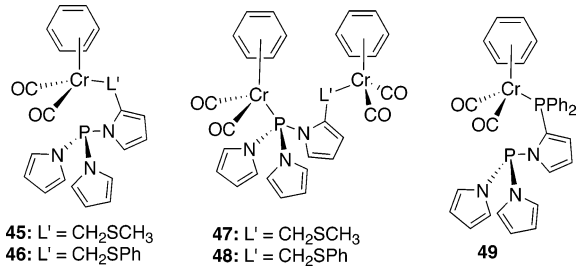
Figure 8. Yields of the monosubstituted tris(pyrrolyl)phosphines.



44

a: L' = SMe (66%)
b: L' = SCF_3 (83%)
c: L' = SPh (65%)
d: L' = CH_2SCH_3 (80%)
e: L' = CH_2SPh (55%)
f: L' = $C(O)NMe_2$ (88%)
g: L' = S-tBu (86%)
h: L' = CO_2Me (69%)
i: L' = PPh_2 (see text)
j: L' = 2-Py (59%)

Figure 9. Structures and yields of the benzene complexes.



45: L' = CH_2SCH_3
46: L' = CH_2SPh

47: L' = CH_2SCH_3
48: L' = CH_2SPh

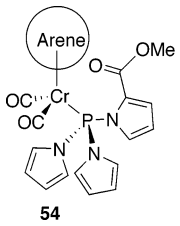
49

Figure 10. Variations in ligand binding.

preferential attachment of the chromium to the side chain phosphorus is consistent with higher electron density at that site.

The apparent kinetic preference for initial side-chain coordination and slow equilibration in the phenylthiomethyl and the methylthiomethyl examples appeared again in the formation of the corresponding complexes with fluorobenzene, **50**. In this case, ^{19}F NMR provided additional information. Working with mixtures whose composition changed slowly with time and monitoring by ^{19}F, ^{31}P, and ^{1}H NMR, tentative correlations of the peaks in the ^{19}F NMR spectrum are suggested as shown in Scheme 9. The P-bound complex **50e** was isolated and fully characterized. The S-bound complex **51** was the major product at the beginning of the reaction, but it slowly converted to the P-bound complex **50e**. Two small peaks of approximately the same intensity, one close to the peak for the P-bound complex **50e** and the other close to the peak for the S-bound complex **51**, were tentatively assigned to the bridged species **52**. Another peak, which appeared between the S-bound and P-bound clusters of peaks, was assigned to the transient COE intermediate **53**. After 2 h, most of the COE adduct **53** was converted to a mixture of species **51** (S-bound), **50e** (P-bound), and **52** (bridged) in an approximate ratio of 1:2:5. The area of the peaks corresponding to S-bound (**51**) and the bridged (**52**) species decreased with time, while the area of the P-bound species (**50e**) increased. The estimated half lifetimes are about 10 h (**51**) and 14 h (**52**) at 23 °C.

A series of complexes was synthesized employing the 2-(methoxycarbonyl)pyrrolylphosphine ligand **43h** with differing arene rings. The standard protocol (eq 4) gave the complexes **54a**−**d** as orange solids in the yields shown in Figure 11. The fluorobenzene complex **54a** was too unstable to obtain completely pure. It was tentatively characterized by ^{1}H NMR and ^{31}P NMR spectral data.

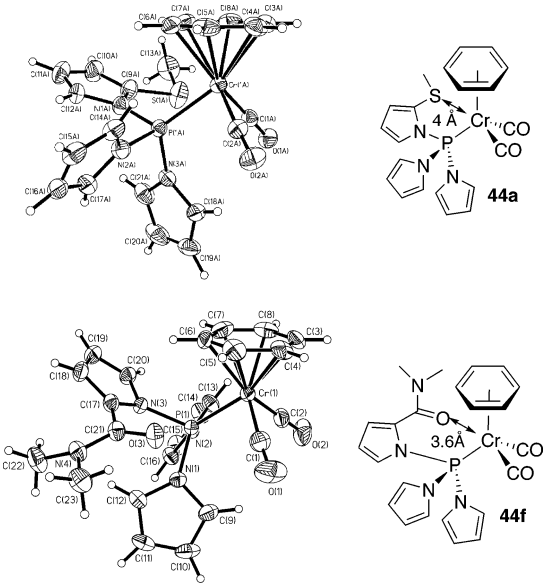


54

Arene

a: fluorobenzene (66%)
b: o-xylene (83%)
c: m-xylene (65%)
d: p-xylene (86%)

Figure 11. Substituted arene ligands on the 2-(methoxycarbonyl)pyrrolylphosphine complexes.



44a

44f

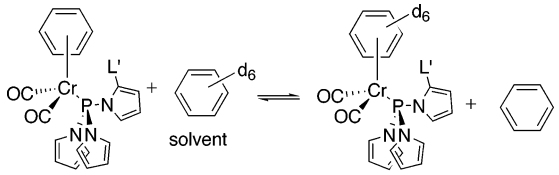
Figure 12. X-ray structures of the complexes **44a** and **44f**.

The structures of complexes **44a** and **44f** were determined by single-crystal X-ray diffraction (Figure 12). An important feature in **44a** is the position of the sulfur about 4 Å away from the metal center. It is poised to make the interaction leading to side chain coordination. In **44f**, the corresponding oxygen−chromium distance is even shorter (3.6 Å). In **44a**, the arene ligand is observed only in the staggered conformation with respect to the CO ligand, while in **44f**, there is evidence for a low barrier to rotation with the population of both the staggered (64%) and eclipsed (36%) conformations.

(b) Arene Exchange Rates. Effect of the Side Chain. The ability of the side chain of the ligand to facilitate arene exchange was determined by measurement of the rate of the arene exchange reaction in neat perdeuteriobenzene (Table 1). The reaction was continuously monitored by ^{1}H NMR at elevated temperature (typically at 70 °C) following the disappearance of the complexed benzene peak at around δ 4 ppm in **44**. Signals due to the phosphine remained unchanged, consistent with the formation of the perdeuterated benzene complex **55** with essentially identical environment compared to the starting material.

As a reference point, the complex with L′ = H shows no arene exchange after many hours at 150 °C. For the trifluoromethylthio complex **44b**, no change in the ^{1}H spectrum was observed after 12 h at 70 °C, and for the phenylthiomethyl complex **44e**, no exchange was observed after 60 h at 70 °C. For **44e**, partial decomposition of the starting material led to severe line broadening in the ^{1}H NMR spectrum and did not allow an investigation of the reaction for longer time. The dimethylamide and pyridine complexes **44f** and **44j** decomposed

Table 1. Ligand Effects on the Rate of Arene Exchange of (Arene)Cr(CO)$_2$(L−L′) 44 with Benzene-d_6



44 **55**

complex	half life at 70.0 °C
44a L = SMe	8.7 h
44b L = SCF_3	<5% conversion/12 h
44c L = SPh	30.6 h
44d L = CH_2SMe	28.7 h
44e L = CH_2SPh	very slow (decomp)
44f L = $CONMe_2$	9 h at 22 °C[a]
44g L = St-Bu	9.91 h
44h L = CO_2Me	0.5 h (∼115 h at 23 °C)
44j L = 2-Py	8 h at 22 °C[a]

[a] Too fast to measure at 70 °C.

quickly at 70 °C. However, when arene exchange was performed at 22 °C, clean formation of the corresponding C_6D_6 complex was observed. The following reactivity order is evident (from Table 1)

$$\text{2-Py} > CONMe_2 > CO_2Me \gg SMe > \text{S-}t\text{-Bu} > CH_2SMe > SPh \gg CH_2SPh, SCF_3$$

Summary of the Rate Data. (a) Arene exchange is much faster when the side chain heteroatom possesses an available π^* orbital (L′ = 2-Py, C(O)NMe_2, CO_2Me). Sulfur-based σ donors, which do not have a low energy π^* (L′ = SR and CH_2SR), were much slower. (b) Exchange in a complex with a large t-BuS side chain is only slightly slower than that for the MeS analogue, suggesting that steric effects play only a minor role. However, the electronic effect is very dramatic. The SCF_3 complex is much slower than the SMe analogue. Also, SMe is faster than SPh and CH_2SMe is faster than CH_2SPh, consistent with partial electron delocalization from the sulfur into the phenyl ring as a negative factor. (c) The formation of a five-membered vs a six-membered chelate ring does not show an obvious difference (compare **44a** vs **44d** and **44c** vs **44e**. (d) Among carbonyl donors, the more electron-rich amide is significantly faster than the ester. Pyridine is faster still, although the difference between pyridine and amide is relatively small.

Interpretation of the Rate Data. To reconcile these results, we propose that a chromium side-chain heteroatom bond is present in the rate-determining transition state for arene exchange. The strength of this bond determines the energy of the transition state and therefore the rate of the arene exchange. Even though sulfur is relatively polarizable and a good σ donor, it does not allow for effective back bonding from the metal. Such back bonding is expected to be much more significant in the corresponding transition states for the ester, amide, and the pyridine side chains and may be a dominant factor in stabilizing the transition state in these cases.

Among the sulfur donor ligands, the electron-donating ability of sulfur is of major importance. A substituent which depletes the electron density at sulfur, such as trifluoromethyl or, to a smaller extent, phenyl, reduces the stability of the chromium−sulfur bond and slows the exchange rate.

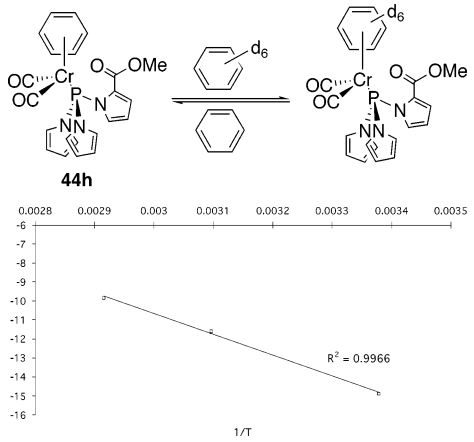


Figure 13. Eyring plot for the arene-exchange reaction of the complex **44h** with C_6D_6.

Among the π-acceptor side chains, pyridine is the fastest. It not only provides a basic lone pair but also possesses a relatively low energy π^* orbital for back bonding from the chromium. The ester also possesses a lower energy π^* then the amide, but the amide provides a much more basic lone pair (on the oxygen); evidently the stronger σ-donating ability of the amide is responsible for a more stable transition state for arene detachment in this case.

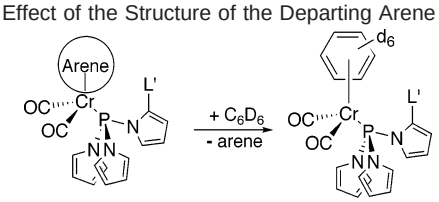
Preliminary Studies of the Temperature Dependence of Arene Exchange: Eyring Plot. Because the complex bearing the carbomethoxy side chain (**44h**) has a relative low barrier to exchange and is easy to prepare and purify, it was chosen as the example for further kinetic studies. By use of the degenerate exchange (except for the deuterium label), the rate of disappearance of **44h** was monitored at 23, 50, and 70 °C and the standard Eyring plot (Figure 13) gave activation parameters of $\Delta H^‡$ 22 kcal/mol (from the slope) and $\Delta S^‡$ −2.8 cal/mol K (from the intercept).

The small value of $\Delta S^‡$ is not consistent with an associative reaction for which a value below −10 eu is expected nor with a dissociative mechanism for which a value above 10 eu is expected.[50] It is consistent with an interchange mechanism, as defined by Atwood, although "one must be careful in interpreting the mechanism for reactions that have $\Delta S^‡$ between −10 and +10 eu because solvent reorganization may also contribute, especially for polar solvents and charged metal complexes".[50]

The Effect of the Structure of the Departing Arene. The departing arene has a dramatic effect on the rate of the exchange reaction (Table 2). Fluorobenzene was replaced much faster than benzene from (arene)Cr(CO)$_2$L−L′ (L′ = SMe, CO_2Me), compare **50a** vs **44a** and **54a** vs **44h**. The half life of the fluorobenzene complex with the methylthio side chain (**50a**) was 45 min at 60 °C, while for the benzene complex **44a**, it was 2 h at 80 °C. With the fluorobenzene ligand and ester side chain (**54a**), much faster exchange rates prevented a precise determination of exchange kinetics; the half life was estimated to be less than 1 h at 23 °C, whereas the corresponding benzene complex **44h** has a half life of about 115 h at the same temperature. Xylene complexes **54b**−**d** exchanged the arene ligand even more slowly than the corresponding benzene

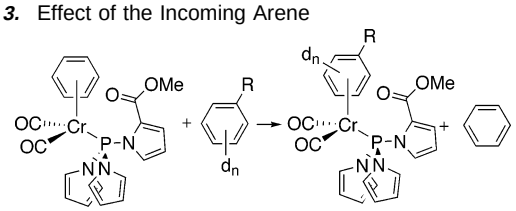
(50) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*, 2nd ed.; VCH Publishers: New York, 1997.

Table 2. Effect of the Structure of the Departing Arene



entry	L	arene	half life time
50a	−SMe,	fluorobenzene	45 min/60 °C
44a	−SMe	benzene	120 min/80 °C
54a	$-CO_2Me$	fluorobenzene	<60 min/23 °C
44h	$-CO_2Me$	benzene	115 h/23 °C
44h	$-CO_2Me$	benzene	1.5 h/60 °C
54b	$-CO_2Me$	*o*-xylene	8.6 h/60 °C
54c	$-CO_2Me$	*m*-xylene	16.2 h/60 °C
54d	$-CO_2Me$	*p*-xylene	9.1 h/60 °C

Table 3. Effect of the Incoming Arene



entry[a]	incoming arene	$t_{1/2}$ (h)
1	chlorobenzene-d_5	0.88
2	anisole-d_8	1.35
3	fluorobenzene-d_5	1.64
4	benzene-d_6	2.45
5	toluene-d_8	2.64
6	*o*-xylene-d_{10}	3.01
7	*m*-xylene-d_{10}	3.80
8	*p*-xylene-d_{10}	4.64
9	mesitylene-d_{12}	10.7

[a] By use of complex **44h** at 50.5 °C.

complex **44h** (Table 2). The half lives were measured for *o*-xylene, **54b**, (8.6 h), *m*-xylene, **54c**, (16.2 h), and *p*-xylene, **54d** (9.1 h) complexes in benzene-d_6 at 60 °C (the half life for the benzene complex at this temperature is about 1.5 h). Different rates may reflect different stabilities of the starting complexes as well as different transition state energies.

The Effect of the Structure of the Incoming Arene. The structure of the incoming arene was also found to affect the rate of the arene exchange reaction for **44h**. In a typical experiment, a perdeuterated arene was used as a solvent and the disappearance of the starting material (**44h**) was monitored by ^{1}H NMR at 50.5 (±0.2) °C in the NMR probe (Table 3). In some cases, the new arene created a sufficiently different environment in the resulting complex **66** so that the ^{1}H NMR peaks of the phosphine in the product **66** could be distinguished. Note that fluorobenzene serves as an effective incoming arene, which bodes well for the proposed goal of a catalytic S_NAr process.

Proposed Ligand-Assisted Arene-Exchange Mechanism. A mechanism consistent with the observations above is presented in Scheme 10. Step **a** is endothermic and involves reversible formation of the η^4 intermediate **A** stabilized by the side chain of the ligand. This stabilization is analogous to an intermolecular stabilization of the η^4-benzene chromium tricarbonyl intermediate by a σ-donor molecule. However, it is likely that the intramolecular stabilization in **A** is much more favorable than intermolecular stabilization, consistent with a lower activation energy for this step in the intramolecular case. Step **b** is highly endothermic; it involves a further dissociation of the arene to give the η^2 intermediate **B** which is formally a 16-electron complex. Loss of arene coordination may be compensated by an additional interaction with the side-chain heteroatom, as is possible with the $-CO_2Me$, $-CONMe_2$, or 2-pyridyl side chains. This interaction can be viewed as a back bond from the zerovalent chromium metal to LUMO of the heteroatom group. Step **c** is proposed to be rate determining and involves an associative step to generate an η^2, η^2 intermediate, **C**. The kinetic significance of this step is implied by a dependence on the structures of both the departing and incoming arenes. The following steps **d** and **e** are fast and highly exothermic overall to give the stable product, **E**. An alternative (steps **f** and **g**) with complete dissociation of the departing arene to give **F** is considered unlikely due to the lack of stabilization of this intermediate and the less direct relationship to the nature of the departing and incoming arenes.

Summary. The hypothesis that temporary coordination from an internal ligand can lower the barrier to detachment of an arene ligand and facilitate arene exchange in arene−metal π complexes was explored systematically. A series of 2-L′-pyrroles exhibiting a range of steric and electronic properties was prepared and converted to (2-L′-pyrrolyl)-(pyrrolyl)$_2$phosphines (L−L′), which were then used to replace a CO ligand in (arene)Cr(CO)$_3$ complexes and create a series of (arene)Cr(CO)$_2$(L−L′) complexes. Significant increases in the rate of arene exchange were observed with these (arene)-Cr(CO)$_2$(L−L′) complexes, from a slow reaction at 150 °C for the parent tris(pyrrolyl)phosphine to reactions which proceeded measurably at 23 °C. It was further demonstrated that the rate of arene exchange in the system with L′ = CO_2Me shows a significant dependence on the structure of both the incoming arene and the departing arene. A mechanism is proposed which accounts for this rate dependence on both arenes as well as the side chain ligand. With arene exchange now operating at close to room temperature in these systems, useful catalytic S_NAr reactions may be realized.

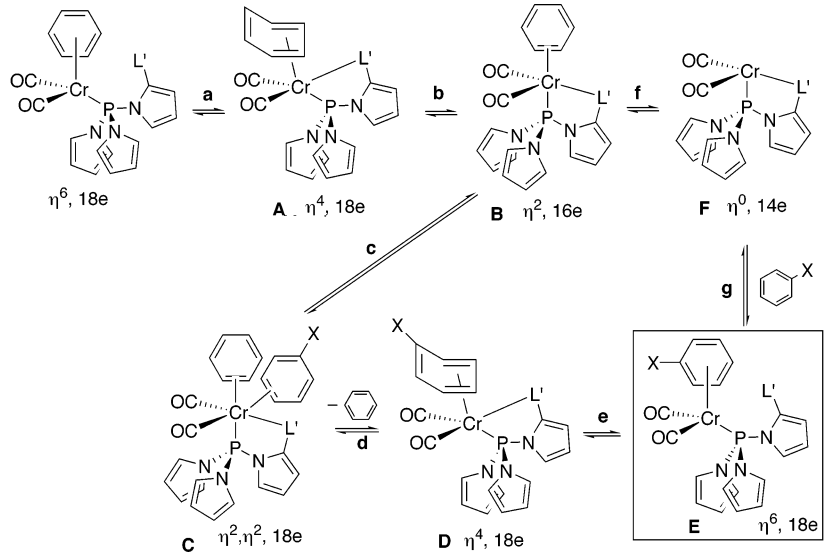
Experimental Procedures.

Analytical Data. Proton (^{1}H), carbon (^{13}C), fluorine (^{19}F), and phosphorus (^{31}P) NMR spectra were recorded on a Varian 500 (500 MHz, ^{1}H), Inova 400 (400 MHz, ^{1}H), or Mercury 300 (300 MHz, ^{1}H) spectrometers. Fluorine resonances were indirectly referenced to external fluorotrichloromethane. Phosphorus resonances were indirectly referenced to external phosphoric acid. Infrared (IR) spectra were recorded on a Nicolet 730 FTIR spectrometer with internal calibration. Mass-spectral data were obtained using a Kratos MS 80 RFA spectrometer operating in electron impact (EI) mode at 70 eV or fast atom bombardment (FAB) mode. High-resolution mass spectra were obtained at the UCR Mass Spectrometry Facility, Department of Chemistry, University of California, Riverside CA, 92521. Peaks are identified by mass/charge (*m*/*z* (%)) and relative abundance to base peak (%). Melting points are uncorrected and were recorded on an Electrothermal Melting Point Apparatus model #IA6304 using open capillary tubes.

Reagents. Commercial reagents were purchased from Aldrich Chemical Co., Fluka, or Strem and used without further purification, unless otherwise noted.

Solvents. Anhydrous diethyl ether and tetrahydrofuran (THF) were obtained by distillation from sodium benzophenone ketyl. Benzene, toluene, dichloromethane, methanol, hexanes (hex), and acetonitrile

Scheme 10. Proposed Mechanism of Ligand-Assisted Arene Exchange



were distilled from calcium hydride under Ar. Fluorobenzene, *N*-methylpyrrolidinone (NMP), and dimethylformamide (DMF) were distilled over calcium hydride and stored under Ar over molecular sieves (4 Å). Deuterated NMR solvents were stored over activated molecular sieves (4 Å).

General Procedures. Operations with air-sensitive compounds were performed under Ar using double manifold techniques. A reaction flask was placed "under Ar" by sequentially evacuating it with an oil pump (0.1 Torr) and then filling it with Ar three times. Flash chromatography was performed using Merck Silica Gel 60 (230−400 mesh). For photochemical reactions, irradiation was performed with a 450-W low-pressure Hg lamp held in a water-cooled quartz jacket.

Preparation of 2-Allylpyrrole (27). (a) Preparation of 2-Allylpyrrole-1-*tert*-butylcarboxylate. A 100-mL two-neck flask equipped with a magnetic stirring bar, a reflux condenser, and a vacuum adapter was charged with palladium(II) chloride (0.27 g, 1.5 mmol), lithium chloride (68 mg, 1.6 mmol), and 2-trimethylstannyl-N-boc-pyrrole[51] (9.4 g, 30 mmol) under Ar. Toluene (50 mL) was added followed by allyl bromide (5.2 mL, 60 mmol), and the mixture was heated at reflux for 24 h at which time it acquired a dark color. It was allowed to cool to 23 °C, filtered through a silica gel plug, and concentrated by rotary evaporation to yield the greenish oil. It was chromatographed on a silica gel column (hex:EtOAc 50:1) to give a title compound (2.8 g, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 (s, 9H), 3.62 (dd, J = 8 Hz, J = 2.4 Hz, 2H), 5.04−5.10 (m, 2H), 5.97−6.11 (m, 3H), 7.22−7.24 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.2, 33.4, 83.5, 110.2, 111.8, 116.1, 121.3, 134.0, 136.0, 149.6.

(b) Preparation of 2-Allylpyrrole (27). A Standard Procedure for Boc-Deprotection. A 250-mL round-bottom flask equipped with a magnetic stirring bar under Ar was charged with N-Boc-2-allylpyrrole (6.5 g, 34 mmol) and THF (20 mL). The resulting solution was cooled to 0 °C, and NaOMe (40 mL of 25% soln in MeOH, 190 mmol) was added slowly via syringe. The solution was stirred for 10 min at 0 °C and then allowed to warm to 23 °C over 30 min. The resulting solution was poured into water (100 mL) and extracted with ether (100 mL). The organic layer was collected, washed with water (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation followed by a flash distillation at 24 Torr/50 °C to yield **27** (2.0 g, 56% yield). The ^{1}H NMR data were consistent with literature values.[33]

Preparation of 2-(Methylthio)pyrrole (24). (a) Preparation of N-Boc-2-(methylthio)pyrrole. This method is based on a general procedure for metalation/trapping/deprotection of N-bocpyrrole.[52] A three-neck flask equipped with a stirring bar and a thermometer was placed under Ar, and a solution of *n*-butyllithium (31 mL, 50 mmol, 1.6 M in hexane) was added dropwise via syringe to a stirred solution of TMP (8.4 mL, 50 mmol) in THF (50 mL) at −78 °C. The mixture was allowed to stir for 10 min at −78 °C and then 10 min at −10 °C, whereupon it was cooled to −78 °C. To the resulting yellow solution was added N-(boc)pyrrole (8.4 mL, 50 mmol) dropwise via syringe. The solution was stirred for 1 h at −78 °C and then was quenched by rapid addition (<2 s) of dimethyl disulfide (9.9 mL, 110 mmol) at −78 °C. If dimethyl disulfide is added slowly, the 2,5-disubstituted product formed in significant amounts. The mixture was warmed to 23 °C slowly and then stirred for 1 h. The mixture was diluted with ether (50 mL), washed with water (50 mL) and saturated NaCl solution, and then dried over anhydrous Na_2SO_4. The solution was filtered, and the filtrate was concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel (50:1 hex:EtOAc) to give the title compound as a colorless oil (6.1 g, 57% yield), homogeneous by TLC (silica gel, R_f 0.4, 20:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.62 (s, 9H), 2.42 (s, 3H), 5.96 (dd, J = 3.6 Hz, J = 1.8 Hz, 1H), 6.20 (t, J = 3.3 Hz, 1H), 7.25 (dd, J = 3.3 Hz, J = 1.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.2, 28.2, 84.5, 110.4, 111.6, 121.7, 129.5, 149.2. MS (+EI): m/z (%) 213 (4), 157 (34), 113 (100), 84 (19). HRMS (+EI): found 213.0832 (calcd 213.0823). IR (KBr): 2981 (s), 2923 (s), 1737 (s), 1333 (s), 1158 (s) cm^{-1}.

(b) Deprotection. This product was previously prepared by a different method.[53] Deprotection of N-Boc-2-(methylthio)pyrrole using a standard procedure (see above) yielded a yellow oil which was purified by chromatography on silica gel with hex:EtOAc 50:1 to yield 2-methylthiopyrrole **24** as a colorless oil, 2.3 g (70% yield), homogeneous by TLC (R_f 0.33, 10:1 hex:EtOAc).

Preparation of 2-(Methylthiomethyl)pyrrole (41a). This compound was prepared by analogy to 2-allylpyrrole.[54] A 250-mL three-neck flask equipped with a magnetic stirring bar, an addition funnel, and a vacuum adapter was placed under Ar and then charged with 3 mol equiv of pyrrole (16 g, 17 mL, 0.24 mol), aqueous potassium carbonate (5.6 g in 50 mL of H_2O), and toluene (50 mL). To the resulting two-phase mixture, chloromethyl methyl sulfide (7.7 g, 6.7 mL, 80 mmol) was added dropwise (via the addition funnel) over 10 min with vigorous

(51) Martina, S.; Enkelmann, V.; Wegner, G.; Schluter, A.-D. *Synthesis* **1991**, 613.

(52) Gharpure, M.; Stoller, A.; Bellamy, F.; Firnau, G.; Snieckus, V. *Synthesis*, **1991**, 1079.

(53) Nedolya, N. A.; Brandsma, L.; Verkruijsse, H. D.; Trofimov, B. A. *Tetrahedron Lett.* **1997**, *38*, 7247.

(54) Papdopoulos, E. P.; VanderWerf, C. A. *Heterocycles* **1982**, *19*, 343.

stirring. The resulting mixture was allowed to stir for 4 h at which time the layers were separated, toluene was partially removed from the organic layer on a rotary evaporator, and the resulting oil was fractionally distilled at 1 Torr to yield 2-(methylthiomethyl)pyrrole (4.4 g, 43% yield) as a colorless oil (bp 55 °C at 1 Torr). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.00 (s, 3H), 3.73 (s, 2H), 6.07−6.11 (m, 1H), 6.12−6.17 (m, 1H), 6.76−6.81 (m, 1H), 8.37 (br s, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 14.8, 30.7, 108.2, 108.3, 118.1, 127.5. MS (+EI): m/z (%). 127 (13), 80 (100). HRMS (+EI): m/z found 127.04608 (calcd 127.04557). IR (KBr): 3384 (s, br), 2914 (m), 1254 (m), 1090 (m), 1027 (m), 723 (m) cm^{-1}.

Preparation of 2-(Phenylthiomethyl)pyrrole (41b). This compound was prepared by analogy to 2-allylpyrrole.[54] A 250-mL three-neck flask equipped with a magnetic stirring bar, an addition funnel, and a vacuum adapter was placed under Ar and then charged with 3.00 mol equiv of pyrrole (10.5 mL, 10.2 g, 151 mmol), aqueous potassium carbonate (6.9 g in 50 mL of H_2O), and toluene (50 mL). The resulting mixture was heated to 80 °C, and chloromethyl phenyl sulfide (6.7 mL, 7.9 g, 50 mmol) was added dropwise (via the addition funnel) over 10 min with vigorous stirring. The resulting mixture was allowed to stir for 6 h at 80 °C. The mixture was then allowed to cool to 23 °C, the layers were separated, and the organic layer was collected. The volatiles were removed in vacuo, and the resulting brownish oil was dissolved in Et_2O and cooled to −5 °C whereupon crystallization occurred to yield 6.0 g (68% yield) of 2-(phenylthiomethyl)pyrrole as a white solid. The ^{1}H NMR data were consistent with literature values.[55]

Preparation of 2-*t*-Butylthiopyrrole (41d). A three-neck flask equipped with a magnetic stirrer bar and a vacuum adapter under Ar was charged with excess of 1 M solution of *t*-BuMgCl in THF (7.6 mL, 7.6 mmol). The solution was cooled to 0 °C whereupon 2-thiocyano-pyrrole (0.34 g, 2.7 mmol)[56,57] was added slowly via syringe as a solution in THF (15 mL). The resulting solution was allowed to warm to 23 °C over 4 h at which time it was poured into chilled water and extracted with EtOAc. The volatiles were removed on a rotary evaporator and the residue was dissolved in dichloromethane and filtered through a plug of silica gel. Evaporation of the solvent in vacuo yielded 327 mg (78% yield) of 2-*tert*-butylthiopyrrole as a colorless oil. It can be further recrystallized from hexane to yield a white solid, mp 39−40 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 9H), 6.25−6.28 (m, 1H), 6.39−6.42 (m, 1H), 6.87−6.90 (m, 1H), 8.2 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.9, 46.8, 110.0, 118.3, 118.7, 120.8. MS (+EI): *m*/*z* (%) 155 (6), 99 (100), 84 (15). HRMS (+EI): *m*/*z* found 155.07519 (calcd 155.07687). IR (KBr): 3348 (br, m), 2964 (m), 2925 (m), 2898 (m), 2863 (m), 1531 (m), 1363 (m), 738 (m) cm^{-1}.

Preparation of 2-(Diphenylphosphino)pyrrole (41f). (a) Preparation of N-Boc-2-(diphenylphosphino)pyrrole. A 500-mL four-neck flask equipped with a thermometer adapter, magnetic stirrer, and vacuum adapter, and an addition funnel was placed under Ar and subsequently charged with TMP (8.9 mL, 5.2 mmol) and THF (50 mL). The solution was cooled to −78 °C and *n*-butyllithium (34 mL, 55 mmol, 1.6 M in hex) was added dropwise via an addition funnel. The reaction temperature was maintained below −65 °C. The mixture was stirred for 10 min at −78 °C and was then allowed to warm to 0 °C in 30 min. It was then cooled to −78 °C, and a solution of N-(boc)-pyrrole (8.4 g, 50 mmol in 50 mL THF) was added dropwise via an addition funnel again maintaining the temperature below −65 °C. The mixture was then stirred for 20 min at −78 °C and then was transferred via cannula to a solution of chlorodiphenylphosphine (2.00 mol equiv, 100 mmol, 18 mL) in THF (50 mL) kept at −30 °C. Upon addition, the mixture was allowed to warm to 23 °C over 21 h. The solvent was then removed on a rotary evaporator and the residue taken up in Et_2O (100 mL) and washed with H_2O (100 mL). The resulting aqueous layer was extracted with Et_2O (2 × 100 mL). The organic layers were combined and washed with brine. The resulting organic layer was dried over Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue was purified by column chromatography (4:1 hex:CH_2Cl_2) to give N-Boc-2-(diphenylphosphino)pyrrole as a colorless oil (8.8 g, 52% yield), homogeneous by TLC (silica gel, R_f 0.5, 20:1 hex:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.41 (s, 9H), 5.57 (dd, J = 3.3 Hz, J = 1.8 Hz, 1H), 6.17 (td, J = 3.3 Hz, J = 0.3 Hz, 1H), 7.26−7.36 (m, 10H), 7.54−7.57 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.9, 85.0, 111.8, 123.1, 125.4, 128.4 (d, J^3_{CP} = 7 Hz), 128.8, 130.4 (d, J^1_{CP} = 14 Hz), 133.7 (d, J^2_{CP} = 20 Hz), 138.2 (d, J^1_{CP} = 10 Hz), 149.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ −17.0. MS (+EI): *m*/*z* (%) 351 (0.5), 295 (2.9), 251 (100), 219 (18), 174 (58), 143 (36). HRMS (+EI): *m*/*z* found 351.13935 (calcd 351.13882). IR (KBr): 3070 (m), 3034 (m), 3003 (m), 2982 (m), 2933 (m), 1736 (s), 1478 (m), 1327 (s) cm^{-1}.

(b) Preparation of 2-(Diphenylphosphino)pyrrole (41f). Deprotection of N-Boc-2-(diphenylphosphino)pyrrole using a standard procedure (see above) yielded 2-(diphenylphosphino)pyrrole as a colorless oil in quantitative yield. It can be further purified, if necessary, by chromatography on silica gel with 4:1 hex:CH_2Cl_2. The ^{1}H NMR data were consistent with literature values.[58]

Preparation of N-Boc-2-iodopyrrole (42). According to a modified literature procedure,[59] a 100-mL three-neck flask equipped with a magnetic stirring bar and a vacuum adapter under Ar was charged with 2-trimethylstannyl-pyrrole-1-*tert*-butylcarboxylate[60] (1.3 g, 4.3 mmol) and THF (50 mL). The resulting solution was cooled to −78 °C, and N-iodosuccinimide (0.97 g, 4.3 mmol) was added in small portions while an Ar stream was bubbled through the flask. The vacuum adapter was replaced with a septum, and the resulting yellowish suspension was allowed to warm in the fridge at −5 °C over 1 day. During this time, the solution became colorless and a white precipitate formed. The flask was removed from the cold, anhydrous Na_2CO_3 (about 1 g) was added, and the mixture was filtered through a silica gel plug to yield N-Boc-2-iodopyrrole (1.2 g, 99%) as a colorless oil after rotary evaporation. The ^{1}H NMR data were consistent with literature values.[61]

Preparation of 2-(2′-Pyridino)pyrrole (41i). (a) Preparation of 2-(2′-Pyridino)pyrrole-1-*tert*-butylcarboxylate. A 50-mL two-neck flask equipped with a magnetic stirring bar, a reflux condenser, and a vacuum adapter was charged with tetrakis(triphenylphosphine)palladium-(0) (0.68 g, 0.59 mmol) and placed under Ar. N-Boc-2-iodopyrrole **42** (4.3 g, 15 mmol) was added as a solution in toluene (20 mL) and the mixture was allowed to stir for 25 min. To the resulting orange solution 2-trimethylstannylpyridine (4.4 g, 18 mmol) was added slowly via syringe. The mixture was heated at reflux for 22 h during which time it acquired a dark color. It was allowed to cool to 23 °C, poured into water, and extracted with Et_2O. The organic layer was washed with H_2O and then brine. The organic layer was dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was chromatographed on a silica gel column with hex:EtOAc 5:1 as the mobile phase to give 2-(2′-pyridino)pyrrole-1-*tert*-butylcarboxylate as a colorless oil (2.0 g, 59% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.36 (s, 9H), 6.25 (t, J = 3.3 Hz, 1H), 6.42 (dd, J = 3.3 Hz, J = 1.8 Hz, 1H), 7.20 (ddd, J = 12 Hz, J = 4.8 Hz, J = 1.2 Hz, 1H), 7.36−7.43 (m, 2H), 7.68 (td, J = 7.5 Hz, J = 1.8 Hz, 1H), 8.60−8.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.8, 83.8, 110.8, 115.8, 122.0, 123.7, 123.7, 134.3, 136.0, 149.0, 149.5, 153.2. MS (+EI): *m*/*z* (%) 244 (1), 171 (1), 144 (100), 117 (14), 89 (7). HRMS (+EI): *m*/*z* found 244.1227 (calcd 244.1212). IR (KBr): 2981 (m), 2934 (m), 1741 (s), 1590 (s), 1317 (s), 1153 (s), 783 (s), 731 (s).

(55) Barcock, R. A.; Moorcroft, N. A.; Nicholas, A.; Storr, R. C.; Young, J. H.; Fuller, L. S. *Tetrahedron Lett.* **1993**, *34*, 1187.
(56) Gronowitz, S.; Hornfeldt, A.-B.; Gestblom, B.; Hoffman, R. A. *J. Org. Chem.* **1961**, *26*, 2615.
(57) Matteson, D. S.; Snyder, H. R. *J. Org. Chem.* **1957**, *22*, 1500.
(58) Allen, D. W.; Charlton, J. R.; Hutley, B. G. *Phosphorus* **1976**, *6*, 191.
(59) Groenendaal, L.; Van Loo, M E.; Vekemans, J. A. J. M.; Meijer, E. W. *Synth. Comm.* **1995**, *25*, 1589.
(60) Martina, S.; Enkelmann, V.; Wegner, G.; Schluter, A.-D. *Synthesis* **1991**, 613.
(61) Chen, W.; Cava, M. P. *Tetrahedron Lett.* **1987**, *28*, 6025.

(b) Preparation of 2-(2′-Pyridino)pyrrole (41i). Deprotection of 2-(2′-pyridino)pyrrole-1-*tert*-butylcarboxylate using a standard procedure (see above) yielded 2-(2′-pyridino)pyrrole as an off-white solid in 94% yield. It was further purified by filtering through a silica gel plug using 5:1 hex:EtOAc as a solvent. The ^{1}H NMR data were consistent with literature values.[62,63]

Preparation of Tris(2-methylthiopyrrolyl)phosphine (25). To a suspension of NaH (790 mg, 19.8 mmol, 60% in mineral oil) in THF (15 mL) at 0 °C was added 2-methylthiopyrrole (1.50 g, 13.3 mmol) via syringe. After the reaction mixture had been stirred at 23 °C for 2 h, a solution of PCl_3 (2.1 mL, 4.2 mmol, 2 M in dichloromethane) was added dropwise at 23 °C via syringe. Then the mixture was allowed to stir for 3 h at 23 °C. The mixture was filtered, the filtrate was concentrated by rotary evaporation, and the residue was purified by column chromatography on silica gel (30:1 hex:EtOAc) to give phosphine **25** as a colorless crystals (956 mg, 62%). Recrystallization from hex at −78 °C gave colorless needles, mp 76−77 °C, homogeneous by TLC (R_f 0.60, 10:1 hex:EtOAc). ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.28 (s, 9H), 6.18 (m, 3H), 6.29 (m, 3H), 6.52 (m, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 128.0 (d, J = 28 Hz), 126.0 (d, J = 3.5 Hz), 121.8, 142.2, 22.9. IR (neat, KBr): 1048 (s), 1416 (s), 1743 (s), 2919 (s), 2989 (s), 3126 (s) cm^{-1}. MS (+EI): m/z (%) 367 (M^+, 10.4), 320 (100), 255 (17.5), 207 (89.1), 161 (47.3), 126 (41.6), 112 (31.6), 68 (62.1). Anal calcd for $C_{15}H_{18}N_3PS_3$: C, 49.02; H, 4.94; N, 11.43. Found: C, 48.92; H, 5.09; N, 11.43.

Preparation of Tris(2-allylpyrrole)phosphine (28). A three-neck flask equipped with a magnetic stirring bar was placed under Ar and charged with NaH (700 mg, 17.5 mmol, 60% in mineral oil) and THF (20 mL). The suspension was cooled to 0 °C and 2-allylpyrrole (1.69 g, 15.8 mmol) was added dropwise via syringe. The reaction mixture was allowed to warm to 23 °C over 3 h. It was then filtered, concentrated by rotary evaporation, and purified by chromatography on silica gel (50:1 hex:EtOAc) to yield tris(2-allylpyrrole)phosphine as a colorless oil (690 mg, 41%). Homogeneous by TLC R_f 0.73 (10:1 hex:EtOAc). ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.44 (d, 6H, J = 5.9 Hz), 4.99 (d, 3H, J = 9.9 Hz), 5.29 (d, 3H, J = 4.6 Hz), 5.74−5.86 (m, 3H), 6.05 (m, 3H), 6.19 (t, 3H), 6.24 (m, 3H). ^{13}C NMR (75 MHz, CDCl3): δ 31.7 (d, J = 16 Hz), 111.3, 112.1, 116.6, 122.0, 135.3, 135.7 (d, J = 20 Hz). LRMS (+EI): m/z (%) 349 (M^+, 4.7), 243 (82), 136 (100), 122 (57), 106 (33), 80 (77).

Preparation of Chlorodipyrrolylphosphine (39). A 100-mL Schlenk flask equipped with a stirring bar was placed under argon. It was then charged with pyrrole (2.1 mL, 31 mmol), and triethylamine (4.7 mL, 33 mmol) and THF (50 mL) were added slowly via syringe. The mixture was cooled to −78 °C, and phosphorus trichloride (1.00 mL, 11.5 mmol) was added rapidly via syringe. The mixture was stirred for 15 min and then allowed to warm to 23 °C (over 1 h) and subsequently heated at 60 °C for 24 h. The mixture was then cooled, and the white precipitate was filtered (using a Schlenk line) and washed with THF. The volatiles were removed on a rotary evaporator and the residue distilled at 70 °C at 1 Torr to yield chlorodipyrrolylphosphine as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.39−6.42 (m, 4H), 7.08−7.12 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 113.9 (d, J = 5 Hz), 122.7 (d, J = 17 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 104.3 ppm, consistent with published data.[25]

Preparation of (2-Methylthiopyrrolyl)dipyrrolylphosphine (43a). Procedure A. A 100-ml Schlenk flask equipped with a stirring bar under Ar was charged with DMAP (8.0 mmol, 98 mg), 2-methylthiopyrrole (**24**, 5.0 mmol, 0.57 g), and THF (20 mL) and cooled to 0 °C. Chlorodipyrrolylphosphine (**39**, 5.0 mmol, 0.99 g) was added slowly via syringe, and the solution was allowed to warm to 23 °C over 15 min. It was then heated at 65 °C for 20 h. The resulting mixture was filtered under argon and then concentrated on a rotary evaporator to give a residual oil which was chromatographed on silica gel with hex:EtOAc 50:1 as the mobile phase. The volatiles were removed in vacuo leaving 1.03 g (75% yield) of the title compound as a colorless oil. It was recrystallized from hexane to yield white crystals, mp 45−46 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 3H), 6.24−6.29 (m, 2H), 6.40 (t, J^3_{HH} = 2 Hz, 4H), 6.55 (ddd, J^3_{PH} = 3.2 Hz, J^3_{HH} = 2.4 Hz, J^4_{HH} = 1.6 Hz, 1H), 6.82−6.86 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.7 (d, J^3_{CP} = 3 Hz), 113.3 (d, J^2_{CP} = 5 Hz), 121.3, 122.9, 123.0, 124.7 (d, J^2_{CP} = 4 Hz), 138.7 (d, J^2_{CP} = 24 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 70.1. MS (+EI): m/z (%) 275 (61.3), 228 (38.0), 163 (100). HRMS (+EI): m/z found 275.06438 (calcd 275.06461). IR (KBr): 3130 (m), 3102 (m), 2921 (m), 1453 (s), 1418 (m), 736 (s) cm^{-1}.

Characterization of (2-Trifluoromethylthiopyrrolyl)dipyrrolylphosphine (43b). This was obtained (according to procedure A) from 2-trifluoromethylthiopyrrole **41c** as a colorless oil in 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.38−6.42 (m, 5H), 6.53−6.55 (m, 1H), 6.7−6.80 (m, 4H), 6.84−6.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 113.7 (d, J^3_{CP} = 5 Hz), 114.0, 122.9 (d, J^2_{CP} = 15 Hz), 126.5, 128.1 (q, J^1_{CF} = 310 Hz), 128.3 (d, J^2_{CP} = 4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 74.5 (broad). ^{19}F NMR (376 MHz): δ −45.4 (d, J = 14 Hz). MS (+EI): m/z (%) 329 (7), 228 (75), 193 (8), 163 (100). HRMS (+EI): m/z found 329.03556 (calcd 329.03634). IR (KBr): 3131 (m), 1577 (m), 1454 (s), 1416 (s), 731 (s), 615 (s) cm^{-1}.

Characterization of (2-Phenylthiopyrrolyl)dipyrrolylphosphine (43c). This was obtained (according to procedure A) from 2-phenylthiopyrrole **41e** as a white solid in 63% yield. It was recrystallized from hexane to yield white crystals of mp 60−61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (t, J = 1.5 Hz, 4H), 6.39 (td, J = 2.7 Hz, J = 0.6 Hz, 1H), 6.49−6.51 (m, 1H), 6.68−6.71 (m, 4H), 6.72−6.74 (m, 1H), 6.69−6.72 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 113.2 (d, J = 4 Hz), 113.7, 122.8 (d, J = 14 Hz), 124.1, 126.0, 126.2 (d, J = 6 Hz), 126.4, 129.1, 137.9. ^{31}P NMR (162 MHz, $CDCl_3$): δ 73.1. MS (+EI): m/z (%) 337 (49), 271 (19), 244 (16), 228 (45), 204 (45), 174 (73), 161 (100). HRMS (+EI): m/z found 337.08087 (calcd 337.08025). IR (KBr): 3130 (m), 3101 (m), 3072 (m), 3058 (m), 1583 (m), 1453 (m), 1178 (s), 1165 (s), 729 (s) cm^{-1}.

Characterization of (2-Methylthiomethylpyrrolyl)dipyrrolylphosphine (43d). This was obtained (according to procedure A) from 2-methylthiomethylpyrrole **41a** as a colorless oil in 37% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.88 (s, 3H), 3.72 (s, 2H), 6.15−6.20 (m, 2H), 6.36−6.39 (m, 4H) 6.42−6.45 (m, 1H), 6.81−6.85 (m, 4H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 14.7, 30.1 (d, J = 13 Hz), 11.7, 113.0 (d, J = 4 Hz), 113.8 (d, J = 3 Hz), 123.12 (d, 4 Hz), 123.14, 133.4 (d, J = 16 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 73.0. MS (+EI): m/z (%). 289 (3), 242 (9), 223 (22), 175 (100), 144 (20). HRMS (+EI): m/z found 289.08095 (calcd 289.08025). IR (KBr): 3132 (w), 3100 (w), 2913 (m), 1454 (s), 1179 (s), 1058 (s), 732 (s) cm^{-1}.

Characterization of (2-Methylthiophenylpyrrolyl)dipyrrolylphosphine (43e). This was obtained (according to procedure A) from 2-methylthiophenylpyrrole **41b** as a colorless oil in 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.18 (s, 2H), 6.03−6.07 (m, 1H), 6.12 (td, J = 3 Hz, J = 0.6 Hz, 1H), 6.38−6.40 (m, 4H), 6.45 (td, J = 3.6 Hz, J = 3.3 Hz, 1H), 6.81−6.85 (m, 4H), 7.16−7.28 (m, 5H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 31.8 (d, J = 15 Hz), 112.1, 113.2 (d, J = 4 Hz), 113.9 (d, J = 3 Hz), 123.0, 123.1 (d, 14 Hz), 127.1, 128.9, 131.2, 133.1 (d, J = 19 Hz), 135.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ 73.4. MS (+EI): m/z (%) 351 (0.4), 272 (0.8), 242 (26), 206 (4), 175(100). HRMS (+EI): m/z found 351.09789 (calcd 351.09590). IR (KBr): 3131 (w), 3100 (w), 1454 (s), 1179 (s), 1058 (s), 733 (s) cm^{-1}.

Characterization of (2-(*N*,*N*-Dimethylamido)pyrrolyl)dipyrrolylphosphine (43f). This was obtained (according to procedure A) from pyrrole-2-carboxylic acid *N*,*N*-dimethyl-amide **41h** as a white solid in 79% yield. It was recrystallized from hexane to yield white crystals that turned yellow at 76 °C and then melted between 102 and 106 °C. The solid is easily oxidized in air acquiring a yellow color. ^{1}H NMR

(62) Seki, K.; Ohkura, K.; Terashima, M. *Heterocycles* **1984**, *22*, 2347.
(63) Savoia, D.; Concialini, V.; Roffia, S.; Tarsi, L. *J. Org. Chem.* **1991**, *56*, 1822.

(300 MHz, $CDCl_3$): δ 3.18 (br s, 6H), 6.04 (dt, $J = 3$ Hz, $J = 1.5$ Hz, 1H), 6.26 (td, $J = 2.4$ Hz, $J = 0.6$ Hz, 1H), 6.34 (t, $J = 2.4$ Hz, 4H), 6.72 (dt, $J = 3.6$ Hz, $J = 1.2$ Hz, 1H), 6.74−6.78 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 112.1, 112.2 (d, $J = 4$ Hz), 117.4, 122.7 (d, $J = 15$ Hz), 126.7, 129.8 (d, $J = 5$ Hz), 162.8. ^{31}P NMR (162 MHz, $CDCl_3$): δ 67.4. MS (+EI): *m*/*z* (%) 300 (0.7), 285 (0.9), 256 (4), 250 (6), 234 (100), 189 (43), 180 (84), 141 (70). HRMS (+EI): *m*/*z* found 300.11324 (calcd 300.11400). IR (KBr): 1590 (s), 1425 (s), 1187 (s), 1172 (s), 1153 (s), 1062 (s), 1033 (s), 737 (s) cm^{-1}.

Preparation of (2-*t*-Butylthiopyrrolyl)dipyrrolylphosphine (43 g). Procedure B. To a suspension of NaH (75 mg, 1.9 mmol, 60% in mineral oil) in THF (15 mL) at 0 °C under Ar was added 2-(*tert*-butylthio)pyrrole (**41d**, 0.26 g, 1.7 mmol) via syringe. After the reaction mixture was stirred at 23 °C for 2h, it was cooled to 0 °C and chlorodipyrrolylphosphine (**39**, 0.33 g, 1.7 mmol) was added slowly via syringe. Then the system was allowed to warm to 23 °C over 3 h. It was filtered through a silica gel plug, the filtrate was concentrated on a rotary evaporator, and the residue was purified by column chromatography on silica gel (4:1 hex:CH_2Cl_2) to give 370 mg (69% yield) of the phosphine **43g** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27(s, 9H), 6.32 (td, $J = 3$ Hz, $J = 0.6$ Hz, 1H), 6.35−6.38 (m, 4H), 6.40−6.43 (m, 1H), 6.53−6.56 (m, 1H), 6.72−6.76 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.7 (d, $J = 2$ Hz), 48.6, 113.1 (d, $J = 4$ Hz), 113.3, 122.9 (d, $J = 15$ Hz), 123.7, 124.8 (d, $J = 25$ Hz), 125.2 (d, $J = 4$ Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 72.3. MS (+EI): *m*/*z* (%) 317 (14), 261 (31), 194 (100), 161 (61), 132 (24). HRMS (+EI): *m*/*z* found 317.11110 (calcd 317.11155). IR (KBr): 3101 (w), 2961 (m), 2921 (w), 2896 (w), 2861 (w), 1454 (m), 1163 (s), 729 (s) cm^{-1}.

Characterization of (2-Methylcarboxypyrrolyl)dipyrrolylphosphine (43h). This was obtained (according to procedure B) from methyl pyrrole-2-carboxylate **41g** as a colorless oil that was taken up in hexane and cooled to 0 °C to yield white crystals, in 64% yield. Mp 80−81.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.79 (s, 3H), 6.02 (dt, $J^3_{HH} = 3$ Hz, $J^4_{HH} = J^4_{PH} = 1.8$ Hz, 1H), 6.28 (ddd, $J^3_{HH} = 3.9$ Hz, $J^3_{HH} = 3.0$ Hz, $J^4_{PH} = 0.3$ Hz, 1H), 6.39 (t, $J^3_{HH} = 2.1$ Hz, 4H), 6.78−6.81 (m, 4H), 7.09 (ddd, $J^3_{HH} = 4.8$ Hz, $J^3_{PH} = 2.7$ Hz, $J^4_{HH} = 1.2$ Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.1, 112.8, 113.1 (d, $J^3_{CP} = 4.6$ Hz), 113.3 (d, $J^3_{CP} = 4.6$ Hz), 121.0, 122.9 (d, $J^3_{CP} = 15$ Hz), 123.0. ^{31}P NMR (202 MHz, $CDCl_3$): δ 74.1. MS (+EI): *m*/*z* (%) 287 (M^+, 3.3), 221 (100), 189 (28), 143 (10), 128 (59). HRMS (+EI): *m*/*z* found 287.08236 (calcd 287.08236). IR (KBr, CH_2Cl_2): 1698 (s), 1540 (m), 1445 (s), 1432 (m), 1412 (m), 1344 (m), 1275 (s), 1161 (s), 1058 (s) cm^{-1}.

Characterization of (2-Diphenylphosphinopyrrollyl)dipyrrolylphosphine (43i). This was obtained (according to procedure B) from 2-diphenylphosphinopyrrole **41f** in 50% yield as a colorless oil which solidified at 0 °C. Mp 86−87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.10−6.12 (m, 1H), 6.31 (t, $J = 2$ Hz, 4H), 6.34 (t(br), $J = 3.2$ Hz, 1H), 6.64−6.67 (m, 1H), 6.67−6.70 (m, 4H), 7.24−7.34 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 113.4 (d, $J = 4.5$ Hz), 114.1, 122.9 (d, $J = 14$ Hz), 123.3 (d, 57 Hz), 126.6 (br), 128.9 (d, $J = 29$ Hz), 129.4, 133.8 (d, 78 Hz), 136.8 (t, $J = 25$ Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ −28.2 (d, $J = 340$ Hz), 76.0 (d, $J = 340$ Hz). MS (+EI): *m*/*z* (%) 413 (5.0), 347 (96), 251 (31), 172 (100). HRMS (+EI): *m*/*z* found 413.12137 (calcd 413.12107). IR (KBr): 3100 (m), 3053 (m), 1585 (m), 1453 (s), 1178 (s), 1057 (s), 735 (s) cm^{-1}.

Characterization of (2-(2′-Pyridino)pyrollyl)dipyrrolylphosphine (43j). This was obtained (according to procedure B) in 100% yield as a white solid that was further recrystallized from Et_2O. The solid turned yellow at 146 °C and turned into liquid between 171 and 178 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.84 (dt, $J = 3$ Hz, $J = 1.8$ Hz, 1H), 6.27−6.33 (m, 5H), 6.78−6.82 (m, 4H), 6.87−6.90 (m, 1H), 6.95−7.00 (m, 1H), 7.52−7.64 (m, 2H), 8.25−8.29 (m, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 112.0 (d, $J = 4$ MHz), 112.2, 118.2, 120.6, 122.8 (d, $J = 15$ Hz), 126.0 (d, 3 Hz), 136.3, 137.0, 145.9 (d, 2 Hz), 149.3. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 63.3. MS (+EI): *m*/*z* (%) 306 (3), 240 (100), 174 (88), 147 (63), 120 (75), 96 (49), 70 (63). HRMS (+EI): *m*/*z* found 306.10204 (calcd 306.10343). IR (KBr): 3139 (m), 3103 (w), 1592 (s), 1439 (s), 1154 (s), 1059 (s), 742 (s) cm^{-1}.

Preparative Example of the Standard Ligand Substitution Procedure. Preparation of η^6-Benzene(2-(methylthiopyrrolyl)dipyrrolylphosphine)dicarbonyl Chromium (0) (44a). (a) Preparation of η^2-Cyclooctenedicarbonyl Chromium(0). A 20-ml Schlenk tube, modified to have a flat bottom and equipped with a magnetic stirring bar, was charged with (benzene)tricarbonylchromium(0) (100 mg, 0.47 mmol), and the tube was placed under argon. Freshly distilled benzene (15 mL) was added via syringe followed by cyclooctene (3.0 mL, 23 mmol), and the resulting solution was irradiated using a standard 450-W medium-pressure Hanovia Hg lamp for 1 h while an argon was bubbled through the solution by means of a long needle.

(b) Exchange of the Phosphine for Cyclooctene. Upon completion of irradiation, (2-methylthiopyrrolyl)dipyrrolylphosphine (**43a**, 130 mg, 0.47 mmol) was added via syringe as a solution in benzene (5 mL) and stirred for 30 min. The resulting mixture was filtered through Celite, the solvent was removed on a rotary evaporator, and the resulting yellow oil was chromatographed on a silica gel column with hex:EtOAc 20:1. The yellow fractions were collected and the solvent evaporated in vacuo to yield 143 mg (66% yield) of a yellow solid (mp 147−148 °C dec). ^{1}H NMR (500 MHz, benzene-d_6): δ 1.92 (s, 3H), 4.41 (d, $J^3_{PH} = 2.4$ Hz, 6H), 5.73 (td, $J_1 = 2.8$ Hz, $J_2 = 1.6$ Hz, 1H), 6.03 (dt, $J_1 = 3.2$ Hz, $J_2 = 1.2$ Hz,1H), 6.23−6.28 (m, 5H), 6.88−6.92 (m,4H). ^{13}C NMR (125 MHz, benzene-d_6): δ 21.7, 111.8 (d, $J^3_{CP} = 4.5$ Hz), 112.7 (d, $J^3_{CP} = 5.9$ Hz), 118.9 (d, $J^3_{CP} = 3.2$ Hz), 124.6 (d, $J^2_{CP} = 6.6$ Hz), 130.5 (d, $J^2_{CP} = 9.8$ Hz), 236.2 (d, $J^2_{CP} = 27$ Hz). ^{31}P NMR (162 MHz, benzene-d_6): δ 173.5. MS (+FAB, nitrobenzyl alcohol): *m*/*z* (%) 461 (17), 395 (21), 355 (42), 327 (100), 307 (81), 289 (42). HRMS (+FAB) *m*/*z* found 461.0438 (calc 461.0419). IR (CH_2Cl_2 soln): 1055 (s), 1181 (s), 1444 (s), 1866 (s), 1925 (s), 2925 (m). X-ray determination: see Supporting Information.

Characterization of η^6-Benzene(2-(trifluoromethylthiopyrrolyl)-dipyrrolylphosphine) Dicarbonylchromium(0) (44b). Obtained as a yellow solid in 83% yield. It was recrystallized from CH_2Cl_2/Et_2O to give yellow crystals with mp 211−213 °C (dec). ^{1}H NMR (400 MHz, benzene-d_6): δ 4.26 (d, $J^3_{PH} = 2.4$ Hz, 6H), 5.87 (td, $J^3_{HH} = 3.2$ Hz, $J^4_{PH} = 1.6$ Hz, 1H), 5.91 (td, $J^3_{HH} = 3.6$ Hz, $J^4_{PH} = 1.2$ Hz, 1H), 6.20−6.24 (m, 4H), 6.66 (br s, 1H), 6.87−6.91 (m, 4H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 92.9, 112.7 (d, $J^3_{CP} = 6$ Hz), 124.4 (d, $J^2_{CP} = 7$ Hz), 125.3, 128.1 (q, $J^1_{CF} = 145$ Hz), 128.3, 130.5, 236.2 (d, $J^2_{CP} = 27$ Hz). ^{31}P NMR (162 MHz, benzene-d_6): δ 174.1. ^{19}F NMR (376 MHz): δ −43.7. MS (+EI): *m*/*z* (%) 515 (1.4), 459 (8), 409 (6), 381 (19), 279 (46), 228 (77), 163 (93). HRMS (+EI): *m*/*z* found 515.01058 (calcd 515.01363) IR (KBr): 1921 (s), 1868 (s), 1636 (s), 1175 (s), 1041 (s) cm^{-1}.

Characterization of η^6-Benzene(2-(phenylthiopyrrolyl)dipyrrolylphosphine) Dicarbonylchromium (0) (44c). This was obtained as a yellow solid in 65% yield. Mp 158−159 °C (dec). ^{1}H NMR (300 MHz, benzene-d_6): δ 4.30 (d, 2.4 Hz, 6H), 5.80 (td, $J = 3.3$ Hz, $J = 1.8$ Hz, 1H), 6.04 (td, $J = 3.3$ Hz, $J = 1.2$ Hz, 1H), 6.11−6.17 (m, 4H), 6.62−6.66 (m, 1H), 6.83−6.94 (m, 7H), 7.27−7.33 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 92.6, 112.0 (d, $J = 4$ Hz), 112.2 (d, $J = 6$ Hz), 123.3 (d, $J = 9$ Hz), 124.3 (d, $J = 6$ Hz), 125.7, 126.4, 126.7, 127.7, 129.3, 137.3, 236.5 (d, $J = 27$ Hz). ^{31}P NMR (162 MHz, benzene-d_6): δ 174.5. MS (+EI): *m*/*z* (%) 523(<1), 445(2), 389(15), 337 (45), 271 (15), 204 (32), 161 (63). HRMS (+FAB): *m*/*z* found 523.0561 (calcd 523.0575). IR (KBr): 1920 (s), 1859 (s), 1445 (m), 1171 (m), 1039 (m), 735 (s) cm^{-1}.

Characterization of η^6-Benzene(2-(*tert*-butylthiopyrrolyl)dipyrrolylphosphine) Dicarbonylchromium(0) (44g). This was obtained as a yellow solid in 86% yield. It was recrystallized from Et_2O to yield yellow crystals (decomposed without melting between 150 and 157 °C). ^{1}H NMR (400 MHz, benzene-d_6): δ 1.20 (s, 9H), 4.46

(d, 1.6 Hz, 6H), 5.92 (td, J = 3.6 Hz, J = 1.6 Hz, 1H), 6.06 (td, J = 3.2 Hz, J = 1.2 Hz, 1H), 6.24−6.26 (m, 4H), 6.43−6.46 (m, 1H), 6.95−6.98 (m, 4H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 31.7, 92.8, 111.7, 112.0 (d, J = 9 Hz), 121.1, 124.7 (d, J = 6 Hz), 125.2, 127.8 (d, J = 10 Hz), 236.9 (d, J = 27 Hz). ^{31}P NMR (162 MHz, benzene-d_6): δ 173.4. MS (+EI): m/z (%) 503 (1), 481 (8), 425 (7), 397 (39), 369 (64), 317 (72). HRMS (+EI): found 503.08984 (calcd 503.08884). IR (KBr): 2960 (m), 1923 (s), 1864 (s), 1458 (m), 1056 (s), 738 (s) cm^{-1}.

Characterization of η^6-Benzene(2-(methylthiomethylpyrrolyl)-dipyrrolylphosphine) Dicarbonylchromium(0) (44d). This was obtained as a yellow solid in 80% yield. It was recrystallized from Et_2O to yield yellow crystals (decomposed without melting at 157−160 °C). ^{1}H NMR (400 MHz, C_6D_6): δ 1.82 (s, 3H), 3.86 (s, 2H), 4.41 (d, J = 2.4 Hz, 6H), 5.74−5.76 (m, 1H), 6.06−6.09 (m, 1H), 6.21−6.23 (m, 4H) 6.60−6.62 (m, 1H), 6.93−6.96 (m, 4H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 16.8, 32.0, 93.0, 111.1, 112.6 (d, J = 6 Hz), 114.4, 123.0, 124.3 (d, J = 7 Hz), 133.9, 237.0 (d, J = 27 Hz). ^{31}P NMR (162 MHz, C_6D_6): δ 177.7. MS (+EI): m/z (%): 475 (0.3), 427 (7), 369 (19), 341 (91), 293 (69), 262 (71), 223 (43). HRMS (+EI): found 475.05873 (calcd 475.05754). IR (KBr): 3118 (w), 2905 (w), 1911 (s), 1854 (s), 1445 (m), 1179 (m), 1036 (m), 742 (s) cm^{-1}.

Characterization of η^6-Benzene(2-(phenylthiomethylpyrrolyl)-dipyrrolylphosphine) Dicarbonylchromium(0) (44e). This was obtained as a yellow solid in 55% yield. It was recrystallized from Et_2O to yield yellow crystals. Mp 164−165 °C (dec). ^{1}H NMR (400 MHz, C_6D_6): δ 4.37 (d, J = 2.4 Hz, 6H), 4.43 (s, 2H), 5.71−5.74 (m, 1H), 6.04−6.07 (m, 1H), 6.20−6.23 (m, 4H) 6.63−6.66 (m, 1H), 6.84−7.00 (m, 7H), 7.34−7.38 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 32.1 (d, J = 10 Hz), 92.0, 111.4 (d, J = 5 Hz), 113.2 (d, J = 6 Hz), 115.3 (d, J = 4 Hz), 123.2 (d, J = 3 Hz), 124.5 (d, J = 6 Hz), 126.7, 129.5, 129.6, 132.8 (d, J = 7 Hz), 137.5, 236.6 (d, J = 27 Hz). ^{31}P NMR (162 MHz, C_6D_6): δ 175.3. MS (+EI): m/z (%) 537 (0.5), 481 (0.5), 459 (45), 427 (70), 403 (100), 371 (55). HRMS (+FAB): m/z found 537.0739 (calcd 537.0732). IR (KBr): 3134 (w), 3098 (w), 1913 (s), 1858 (s), 1458 (m), 1174 (m), 1038 (m), 737 (s) cm^{-1}.

Characterization of η^6-Benzene((2-methylcarboxypyrrolyl)dipyrrolylphosphine) Dicarbonylchromium(0) (44h). This was obtained in 69% yield as a yellow solid which was further recrystallized from ether. Mp 146 °C (dec). ^{1}H NMR (300 MHz, benzene-d_6): δ 3.39 (s, 3H), 4.29 (d, J^3_{PH} = 2.4 Hz, 6H), 5.54 (ddd, 1H), 5.86 (dt, 1H), 6.21−6.26 (m, 4H), 6.85−6.91 (m, 4H), 7.20 (dt, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 52.2, 92.1, 111.4, 112.2 (d, 5.3 Hz), 123.6, 124.3 (d, 6.4 Hz), 128.1, 130.0, 160.7, 235.9 (d, 28 Hz). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 177.8. MS (+EI): m/z (%) 473 (M^+, 1.1), 445 (1.6), 424 (24), 417 (13), 367 (36), 339 (62), 221 (58). HRMS (+FAB): m/z found 473.0577 (calcd 473.0600). IR (CH_2Cl_2, KBr): 1917 (m), 1856 (m), 1708 (m), 1653 (m) cm^{-1}.

Characterization of η^6-Benzene(2-(*N*,*N*-Dimethylamidopyrrolyl)-dipyrrolylphosphine) Dicarbonylchromium(0) (44f). This was obtained in 88% yield as a yellow oil which crystallized from CH_2Cl_2/Hex to yield an orange solid. ^{1}H NMR (400 MHz, C_6D_6): δ 2.42 (s, 6H), 4.35 (d, J = 2.4 Hz, 6H), 6.02−6.05 (m, 1H), 6.06−6.09 (m, 1H), 6.14−6.18 (m, 4H), 6.90−6.95 (m, 4H), 6.98−7.02 (m, 1H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 93.5, 110.9, 111.7 (d, J = 5 Hz), 114.3, 124.5 (d, J = 6 Hz), 127.4 (d, J = 10 Hz), 131.1, 162.9, 237.2 (d, J = 28 Hz). IR (KBr): 1913 (s), 1855 (s), 1634 (s), 1456 (s), 1173 (s), 1055 (s), 734 (s) cm^{-1}. X-ray determination: see Supporting Information.

Characterization of η^6-Benzene((2-(2′-pyridino)pyrrolyl)dipyrrolyl) Phosphinedicarbonylchromium(0) (44j). This was obtained as an orange oil which solidified on storage at 0 °C. Rapid chromatography on a short silica gel column yielded **44i** in 59% yield (extended chromatography time led to significant decomposition of the product). Careful recrystallization from ether/hexane gave an orange solid that decomposed at 114 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 4.22 (d, J = 2.4 Hz, 6H), 5.62−5.66 (m, 1H), 6.07−6.10 (m, 1H), 6.22−6.24 (m, 4H), 6.39−6.43 (m, 1H), 6.70−6.80 (m, 1H), 6.93−6.98 (m, 5H), 7.07−7.10 (m, 1H), 8.53−8.55 (m, 1H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 92.3, 111.4, 111.7 (d, J = 5 Hz), 116.0, 120.9, 121.0, 124.6 (d, J = 5 Hz), 127.1, 136.6, 137.7, 148.2, 151.0, 236.8 (d, J = 26 Hz). ^{31}P NMR (162 MHz, C_6D_6): δ 175.9. MS (+FAB): m/z (%) 493 (12), 426 (30), 386 (16), 358 (97), 349 (20), 261 (92), 240 (100). HRMS (+FAB): (MH+) m/z found 493.0872 (calcd 493.0885). IR (KBr): 1914 (s), 1857 (s), 1586 (m), 1435 (m), 1183 (m), 1038 (m), 734 (m) cm^{-1}.

Attempted Formation of η^6-Benzene((2-diphenylphosphinopyrrolyl)dipyrrolylphosphine) Dicarbonylchromium(0) (44i). Characterization of Complex 49. The initial product was obtained as an orange solid (a mixture of PPh_2 and $PPyr_2$ bound ligand in about a 4:1 ratio by NMR). The PPh_2 bound complex **49** was purified by a careful crystallization from CH_2Cl_2/Et_2O as an orange solid; 46% yield. Mp 159−164 (dec). ^{1}H NMR (400 MHz, C_6D_6): δ 4.19 (d, J = 2 Hz, 6H), 6.14 (br s, 1H), 6.20 (t, J = 2 Hz, 4H), 6.48−6.52 (m, 5H), 6.88−7.05 (m, 7H), 7.78 (br t, J = 13 Hz, 4H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 91.0, 113.0, 113.2 (d, J = 5 Hz), 123.3 (d, J = 11 Hz), 125.6−126.0 (m), 128.5 (d, 9 Hz), 128.8 (br), 129.7, 132.8 (d, J = 11 Hz), 241.2 (d, 30 Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 70.6−71.2 (m), 77.7−78.3 (m). MS (+EI): m/z (%) 521 (<1), 465 (10), 398 (8), 347 (20), 269 (5). HRMS (+FAB): m/z found (MH^+) 600.1068 (calcd 600.1062). IR (KBr): 1889 (s), 1832 (s), 1453 (m), 1435 (m), 1176 (m), 1151 (m), 1057 (m), 733 (m) cm^{-1}.

Characterization of η^6-Fluorobenzene((2-phenylthiomethylpyrrolyl)dipyrrolylphosphine) Dicarbonylchromium(0) (50e). This was obtained as a yellow solid in 50% yield. It was recrystallized from Et_2O to yield yellow crystals. Mp 135−136 °C (dec). ^{1}H NMR (400 MHz, C_6D_6): δ 3.97−4.02 (m, 1H), 4.24−4.30 (m, 2H), 4.35−4.37 (br s, 2H), 4.46−4.52 (m, 2H) 5.73−5.76 (m, 1H), 6.02−6.06 (m, 1H), 6.17−6.21 (m, 4H), 6.62−6.65 (m, 1H), 6.84−7.00 (m, 7H), 7.32−7.37 (m, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 32.0, 80.1 (d, J = 20 Hz), 89.0, 92.1 (d, 7 Hz), 111.4 (d, J = 6 Hz), 113.0 (d, 6 Hz), 115.5 (d, 5 Hz), 123.6 (d, 5 Hz), 124.3 (d, 7 Hz), 127.0, 129.5, 129.9, 133.0, 136.8, 235.7 (d, 34 Hz). ^{19}F NMR (376 MHz, C_6D_6): δ −136.6. ^{31}P NMR (162 MHz, C_6D_6): δ 175.5. MS (+FAB): m/z (%) 578 (2), 527 (2), 489 (7), 403 (96), 367 (31), 175 (100). HRMS (+FAB): m/z found (MNa^+) 578.0533 (calcd 578.0535). IR (KBr): 3083 (w), 1925 (s), 1871 (s), 1457 (m), 1181 (m), 1053 (m), 737 (m) cm^{-1}.

Characterization of η^6-Fluorobenzene((2-methylthiopyrrolyl)-dipyrrolylphosphine) Dicarbonylchromium(0) (50e). This was obtained as a yellow solid in 66% yield. Mp 115 °C (dec). ^{1}H NMR (400 MHz, benzene-d_6): δ 1.90 (s, 3H), 3.95−4.00 (m, 1H), 4.30−4.36 (m, 2H), 4.47−4.53 (m, 2H), 5.73 (td, J_1 = 3.2 Hz, J_2 = 2 Hz, 1H), 6.02 (td, J_1 = 3.6 Hz, J_2 = 1.2 Hz, 1H), 6.21−6.27 (m, 5H), 6.86−6.91 (m, 4H). ^{19}F NMR (470 MHz, benzene-d_6): δ −137.2. ^{31}P NMR (202 MHz, benzene-d_6): δ 74.7. ^{13}C NMR (126 MHz, CD_2Cl_2): δ 21.5, 79.8 (d, 20 Hz), 89.0, 92.1, 112.1, 112.6, 118.2, 124.4, 130.6, 235.5 (d, 27 Hz). MS (+FAB) m/z (%) 480 (23), 413 (25), 355 (37), 327 (100), 215 (23). HRMS (+FAB): m/z found (MH^+) 480.0394 (calcd 480.0403). IR (KBr): 3054 (m), 2987 (m), 2305 (w), 1937 (s), 1880 (s), 1458 (s), 1265 (s), 736 (s) cm^{-1}.

Characterization of η^6-(*o*-Xylene)((2-methylcarboxypyrrolyl)-dipyrrolylphosphine) Dicarbonylchromium(0) (54b). This was obtained as a yellow solid in 93% yield. It was recrystallized from Et_2O to yield yellow crystals that turned orange at 124 °C and black at 140 °C. ^{1}H NMR (400 MHz, benzene-d_6): δ 1.65 (s, 6H), 3.40 (s, 3H), 4.27−4.37 (m, 4H), 5.68−5.72 (m, 1H), 5.89 (t, J = 2.8 Hz, 1H), 6.23−6.26 (m, 4H), 6.92−6.95 (m, 4H), 7.28 (dt, J = 3.6 Hz, J = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 19.06, 52.2, 91.9, 94.7, 105.7, 111.3, 112.0 (d, 5.7 Hz), 123.6, 124.2 (d, 6.1 Hz), 130.0, 160.5, 236.4 (d, 24 Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 176.5. MS (+EI): m/z (%) 501 (M^+, 0.1), 445 (5), 367 (1), 339 (16), 303 (6), 221 (89). HRMS (+EI): m/z found 501.09123 (calcd 501.09095). IR (CH_2Cl_2, KBr):

3129 (w), 3121 (w), 2953 (w), 1911 (m), 1849 (m), 1712 (m), 1146 (m), 734 (m) cm^{-1}.

Characterization of η^6-(*m*-Xylene)((2-methylcarboxypyrrolyl)-dipyrrolylphosphine) Dicarbonylchromium(0) (54c). This was obtained as a yellow solid in 97% yield. It was further recrystallized from Et_2O to yield yellow crystals that turned orange at 139 °C and then black at 149 °C. ^1H NMR (400 MHz, benzene-d_6): δ 1.72 (s, 6H), 3.39 (s, 3H), 4.08−4.14 (m, 3H), 4.37−4.43 (m, 1H), 5.56−5.60 (m, 1H), 5.89 (t, J = 3.6 Hz, 1H), 6.22−6.26 (m, 4H), 6.91−6.96 (m, 4H), 7.25−7.28 (m, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 20.8, 52.1, 90.9, 91.2, 94.2, 109.1, 111.2, 112.0 (d, 5.9 Hz), 123.7, 124.2 (d, 6.4 Hz), 128.0, 130.2, 160.6, 236.5 (d, 26 Hz). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 176.7. MS (+EI): *m*/*z* (%) 501 (M^+, 0.1), 445 (8), 367 (5), 339 (25), 287 (55), 221 (100). HRMS (+EI): *m*/*z* found 501.08905 (calcd 501.09095). IR (CH_2Cl_2, KBr): 1914 (m), 1850 (m), 1711 (m), 1147 (m), 732 (m) cm^{-1}.

Characterization of η^6-(*p*-Xylene)((2-methylcarboxypyrrolyl)-dipyrrolylphosphine) Dicarbonylchromium(0) (54d). This was obtained as a yellow solid in 99% yield. It was recrystallized from Et_2O to yield yellow crystals that turned orange at 125 °C and then brown at 133 °C followed by complete decomposition. ^1H NMR (400 MHz, benzene-d_6): δ 1.67 (s, 6H), 3.38 (s, 3H), 4.28 (d, J^3_{PH} = 3.2 Hz, 4H), 5.65−5.67 (m, 1H), 5.90 (t, J = 2.8 Hz, 1H), 6.22−6.25 (m, 4H), 6.94−6.97 (m, 4H), 7.27−7.30 (m, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 20.1, 52.1, 93.3, 106.5, 111.4, 111.9 (d, 5.7 Hz), 123.6, 124.2 (d, 6.6 Hz), 130.1, 160.5, 237.0 (d, 26 Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 176.8. MS (+EI): *m*/*z* (%) 501 (M^+, 0.1), 473 (3), 445 (20), 424 (40), 387 (12), 339 (40), 221 (100). HRMS (+EI): *m*/*z* found 501.08977 (calcd 501.09095). IR (CH_2Cl_2, KBr): 3126 (w), 2949 (w), 1918 (s), 1863 (s), 1724 (m), 1146 (m), 734 (m) cm^{-1}.

General Procedure for Monitoring Arene Exchange. In an NMR tube were put 1−5 mg of (arene)dicarbonyl((2-L-pyrrolyl)dipyrrolylphosphine)chromium(0) and 0.5−1.2 mL of the perdeuterated arene, and the solution was subjected to three freeze−pump−thaw cycles after which the tube was flame sealed under vacuum. The NMR probe was preheated to 40−70 °C, and the tube was inserted (actual probe temperature was assessed via calibration using an ethylene glycol standard). A series of ^1H NMR spectra were collected. Disappearance of the arene peak of the starting material and appearance of the new phosphine peaks of the product (when distinguishable from the starting material) were integrated. The logarithms of the arene areas were plotted vs time to yield a straight line from which half lifetime was calculated. In one case, the *product* of the reaction between η^6-benzene((2-methylcarboxypyrrolyl)dipyrrolylphosphine) dicarbonylchromium(0) (**44h**) and fluorobenzene-d_5 was analyzed by ^{19}F and ^{31}P NMR spectroscopy. Both spectra (^{19}F, δ −138.3 ppm; ^{31}P, δ 177.8 ppm) were consistent with the formation of the expected product η^6-fluorobenzene-((2-methylcarboxypyrrolyl)dipyrrolylphosphine) dicarbonylchromium-(0). From the kinetic plot it was evident that the equilibrium for this arene exchange reaction has been reached after 14 h at 50 °C. An estimate of an equilibrium constant (∼0.004) was made based on the ^1H NMR integrals of the species involved.

Preparative Scale Exchange Experiment. In a 100-mL flask equipped with a magnetic stirring bar was put η^6-fluorobenzene((2-methylthiopyrrolyl)dipyrrolylphosphine) dicarbonylchromiu m(0) (**50a**, 114 mg, 0.240 mmol), and the flask was placed under argon. Then 20 mL of freshly distilled benzene was added and the solution was heated to 60 °C for 3 h. The resulting yellow solution was cooled to room temperature, filtered through Celite, and the filtrate was concentrated on a rotary evaporator to yield yellow solid that was chromatographed on silica gel (hex:EtOAc 10:1) to yield η^6-benzene(2-(methylthiopyrrolyl)dipyrrolylphosphine) dicarbonylchromium(0) **(44a)** (100 mg, 94% yield, pure by ^1H NMR).

Acknowledgment. We wish to thank Drs. Istvan Pelczer and Carlos Pacheco for assistance with the NMR studies, Dr. Dorothy Little for mass spectrometry service, Professor R. Pascal for helpful discussions, and the Bristol-Myers Squibb Company for a graduate fellowship to A.C.

Supporting Information Available: Reproductions of the ^1H NMR and ^{13}C NMR spectra for new compounds studied in this work. CIF files for the X-ray diffraction structure determination. This material is available free of charge via the Internet at http://pubs.acs.org.

JA042705X