*Journal of Organometallic Chemistry*, 165 (1979) 225—231

# THE CHEMISTRY OF CHROMARENES: ORGANIC DERIVATIVES OF 1,2,3,4,5-PENTAFLUORO- AND 1,2,4,5-TETRAFLUORO-CHROMARENE

NGUYEN HAO and MICHAEL J. McGLINCHEY *

*Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1 (Canada)*

(Received July 5th, 1978)

## Summary

$(C_6F_5Li)Cr(C_6H_6)$ can be converted into $(C_6F_5X)Cr(C_6H_6)$, where X is CHO, $CH(OH)CH_3$, $COCH_3$ or $CO_2C_2H_5$. The dilithio derivative $(C_6F_4Li_2)Cr(C_6H_6)$ forms a stable di-ester, but the bis(trimethylsilyl) derivative is very labile. Attempts to synthesise chromarenes with alkenyl substitutents are described.

---

## Introduction

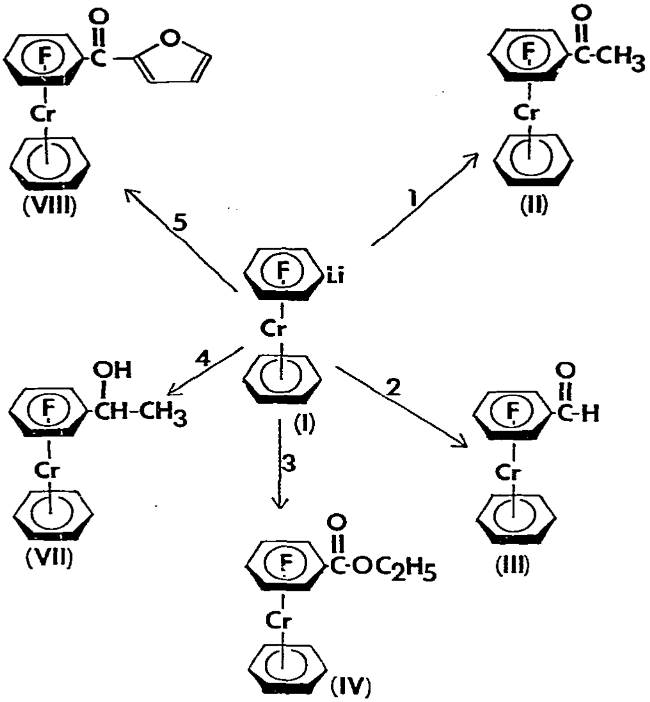
The burgeoning use of metal vapors in synthesis [1—4] has provided convenient routes to otherwise inaccessible organometallic systems. In particular, the chromarene [5] system, whose chemistry at one time seemed to be somewhat restricted, has recently been shown to be readily functionalisable. We now report the syntheses of some simple organic derivatives of 1,2,3,4,5-pentafluoro- and 1,2,4,5-tetrafluorochromarene.

## Discussion

The $pK_a$ values of substituted benzoic acid chromium tricarbonyls [6] and of ferrocene carboxylic acids [7] have been extremely useful indicators of the type of reactivity to be expected for these now almost ubiquitous systems. However, these data are not yet available for the chromarene series and, although we have not yet obtained a chromarenoic acid, we now report the incorporation of a variety of substituents which may eventually lead us to our target.

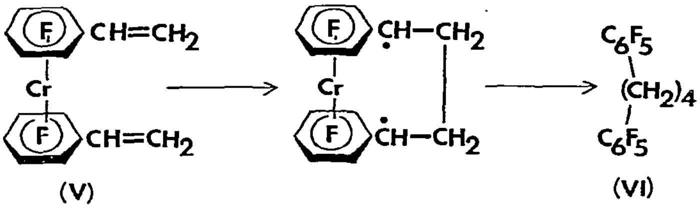
Previous attempts [5] to prepare 2,3,4,5,6-pentafluorochromarenoic acid via the carbonation of the analogous lithiochromarene (I) have been unsuccessful. Some of the more obvious alternate routes which might be viable include, (a) the haloform reaction on the methyl ketone (II), (b) oxidation of the corresponding aldehyde (III), or (c) hydrolysis of an appropriate ester (IV). Reaction of acetyl chloride with I might have been expected to give respectable yields of methyl ketone II, but in fact the desired product was obtained only in small quantities. (The analogous furoyl compound is, however, readily prepared by this route and is discussed below). The reaction of I with ethyl formate gave the corresponding aldehyde (III) while treatment with ethyl chloroformate led to a good yield of ethyl pentafluorochromarenoate (IV) (see Scheme 1). It is to be hoped that, given mild enough conditions, 2,3,4,5,6-pentafluorochromarenoic acid may be obtained from one of these precursors.

SCHEME 1. Reactions of $(C_6F_5Li)Cr(C_6H_6)$ (I). 1. $CH_3COCl$, 2. $HCOC_2H_5$, 3. $ClCO_2C_2H_5$, 4. $CH_3CHO$, 5. $C_4H_3OCOCl$.

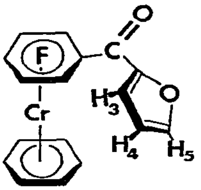


With a view to incorporating unsaturated moieties in the sidechains of chromarenes, a mixture of benzene and pentafluorostyrene was cocondensed with chromium vapor. The only volatile product isolated after removal of the starting materials was identified by mass and NMR spectroscopy as 1,4-bis(pentafluorophenyl)butane (VI). Pentafluorostyrene is known to polymerize [8], albeit less readily than styrene itself, but the product isolated from the cocondensation reaction has not apparently been reported previously. Blank reactions, using the normal cocondensation conditions but with no metal in the crucible gave no VI; likewise, VI was not produced when nickel vapor was used. A possible rationale involves the initial formation of an unstable bis(pentafluorostyrene)chromium complex (V), which then undergoes ligand coupling (see Scheme 2) in a manner analogous to that previously observed for iron vapor and dimethylfulvene [9]. Subsequent hydrogen abstraction from the excess unreacted arenes could then lead to the observed product.

SCHEME 2. Coupling of pentafluorostyrene on a chromium template.



An alternate route to 1-vinyl-2,3,4,5,6-pentafluorochromarene which appeared viable was the dehydration of the appropriate alcohol (VII). Indeed, reaction of the lithiochromarene (I) with acetaldehyde gave the desired alcohol (VII) in good yield, but our attempts to dehydrate the sidechain without thereby destroying the complex have so far been unsuccessful. Furthermore, reaction of I with allyl bromide did not yield a chromarene with an unsaturated sidechain but instead gave a number of products which are still under investigation. A more successful approach was the synthesis of the furoylchromarene (VIII) from the lithio derivative (I) and furoyl chloride. Interestingly, the $^1H$ NMR spectrum of complex VIII showed the absorptions of the furan ring protons to be displaced considerably upfield of their normal resonance positions. We interpret this to mean that the furan is positioned proximate to the chromium atom whose magnetic anisotropy leads to a marked shielding of the furan protons.



The recent synthesis [5] of 1,2,4,5-tetrafluorochromarene opened up the possibility of incorporating two functionalities into the same ring of the sandwich compound. This would require that both protons in the fluorinated ring be readily lithiated as in IX; we find that a three-fold excess of t-butyllithium is required to ensure di-lithiation of 1,2,4,5-tetrafluorochromarene and this is readily confirmed mass spectrometrically after quenching with $D_2O$. Analogously, reaction of an excess of ethyl chloroformate with IX gave good yields of the very air-stable diester X. In contrast, chlorotrimethylsilane gave only traces of the mono-silylated chromarene XI, while the major product was 1,4-bis(trimethylsilyl)-2,3,5,6-tetrafluorobenzene which was readily identified by comparison with the literature data [16]. Apparently, the bis(trimethylsilyl)-tetrafluorochromarene must have dissociated and liberated the parent arene.

It has been noted by ourselves [5,10—12] and by others [13—15] that the oxidative stability of halogenated chromarenes is highly dependent on the electronic properties of the arene substituents. In particular, electro-negative substituents which reduce the $\pi$-basicity of the arene concomitantly retard the oxidation of the formally zero-valent chromium and thus enhance its kinetic rather than its thermodynamic stability. Consequently, the introduction of two electron-releasing trimethylsilyl moieties is apparently not compatible with a kinetically stable fluorochromarene.

Clearly, to produce a stable chromarene, one requires a rather delicate balance of these electronic factors and, pragmatically, one can use Hammett substituent parameters as a guide to the probable stability of a given chromarene [17].

## Experimental

NMR spectra were recorded on a Bruker WH90 spectrometer operating in the FT mode at 90 MHz using tetramethylsilane as the internal reference. Infrared spectra were recorded on a Perkin—Elmer 337 grating spectrometer, and mass spectra were obtained on a C.E.C. 21-110-B spectrometer. Melting points are uncorrected. Elementary analyses were performed by Gygli Microanalysis Laboratory, Toronto.

### *1-Lithio-2,3,4,5,6-pentafluorochromarene, I*

$(C_6F_5Li)Cr(C_6H_6)$ was prepared by the lithiation of $(C_6F_5H)Cr(C_6H_6)$ as described previously [5].

### *Reactions of I with various reagents*

(*a*) *Acetyl chloride.* To a solution of I (0.335 mmol) in ether was added a very slight excess of acetyl chloride at —78° C under a nitrogen atmosphere. The solution was stirred at —78° C for 1 h, by which time the initially red-brown solution had turned yellow. The solution was allowed to warm to room temperature, filtered under nitrogen and the solvent and excess $CH_3COCl$ removed in vacuo. The product was purified by sublimation at 50° C/$10^{-2}$ mmHg to give yellow, air-stable 1-acetyl-2,3,4,5,6-pentafluorochromarene (II) (23 mg, 0.068 mmol; 20%), m.p. 92° C, whose IR spectrum showed $\nu$(CO) at 1741 $cm^{-1}$. Mass spectral data: *m/e* 340, $C_{14}H_9F_5CrO^+$ (12); 325, $C_{13}H_5F_5CrO^+$ (2.5); 298, $C_{12}H_7F_5Cr^+$ (45); 262, $C_8H_3F_5CrO^+$ (14); 168, $C_6F_5H^+$ (23); 149, $C_6F_4H^+$ (40); 130, $C_6H_6Cr^+$ (100); 78, $C_6H_6^+$ (65); 52, $Cr^+$ (63). Anal. Found: C, 49.5; H, 2.6. $C_{14}H_9F_5CrO$ calcd: C, 49.4; H, 2.6%.

(*b*) *Ethyl formate.* To a solution of I (0.335 mmol) in ether was added ethyl formate (0.40 mmol) in ether at —78° C under a nitrogen atmosphere. The red-brown solution gradually became yellow and, after stirring for 1 h at —78° C it was allowed to warm to room temperature and filtered under nitrogen. Ether and excess ethyl formate were removed in vacuo and the residue sublimed at 45° C/$10^{-2}$ mmHg to give yellow, air-stable 1-formyl-2,3,4,5,6-pentafluorochromarene (III) (33 mg, 0.101 mmol; 30%), m.p. 85° C (decomposes) whose IR spectrum showed $\nu$(CO) at 1680 $cm^{-1}$. Mass spectral data: *m/e* 326, $C_{13}H_7F_5CrO^+$ (10); 298, $C_{12}H_7F_5Cr^+$ (35); 248, $C_7HF_5CrO^+$ (8); 168, $C_6F_5H^+$ (40); 149, $C_6F_4H^+$ (55); 130, $C_6H_6Cr^+$ (70); 78, $C_6H_6^+$ (53); 52, $Cr^+$ (100). Anal. Found: C, 47.7; H, 2.0. $C_{13}H_7F_5CrO$ calcd: C, 47.8; H, 2.1%.

(*c*) *Ethyl chloroformate.* To a solution of I (0.335 mmol) in ether was added ethyl chloroformate (0.40 mmol) in ether at —78° C under a nitrogen atmosphere. The initially red-brown solution was stirred at —78° C for 30 min and then slowly allowed to warm to room temperature by which time the solution had become orange-yellow. After filtration under nitrogen and removal of ether and excess ethyl chloroformate in vacuo, the residue was sublimed at 50—60° C/10$^{-2}$ mmHg to give orange, air-stable ethyl 2,3,4,5,6-pentafluorochromarenoate (IV) (99 mg, 0.268 mmol; 80%), m.p. 92—95° C, showing $\nu$(CO) at 1725 cm$^{-1}$. The $^1$H NMR spectrum in $C_6D_6$ exhibited a multiplet at $\delta$ (ppm) 4.63 (6H), a quartet at $\delta$ 4.22 (2H) and a triplet at $\delta$ 1.10 (3H). Mass spectral data: *m/e* 370, $C_{15}H_{11}F_5CrO_2^+$ (25); 325, $C_{13}H_6F_5CrO^+$ (3); 298, $C_{12}H_7F_5Cr^+$ (27); 292, $C_9H_5F_5CrO_2^+$ (11); 264, $C_8H_5F_5CrO^+$ (8.5); 168, $C_6F_5H^+$ (14); 149, $C_6F_4H^+$ (58); 130, $C_6H_6Cr^+$ (100); 111, $C_6F_2H^+$ (42); 78, $C_6H_6^+$ (45); 52, $Cr^+$ (61). Anal. Found: C, 48.8; H, 3.0. $C_{15}H_{11}F_5CrO_2$ calcd: C, 48.6; H, 3.0%.

*(d) Furoyl chloride.* To a solution of I (0.335 mmol) in ether was added furoyl chloride (0.40 mmol) in ether at —78° C under nitrogen atmosphere. The red-brown solution turned yellow-brown after stirring at —78° C for 45 min and was then allowed to warm to room temperature and was stirred for another hour. After filtering under nitrogen and removal of solvent and excess furoyl chloride in vacuo, the product was sublimed at 55—60° C/10$^{-2}$ mmHg to give yellow-brown, air stable 1-furoyl-2,3,4,5,6-pentafluorochromarene (VIII) (98 mg, 0.25 mmol; 75%), m.p. 100° C, which exhibited $\nu$(CO) at 1648 cm$^{-1}$. The $^1$H NMR spectrum in $C_6D_6$ showed a doublet (1.7 Hz) of doublets (<1.0 Hz) at $\delta$ 6.92 ($H_5$), a doublet (3.7 Hz) of doublets (<1.0 Hz) at $\delta$ 6.88 ($H_3$), a doublet (3.7 Hz) of doublets (1.7 Hz) at $\delta$ 5.91 ($H_4$), and a multiplet at $\delta$ 4.80 (6H). Mass spectral data: *m/e* 392, $C_{17}H_9F_5CrO_2^+$ (40); 314, $C_{11}H_3F_5CrO_2^+$ (100); 298, $C_{12}H_7F_5Cr^+$ (10); 262, $C_{11}H_3F_5O_2^+$ (27); 244, $C_{11}HF_5O^+$ (8); 196, $C_7HF_5O^+$ (21); 177, $C_7HF_4O^+$ (15); 168, $C_6F_5H^+$ (12); 149, $C_6F_4H^+$ (20); 130, $C_6H_6Cr^+$ (62); 78, $C_6H_6^+$ (57); 52, $Cr^+$ (61). Anal. Found: C, 52.4; H, 2.6. $C_{17}H_9F_5CrO_2$ calcd: C, 52.0; H, 2.3%.

*(e) Acetaldehyde.* To a solution of I (0.335 mmol) in ether was added acetaldehyde (0.4 mmol) in ether at —78° C under a nitrogen atmosphere and the red-brown solution rapidly turned yellow. The solution was stirred at —78° C for 1 h, allowed to warm to room temperature and acidified with dilute HCl. After filtration, the solvent and excess acetaldehyde were removed in vacuo and the product sublimed at 30° C/10$^{-2}$ mmHg to give yellow 1-(2,3,4,5,6-pentafluorochromarenyl)ethanol (VII) (91 mg, 0.266 mmol; 80%), m.p. 52—55° C. The product is stable in air for about 1—2 days, and shows $\nu$(OH) at 3400 cm$^{-1}$. Mass spectral data: *m/e* 342, $C_{14}H_{11}F_5CrO^+$ (35); 324, $C_{14}H_9F_5Cr^+$ (6); 264, $C_8H_5F_5CrO^+$ (16); 246, $C_8H_3F_5Cr^+$ (3); 212, $C_8H_5F_5O^+$ (2); 196, $C_7HF_5O^+$ (11); 149, $C_6F_4H^+$ (32); 130, $C_6H_6Cr^+$ (100); 78, $C_6H_6^+$ (80); 52, $Cr^+$ (71). Anal. Found: C, 48.8; H, 3.1. $C_{14}H_{11}F_5CrO^+$ calcd.: C, 49.1; H, 3.2%.

### *Reaction of chromium vapor with benzene and pentafluorostyrene*

Chromium vapor and 50 ml of a 60/40 v/v mixture of pentafluorostyrene and benzene were cocondensed over a 1 h period in the apparatus previously described [11]. Removal of unreacted benzene and pentafluorostyrene and subsequent heating of the residue using a water bath at 60—70° C gave a white material (VI), which sublimed onto the water-cooled surface of the reaction apparatus. The air-stable product, m.p. 65° C, exhibited two $^1$H NMR peaks of equal area at $\delta$ 2.73 (triplet) and $\delta$ 1.63 (quintet). Mass spectral data: *m/e* 390, $C_{16}F_{10}H_8^+$ (40); 372, $C_{16}F_9H_9^+$ (30); 222, $C_{10}F_5H_7^+$ (8); 207, $C_9F_5H_4^+$ (25); 194,

$C_8F_5H_3^+$ (60); 181, $C_7F_5H_2^+$ (100); 176, $C_8F_4H_4^+$ (52); 167, $C_6F_5^+$ (25); 162, $C_7F_4H_2^+$ (63); 150, $C_6F_4H_2^+$ (23); 143, $C_7H_2F_3^+$ (45); 131, $C_3F_5^+$ (20).

### *Lithiation of (p-$C_6F_4H_2$)Cr($C_6H_6$)*

1,2,4,5-Tetrafluorochromarene (100 mg, 0.357 mmol), prepared as described previously [5], was dissolved in 60 ml sodium-dried diethyl ether and 40 ml THF. The solution was flushed with dry nitrogen for 20 min, cooled to —78° C and treated with t-butyllithium (1.80 mmol) in hexane. The initially pale-red solution became red-brown, indicative of the formation of the dilithio derivative IX.

### *Reactions of IX with various reagents*

*(a) Deuterium oxide.* Addition of excess $D_2O$ to a solution of IX at —78° C, followed by stirring for 1 h and gradual warming to room temperature produced a pale-orange solution. Removal of solvent and excess $D_2O$ in vacuo followed by sublimation at 35° C/$10^{-2}$ mmHg returned the tetrafluorochromarene essentially quantitatively. Mass spectral data: *m/e* 282, $C_{12}D_2H_6F_4Cr^+$ (45); 281, $C_{12}DH_7F_4Cr^+$ (35); 263, $C_{12}D_2H_6F_3Cr^+$ (12); 262, $C_{12}DH_7F_3Cr^+$ (8); 152, $C_6F_4D_2^+$ (30); 151, $C_{12}F_4HD^+$ (28); 150, $C_6F_4D^+$, $C_6F_4H_2^+$ (15); 149, $C_6F_4H^+$ (8); 133, $C_6F_3D_2^+$ (20); 132, $C_6F_3DH^+$ (22); 131, $C_6F_3D^+$, $C_6F_3H_2^+$ (30); 130, $C_6H_6Cr^+$ (100); 78, $C_6H_6^+$ (86); 52, $Cr^+$ (72). An increased ratio of t-BuLi: ($C_6F_4H_2$)Cr($C_6H_6$) gave an increased percentage of the di-deuterated chromarene.

*(b) Ethyl chloroformate.* To a solution of IX (0.357 mmol) in ether was added ethyl chloroformate (0.80 mmol) at —78°C under nitrogen atmosphere. After stirring for 1 h at —78° C the red-brown solution had turned brown-yellow. The solution was allowed to warm to room temperature, filtered, and the solvent and excess ethyl chloroformate removed in vacuo. The product was sublimed at 90° C/$10^{-2}$ mmHg to give, by mass spectrometry, a mixture of mono- and di-ester which showed $^1$H NMR peaks in $C_6D_6$ at $\delta$ 4.73 and $\delta$ 4.55, in the ratio 2.2/1, and also a quartet at $\delta$ 4.27 and a triplet at $\delta$ 1.14. The monoester (approximately 30% yield) decomposed in air in about 2 days while the diester, which was purified by resublimation, is remarkably air-stable. Thus, 1,4-bis(carbethoxy)-2,3,5,6-tetrafluorochromarene (X), m.p. 105° C, exhibiting $\nu$(CO) at 1720 cm$^{-1}$ was obtained in 65% yield. Mass spectral data: *m/e* 424, $C_{18}H_{16}F_4CrO_4^+$ (40); 386, $C_{18}H_{16}F_2CrO_4^+$ (6); 379, $C_{16}H_{11}F_4CrO_3^+$ (10); 351, $C_{15}H_{11}F_4CrO_2^+$ (2); 346, $C_{12}H_{10}F_4CrO_4^+$ (77); 318, $C_{10}H_6F_4CrO_4^+$ (50); 290, $C_9H_6F_4CrO_3^+$ (12); 274, $C_9H_6F_4CrO_2^+$ (4); 246, $C_7H_2F_4CrO_2^+$ (2); 157, $C_7H_3F_2O_2^+$ (6); 149, $C_6F_4H^+$ (50); 130, $C_6H_6Cr^+$ (100); 78, $C_6H_6^+$ (71); 52, $Cr^+$ (63). Anal. Found: C, 51.0 H, 3.8. $C_{18}H_{16}F_4CrO_4$ calcd.: C, 50.9; H, 3.8%.

*(c) Chlorotrimethylsilane.* To a solution of IX (0.357 mmol) in ether was added $Me_3SiCl$ (0.80 mmol) at —78° C under a nitrogen atmosphere. After stirring at —78° C for 30 min and for 1 h at room temperature, the now orange solution was filtered and the solvent and excess chlorotrimethylsilane removed in vacuo. Fractional sublimation gave the known [16] 1,4-bis(trimethylsilyl)-2,3,5,6-tetrafluorobenzene and traces of 1,2,4,5-tetrafluoro-3-trimethylsilylchromarene (XI) identified mass spectrometrically. Mass spectral data: *m/e* 352, $C_{15}H_{16}F_4CrSi^+$ (6); 280, $C_{12}F_4H_2Cr^+$ (40); 274, $C_9H_{10}F_4CrSi^+$ (8); 261,

$C_{12}H_2F_3Cr^+$ (13); 149, $C_6F_4H^+$ (50); 130, $C_6H_6Cr^+$ (100); 78 $C_6H_6^+$ (80); 73, $C_3H_9Si^+$ (40); 52, $Cr^+$ (50).

## Acknowledgement

We thank the National Research Council of Canada for financial support.

## References

1 P.L. Timms in G.A. Ozin and M. Moskovits (Eds.), Cryochemistry, John Wiley, New York, 1976 p. 61—136.
2 M.J. McGlinchey and P.S. Skell in ref. 1., p. 137—194.
3 K.J. Klabunde, Accounts Chem. Res., 8 (1975) 383.
4 Merck Symposium Proceedings, Metal Atoms in Chemical Synthesis, Angew. Chem., Int. Ed. Engl., 14 (1975) 193—222; 273—321.
5 A. Agarwal, M.J. McGlinchey and T.-S. Tan, J. Organometal. Chem., 141 (1977) 85.
6 B. Nicholls and M.C. Whiting, J. Chem. Soc., (1959) 551.
7 J. Tirouflet, E. Laviron, R Dabard and J. Komenda, Bull. Soc. Chim. France, (1963) 857.
8 W.A. Pryor, M Iino and G R. Newkome, J Amer. Chem. Soc., 99 (1977) 6003.
9 T.-S. Tan, J.L Fletcher and M.J McGlinchey, J. Chem. Soc., Chem. Commun., (1975) 771.
10 P.S. Skell, D.L. Williams-Smith and M.J. McGlinchey, J. Amer. Chem. Soc., 95 (1973) 3337.
11 M.J. McGlinchey and T.-S. Tan, Can. J. Chem., 52 (1974) 2439.
12 M.J. McGlinchey and T.-S Tan, J Amer. Chem. Soc., 98 (1976) 2271.
13 R. Middleton, J.R. Hull, S.R. Simpson, C.H. Tomlinson and P.L. Timms, J. Chem. Soc., Dalton Trans., (1973) 120.
14 K.J. Klabunde and H.F. Efner, Inorg. Chem., 14 (1975) 789.
15 V. Graves and J.J. Lagowski, Inorg. Chem., 15 (1976) 577.
16 F.W.G. Gearon and H. Gilman, J. Organometal. Chem., 10 (1967) 535.
17 M.J. McGlinchey and N. Hao, J. Organometal. Chem., in press.