

Reaction of ($\eta^6:\eta^6$ -Biphenyl)bis(tricarbonylchromium) with Nucleophiles. A Selective Method for the Preparation of Substituted Biphenyls

Reuben D. Rieke* and Khushroo P. Daruwala

Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0304

Received October 26, 1987

Nucleophilic addition of α -nitrile carbanions to ($\eta^6:\eta^6$ -biphenyl)bis(tricarbonylchromium) takes place in a highly stereoselective and regioselective manner. The organometallic intermediate obtained in the addition has been characterized by means of ^{13}C NMR spectroscopy. Depending upon the type of nucleophile used, oxidation of these intermediates with iodine results in the formation of 2- and 4-substituted biphenyls. Oxidation of the intermediate with trifluoroacetic acid results in the formation of phenyl conjugated dienes.

Introduction

The investigation of the reactivity of arene metal complexes with nucleophiles has been well developed by Semmelhack and his co-workers.¹ It was demonstrated that the addition of nucleophiles to (η^6 -benzene)tricarbonylchromium produces a stable (η^5 -cyclohexadienyl)chromium complex.¹ Oxidation of this complex causes loss of the metal and an endo hydrogen atom, thus resulting in an overall nucleophilic substitution for hydrogen.

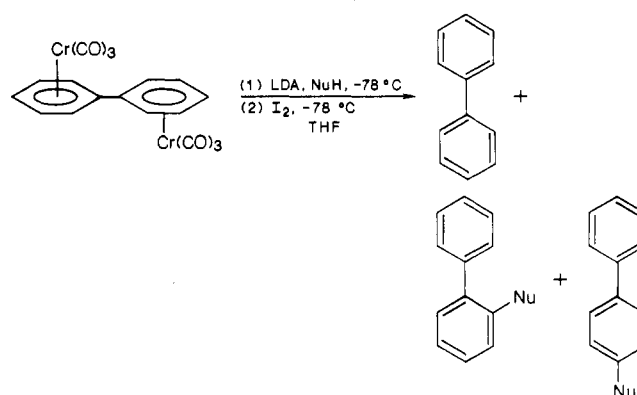
The electrochemistry of (arene)tricarbonylchromium complexes of arene compounds has been studied by several groups.^{2,3} In marked contrast to the monocomplexes, the bis(tricarbonylchromium) complexes of arene compounds with two conjugated phenyl rings reduced electrochemically or chemically in a two-electron ECE process to yield very stable dianions.⁴ These dianions were then trapped with various alkyl halides to give alkylated complexes, which, upon reoxidation with iodine, resulted in high yields of alkylated biphenyls.⁵

In a continuation of the study of the chemistry of ($\eta^6:\eta^6$ -biphenyl)bis(tricarbonylchromium), we were interested in exploring the role of the bis complex as a potential electrophile and in seeing whether Semmelhack's chemistry of the addition of nucleophiles to (η^6 -benzene)tricarbonylchromium complexes could be extended to the bis(tricarbonylchromium) complexes of biphenyl.

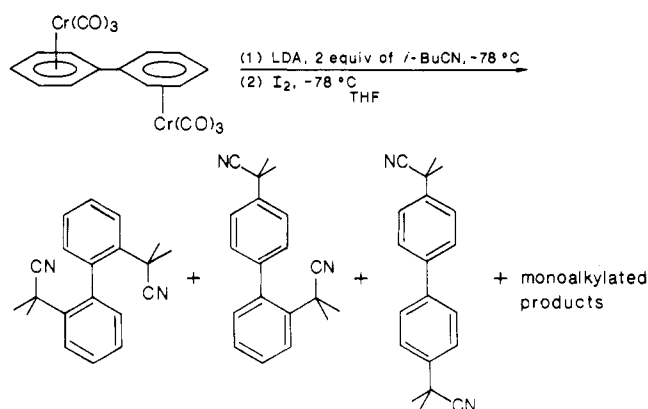
Results and Discussion

The preparation of ($\eta^6:\eta^6$ -biphenyl)bis(tricarbonylchromium) was carried out by standard methods.^{3b} Re-

Scheme I



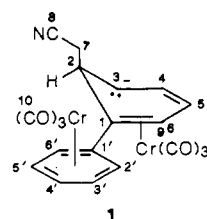
Scheme II



action of the bis complex with various nucleophiles at -78°C , followed by oxidation of chromium tricarbonyl with iodine, resulted in the formation of substituted biphenyls (Scheme I and II).

Using a procedure similar to that of Semmelhack,^{1b} the results of the addition of various nucleophiles to ($\eta^6:\eta^6$ -biphenyl)bis(tricarbonylchromium) are shown in Table I.

In order to prove the structure of the intermediate (structure 1), the ($\eta^6:\eta^6$ -biphenyl)($\text{Cr}(\text{CO})_3$)₂ was reacted with 1 equiv of acetonitrile anion and the reaction monitored by ^{13}C NMR (Table II). Addition of the solution of the bis complex in THF-*d*₃ to the acetonitrile anion solution resulted in an instantaneous color change from orange to dark brown.



(1) (a) Semmelhack, M. F.; Hall, H. T. *J. Am. Chem. Soc.* 1974, 96, 7091. (b) Semmelhack, M. F.; Hall, H. T. *J. Am. Chem. Soc.* 1974, 96, 7092. (c) Semmelhack, M. F. *J. Organomet. Chem. Libr.* 1976, 1, 361. (d) Semmelhack, M. F.; Yoshifuji, M.; Clark, G. *J. Am. Chem. Soc.* 1977, 99, 6387. (e) Semmelhack, M. F.; Clark, G. *J. Am. Chem. Soc.* 1977, 99, 1675. (f) Semmelhack, M. F.; Harrison, J. J.; Thebtaronth, Y. *J. Org. Chem.* 1979, 44, 3275. (g) Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Thebtaronth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* 1981, 37, 3957. (h) Semmelhack, M. F.; Hall, H. T.; Farina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* 1979, 101, 3535.

(2) (a) Cecon, A.; Coroaja, C.; Giacometti, G.; Venzo, A. *J. Chim. Phys.* 1975, 72, 23. (b) Cecon, A.; Coroaja, C.; Giacometti, G.; Venzo, A. *J. Chem. Soc., Perkin Trans. 2* 1978, 283. (c) Khandkarova, V. S.; Gubin, S. P. *J. Organomet. Chem.* 1970, 22, 149. (d) Gubin, S. P. *Pure Appl. Chem.* 1970, 23, 463. (e) Howel, J. O.; Goncalves, J. M.; Amatore, G.; Klasine, L.; Wrightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* 1984, 106, 3968. (f) Degrand, G.; Radecki-Sudre, A. *J. Organomet. Chem.* 1984, 268, 63.

(3) (a) Rieke, R. D.; Milligan, S. N.; Tucker, I.; Dowler, K. A.; Willeford, B. R. *J. Organomet. Chem.* 1981, 218, C25. (b) Rieke, R. D.; Tucker, I.; Milligan, S. N.; Wright, D. R.; Willeford, B. R.; Radonovich, L. J.; Eyring, M. W. *Organometallics* 1982, 1, 938. (c) Milligan, S. N.; Rieke, R. D. *Organometallics* 1983, 2, 171. (d) Rieke, R. D.; Arney, J. S.; Rich, W. E.; Willeford, B. R.; Poliner, B. S. *J. Am. Chem. Soc.* 1975, 97, 5951. (e) Henry, W. P.; Rieke, R. D. *J. Am. Chem. Soc.* 1983, 105, 6314. (f) Milligan, S. N.; Tucker, I.; Rieke, R. D. *Inorg. Chem.* 1983, 22, 987. (g) Rieke, R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* 1987, 26, 420.

(4) Rieke, R. D.; Milligan, S. N.; Schulte, L. D. *Organometallics* 1987, 6, 699.

(5) Schulte, L. D.; Rieke, R. D. *J. Org. Chem.* 1987, 52, 4827.

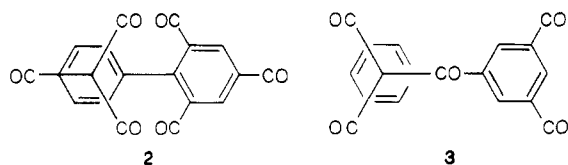
Table I. Reaction of (η^6 : η^6 -Biphenyl)[Cr(CO)₃]₂ with Nucleophiles Followed by Oxidation with Iodine

nucleophile	no. of equiv	product distribution			
		biphenyl	ortho	para	di
H ₃ CCN	2.0	8	69		
	1.0	68	32		
H ₃ CCH ₂ CN	2.0	20	41 ^a		
	1.5	36	27 ^a		
	1.0	67	11 ^a		
	2.0	12	9 ^a		33 ^b
H ₃ CCH ₂ CH ₂ CN	1.5	8	50 ^a		
	1.0	23	34 ^a		
H ₃ CCH(CH ₃)CN	2.0	00	13	12	70 ^c
	1.5	10	20	59	
	1.0	7	15	50	
	1.0 ^d	7	13	41	
	1.0 ^e	43	9	31	

^a Minor amounts of unidentifiable byproducts were also formed.

^b Three peaks observed by GC were identified by mass spectrometry as products of dialkylation. Mass spectrum of the mixture, *m/e* (relative intensity) 288 (M⁺, 49), 273 (5), 259 (100), 230 (20); calcd for C₂₀H₂₀N₂ 288.1626, found 288.1619. ^c Three product peaks observed by GC in the ratio 1:6:0.5 were separated by means of preparative GC and the compounds identified and characterized as the 2,2', 2,4', and 4,4'-bis(1-methyl-1-cyanoethyl)biphenyls respectively (Scheme II). ^d The reaction was warmed up to room temp. after the addition of the bis complex soln. to the anion soln. ^e Inverse addn., i.e., the generated anion was transferred to the bis complex solution.

The attack of the nucleophile was also found to be highly regioselective. This was evidenced by the formation of a single regioisomer, where the attack took place at the 2-position. The assignment of chemical shifts was found to be consistent with previous work.^{1h,3e,g,4,5,11} The carbon atoms of the attacked anionic ring were found to be markedly upfield relative to those of the unattacked neutral ring. It has been shown in (arene)Cr(CO)₃ compounds where the Cr(CO)₃ group adopts a highly preferred conformation either for steric or for electronic reasons that reactions with electrophiles occur at carbon atoms not eclipsed by metal-carbonyl bonds, while reactions with nucleophiles occur at carbon atoms eclipsed by metal-carbonyl bonds.⁶ For the (η^6 : η^6 -biphenyl)bis(tricarbonylchromium) complex the two Cr(CO)₃ groups adopt an anti-eclipsed conformation (structure 2) rather than



a syn-eclipsed conformation (structure 3). This is because in (arene)tricarbonylchromium complexes the arene ring is electron donating relative to the chromium, while on the other hand, the chromium is electron withdrawing toward the arene ring, with its electron-withdrawing power similar to that of a *p*-nitro group. Furthermore, nucleophilic and electrophilic substitution patterns of (η^6 -arene)Cr(CO)₃ complexes have been correlated with the coefficient of the LUMO and HOMO, respectively, of the arene ligand. Hückel calculations for LUMO of the biphenyl system shows that positions 2,4 have the larger coefficients.⁷ Thus for charge-controlled reactions, addition of the nucleophile

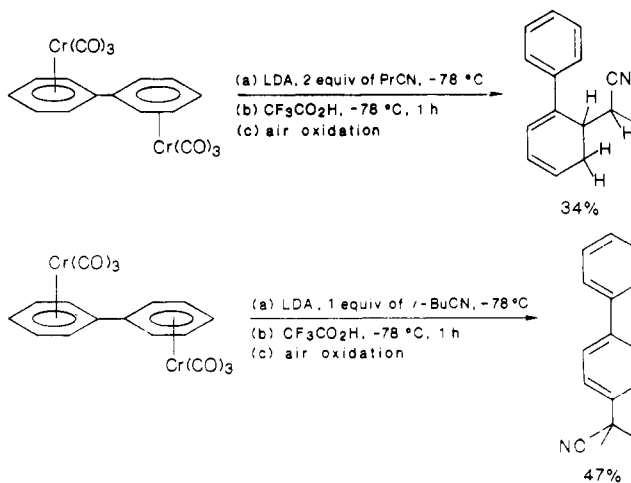
Table II. ¹³C NMR Shifts (ppm) and ¹J_{CH} Coupling Constants (Hz) of the Intermediate Obtained by the Reaction of the Anion of Acetonitrile with (η^6 : η^6 -Biphenyl)[Cr(CO)₃]₂^a

C ^b	chem shift	mult	¹ J _{CH}
2	35.54	d	138
3	50.17	d	173
5	79.93	d	172
7	24.44	t	134
8	118.70	s	
9	240.56	s	
10	236.14	s	
1'	123.21	s	

^a The spectrum was obtained in and referenced to THF-*d*₆ (67.40 ppm) by using a Varian VXR-200 NMR spectrometer. ^b Seven signals are not unambiguously assigned at present. The signals observed at 85.16 (d, *J* = 169 Hz), 88.87 (d, *J* = 172 Hz), 95.58 (d, *J* = 163 Hz), 96.72 (d, *J* = 169 Hz), 95.18 (d, *J* = 169 Hz), 96.83 (d, *J* = 168 Hz) and 88.14 (d, *J* = 163 Hz) correspond to C₄, C₆, C₂', C₃', C₄', C₅', and C₆'. The signal for C₁ could not be easily identified.

Table III. Reaction of (η^6 : η^6 -Biphenyl)[Cr(CO)₃] with 1 equiv of *i*-BuCN in the Presence of Solvent Additives

solvent	product distribution		
	biphenyl	ortho	para
1,2-dimethoxyethane (DME)	38	17	56
hexamethylphosphoric triamide (HMPA)	21	37	41
<i>N,N,N',N'</i> -tetramethylethylenediamine (TMEDA)	26	20	57
1 equiv of 15-crown-5 ether in THF	11	43	60
1 equiv of 18-crown-6 ether in THF	13	22	61

Scheme III

would prefer to take place at the 2-position. This is indeed the case (Table I) with attack at the 2-position being more dominant except for tertiary nucleophiles where para alkylation is preferred for steric reasons.⁸

In an effort to see any changes in the ortho:para distribution ratio for tertiary nucleophiles, the reactions with isobutyronitrile were carried out in the presence of solvent additives (one-sixth in volume to that of THF) (see Table III).⁹

While the addition of DME, TMEDA, and 18-crown-6 ether in THF to the reaction mixture gave a similar ratio of products to that of the pure THF reaction, the addition

(6) (a) Solladie-Cavallo, A.; Wipff, G. *Tetrahedron Lett.* 1980, 3047. (b) Roy Jackson, W.; Rae, I. D.; Wong, M. G.; Semmelhack, M. F.; Garcia, J. N. *J. Chem. Soc. Chem. Comm.* 1982, 1359. (c) Roy Jackson, W.; Rae, I. D.; Wong, M. G., *Aust. J. Chem.* 1986, 39, 303.

(7) Albright, T. A.; Carpenter, B. K. *Inorg. Chem.* 1980, 19, 3092 and references therein.

(8) Similar results have been obtained by Semmelhack, M. F.; Garcia, J. L.; Cortes, D.; Farina, R.; Hong, R.; Carpenter, B. K. *Organometallics* 1983, 2, 467.

(9) Addition of the solvent additive was made after the generation of the anion, i.e., prior to the addition of the bis complex solution to that of the anion.

of HMPA and 15-crown-5 in THF resulted in a near equal amount of the two product isomers.

Attempts were also made to see if metalation could be effected. This was achieved by the direct addition of *n*-butyllithium to the (η^6 : η^6 -biphenyl)[Cr(CO)₃]₂ solution, followed by addition of acetaldehyde to the resultant dark brown solution. However, no addition products were isolated. Only minor amounts of 2- and 4-substituted *n*-butylbiphenyl were obtained.¹⁰

Treatment of (η^5 : η^5 -biphenyl)[Cr(CO)₃]₂ with the nucleophiles, followed by protonation with trifluoroacetic acid instead of oxidation with iodine gave phenyl-conjugated dienes. The loss of the Cr(CO)₃ moiety was achieved by air oxidation of the quenched solution to give the thermodynamically more stable conjugated cyclohexadiene (Scheme III).

In summary, nitrile-stabilized anions undergo a facile nucleophilic addition to (η^6 : η^6 -biphenyl)bis(tricarbonylchromium) to give moderate to good yields of substituted biphenyls, upon oxidation with iodine. While the addition of primary and secondary anions takes place principally in the ortho position, tertiary nucleophiles prefer to attack at the less hindered para position. Addition of 2 mol of the anion leads to the formation of disubstituted biphenyls, while workup of the monoadduct with acid produces phenyl conjugated cyclohexadienes. It appears that the bis complexes are not metalated readily by *n*-butyllithium.

Experimental Section

General Procedures. ¹H NMR and ¹³C NMR were obtained on a NIC-360 and Varian VXR-200 superconducting NMR spectrometers. Double intensity peaks in ¹³C NMR are referred to as 2X. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer, neat between NaCl plates or as KBr disks. High-resolution mass spectra were performed by the Midwest Regional Center for Mass Spectrometry, University of Nebraska, Lincoln, NE. GC analyses were done on a Hewlett-Packard 5890A gas chromatograph (interfaced with a Perkin-Elmer LC-100 integrator) equipped with a 10 ft × 1/8 in. column of 10% SP2100 on 100-120 Supelcoport. Preparative GC work was done on a Varian 920 gas chromatograph equipped with a 12 ft × 1/4 in. column of 10% SP2100 on 100-120 Supelcoport. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Oneida Research Services Inc., Whitesboro, NY.

All manipulations were carried out on a dual manifold providing vacuum and dry argon. The Linde prepurified grade argon was further purified by passing it through a 150 °C catalyst column (BASF R3-11) and then through a column of phosphorus pentoxide followed by a column of granular potassium hydroxide. Tetrahydrofuran (THF), *n*-butyl ether, and 1,2-dimethoxyethane (DME) were freshly distilled under argon from sodium/potassium alloy. Hexamethylphosphoric triamide (HMPA) was dried by storing over 13X molecular sieves (predried under nitrogen at 350 °C for 4 h). *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was freshly distilled under argon from sodium, after being refluxed over potassium hydroxide for 2 h.

The preparation of (η^6 : η^6 -biphenyl)bis(tricarbonylchromium) was carried out by standard methods. The reaction product was purified by subliming off the unreacted Cr(CO)₆ at 50 °C (3 mm) and the mono complex (η^6 -biphenyl)tricarbonylchromium at 100 °C (3 mm).

General Procedure for the Reaction of Nucleophiles with (η^6 : η^6 -Biphenyl)bis(tricarbonylchromium). Lithium diisopropylamide was prepared from *n*-butyllithium (0.8 mL of 2.5

M solution in hexane, 2 mmol) and diisopropylamine (0.3 mL, 2.2 mmol) in THF (3 mL) by mixing the reagents at -78 °C under argon and allowing the mixture to stir at 0 °C for 15 min. The colorless solution was cooled to -78 °C, the nucleophile (RCN) (2 mmol) was added and the solution stirred at 0 °C for 15 min. The orange-colored solution of (η^6 : η^6 -biphenyl)[Cr(CO)₃]₂ (0.852 g, 2 mmol) in dry THF (15 mL) was then added. The orange solution turned yellow and then gradually darkened to red as it was stirred at 0 °C for 45 min, after which it was once again cooled to -78 °C and quenched with a solution of iodine (3.556 g, 14 mmol) in THF (15 mL). The dark black solution that resulted was stirred overnight for 12 h. The reaction mixture was then partitioned between ether (30 mL) and saturated Na₂S₂O₃ solution (50 mL). The ether layer was washed twice with saturated Na₂S₂O₃ solution, twice with water, and once with saturated NaCl solution and dried over MgSO₄. GC analysis of the product mixture was performed by injecting naphthalene (0.256 g, 2 mmol) as an internal standard into the reaction mixture prior to the workup.

2-(1-Cyanomethyl)biphenyl. ¹H NMR (acetone-*d*₆) δ 7.25–7.60 (m, 9 H), 3.77 (s, 2 H); ¹³C NMR (CDCl₃) δ 142.51, 140.75, 130.97, 129.75, 129.56, 129.40, 129.24, 128.78, 128.76, 128.27, 118.96, 22.10; IR (neat) 3070, 3030, 2980, 2930, 2250, 1600, 1485, 1270, 1075, 1010, 775 cm⁻¹; mass spectrum, calcd for C₁₄H₁₁N 193.0891, found 193.0887. Anal. Calcd for C₁₄H₁₁N: C, 87.05; H, 5.70; N, 7.25. Found: C, 87.10; H, 5.87; N, 6.91.

2-(1-Cyanoethyl)biphenyl. ¹H NMR (acetone-*d*₆) δ 7.25–7.70 (m, 9 H), 4.08 (q, 1 H), 1.47 (d, 3 H); ¹³C NMR (CDCl₃) δ 141.07, 140.07, 135.16, 130.48, 128.99, 128.59, 128.46, 127.86, 127.69, 127.06, 122.12, 29.91, 21.30; IR (neat) 3070, 3030, 2990, 2940, 2240, 1610, 1485, 1440, 1010, 760, 745, 700 cm⁻¹; mass spectrum, calcd for C₁₅H₁₃N 207.1048, found 207.1050.

2-(1-Cyanopropyl)biphenyl. ¹H NMR (acetone-*d*₆) δ 7.62 (d, 1 H, *J* = 7.56 Hz), 7.40–7.53 (m 5 H), 7.34 (d, 2 H, *J* = 6.84 Hz), 7.28 (dd, 1 H, *J* = 7.56, 1.08 Hz), 3.94 (dd, 1 H, *J* = 8.64, 6.48 Hz), 1.71–1.93 (m, 2 H), 0.87 (t, 3 H); ¹³C NMR δ 141.52, 136.55, 133.87, 130.49, 129.09, 128.59, 128.30, 127.83, 127.66, 127.56, 120.80, 35.38, 28.95, 11.60; IR (neat) 3065, 3040, 2980, 2940, 2885, 2245, 1605, 1485, 1470, 1010, 760, 710 cm⁻¹; mass spectrum, calcd for C₁₆H₁₅N 221.1204, found 221.1196.

2-(1-Methyl-1-cyanoethyl)biphenyl. ¹H NMR (CDCl₃) δ 7.34–7.70 (m, 9 H), 1.78 (s, 6 H); ¹³C NMR (CDCl₃) δ 142.20, 142.11, 140.77, 129.35, 128.86, 127.66, 127.30, 127.00, 124.44, 124.06, 123.88, 37.32, 29.26; IR (neat) 3060, 3030, 2990, 2930, 2240, 1610, 1580, 760, 700 cm⁻¹; mass spectrum, calcd for C₁₆H₁₅N 221.1204, found 221.1195.

4-(1-Methyl-1-cyanoethyl)biphenyl. mp 87.5–88.5 °C; ¹H NMR (CDCl₃) δ 7.50–7.62 (m, 6 H), 7.43 (t, 2 H), 7.35 (t, 1 H), 1.75 (s, 6 H); ¹³C NMR (CDCl₃) δ 140.85, 140.53, 140.28, 128.81, 127.57, 127.54, 127.03, 125.50, 124.38, 36.94, 29.14; IR (KBr pellet) 3075, 3040, 2980, 2930, 2230, 1930, 1600, 1565, 765, 690 cm⁻¹; mass spectrum, calcd for C₁₆H₁₅N 221.1204, found 221.1191. Anal. Calcd for C₁₆H₁₅N: C, 86.88; H, 6.79; N, 6.33. Found: C, 86.88; H, 6.93; N, 6.15.

2,2'-Bis(1-methyl-1-cyanoethyl)biphenyl. ¹H NMR (CDCl₃) δ 7.65 (s, 2 H), 7.57–7.51 (m, 3 H), 7.48 (d, 3 H), 1.79 (s, 12 H); ¹³C NMR δ 142.30, 141.73, 129.50, 126.88, 124.31, 124.16, 37.33, 29.26; IR (neat) 3050, 2990, 2940, 2240, 1610, 1585, 1480, 1465, 1240, 1070 cm⁻¹; mass spectrum, calcd for C₂₀H₂₀N₂ 288.1626, found 288.1619.

2,4'-Bis(1-methyl-1-cyanoethyl)biphenyl. ¹H NMR (CDCl₃) δ 7.67 (s, 1 H), 7.61 (d, 2 H, *J* = 8.35 Hz), 7.56 (d, 2 H, *J* = 8.41 Hz), 7.53–7.50 (m, 1 H), 7.47 (d, 2 H, *J* = 4.93 Hz), 1.78 (s, 6 H), 1.77 (s, 6 H); ¹³C NMR (CDCl₃) δ 142.23, 141.18, 141.00, 140.31, 129.44, 127.74, 126.58, 125.62, 124.15, 123.98, 37.28, 36.96, 29.19, 29.14; IR (neat) 3050, 3000, 2950, 2250, 1620, 1490, 1470, 1020 cm⁻¹; mass spectrum, calcd for C₂₀H₂₀N₂ 288.1626, found 288.1619. Anal. Calcd for C₂₀H₂₀N₂: C, 83.34; H, 6.94; N, 9.72. Found: C, 82.32; H, 7.14; N, 9.23.

4,4'-Bis(1-methyl-1-cyanoethyl)biphenyl. ¹H NMR (CDCl₃) δ 7.61 (d, 4 H, *J* = 8.41 Hz), 7.55 (d, 4 H, *J* = 8.46 Hz), 1.77 (s, 12 H); ¹³C NMR (CDCl₃) δ 140.97, 139.85, 127.61, 125.69, 37.04, 29.21; IR (neat) 3040, 2990, 2920, 2240, 1610, 1465, 830 cm⁻¹; mass spectrum, calcd for C₂₀H₂₀N₂ 288.1626, found 288.1629.

Preparation of 1-Phenyl-6-(1-cyanoethyl)cyclohexa-1,3-diene. Lithium diisopropylamide was generated from *n*-butyl-

(10) (a) Card, R. J.; Trahanovsky, W. S. *J. Org. Chem.* **1980**, *45*, 2555. (b) Card, R. J.; Trahanovsky, W. S. *J. Org. Chem.* **1980**, *45*, 2560.

(11) For ¹³C NMR of isoelectronic (η^5 -cyclohexadienyl)metal-carbonyl complexes, see: (a) Whitesides, T. H.; Budnik, R. A. *Inorg. Chem.* **1976**, *15*, 874 and references therein. (b) Dobish, P. A.; Areshem, D. G.; Konealski, D. J.; Lillya, C. P.; Magyar, E. S., *Inorg. Chem.* **1978**, *17*, 1775 and references therein.

lithium (1.2 mL of 2.5 M solution in hexane, 3.0 mmol) and diisopropylamine (0.46 mL, 3.3 mmol), in THF (4 mL), by mixing the reagents at -78°C under argon and stirring at 0°C for 15 min. The colorless solution was cooled to -78°C , propionitrile (0.21 mL, 3.0 mmol) added, and the resultant solution stirred at 0°C for 15 min. The orange-colored solution of $(\eta^6\text{-}\eta^6\text{-biphenyl})[\text{Cr}(\text{CO})_3]_2$ (0.639 g, 15 mmol) in THF (12 mL) was added. The mixture was stirred at 0°C for 45 min, during which time it turned red. This solution was then cooled to -78°C , quenched with trifluoroacetic acid (0.69 mL, 9 mmol), and stirred at -78°C for 1 h, after which it was poured into NH_4OH (50 mL). The orange solution was filtered to remove the precipitated white solids, washed twice with saturated NaCl solution, and dried over MgSO_4 . The dried solution was left at room temperature 4 days, during which time it became colorless. Filtration, followed by evaporation of the solvent, gave 0.490 g of an oily gray compound. The crude material was purified on the silica gel column, by using 4% ethyl acetate in hexane as the eluant, to give 24 mg of the pure product and 84 mg of contaminated product.

1-Phenyl-6-(1-cyanoethyl)cyclohexa-1,3-diene. ^1H NMR (CDCl_3) δ 7.41 (d, 2 H, $J = 7.20$ Hz), 7.35 (t, 2 H, $J = 7.49$ Hz), 7.26 (t, 1 H, $J = 7.23$ Hz), 6.38 (d, 1 H, $J = 5.41$ Hz), 6.10–6.18 (ddd, 1 H, $J = 5.81, 5.41$ Hz), 5.85–5.93 (m, 1 H), 2.97–3.05 (m, 1 H), 2.87–2.97 (m, 1 H), 2.74–2.86 (ddd, 1 H, $J = 18.21, 5.82, 1.68$ Hz) 2.60–2.72 (ddd, 1 H, $J = 18.22, 7.36, 2.96$ Hz) 1.06 (d, 3 H, $J = 6.98$ Hz); ^{13}C NMR (CDCl_3) δ 140.24, 136.82, 136.61, 128.34, 127.22, 124.93, 123.24, 120.13, 120.05, 41.86, 25.88; IR (neat) 3040, 2980, 2940, 2860, 2820, 2230, 1600, 1490, 1450, 1440, 790, 690 cm^{-1} ; mass spectrum, calcd for $\text{C}_{15}\text{H}_{15}\text{N}$ 209.1204, found 209.1211.

Preparation of 1-Phenyl-4-(1-methyl-1-cyanoethyl)cyclohexa-1,3-diene. Lithium diisopropylamide was generated from *n*-butyllithium (0.60 mL of 2.5 M solution in hexane, 1.572 mmol) and diisopropylamine (0.23 mL, 1.65 mmol) in THF (4 mL) by mixing the reagents at -78°C under argon and stirring at 0°C for 15 min. The colorless solution was cooled to -78°C , isobutyronitrile (0.136 mL, 1.5 mmol) was added, and the resultant solution was stirred at 0°C for 15 min. The orange-colored solution of $(\eta^6\text{-}\eta^6\text{-biphenyl})[\text{Cr}(\text{CO})_3]_2$ (0.639 g, 1.5 mmol) in THF (12 mL) was then added. The reaction mixture was stirred at 0°C for 45 min, during which time it turned red. This red solution was then cooled to -78°C , quenched with trifluoroacetic acid (0.69 mL, 9 mmol), stirred at -78°C for 1 h, and then poured into NH_4OH (50 mL). The orange solution was filtered, washed twice with saturated NaCl, dried over MgSO_4 , and left at room temperature 4 days, during which time it became colorless. Filtration followed by rotary evaporation of the solvent gave 0.215 g of a colorless oil. Purification of the crude product by column chromatography using 4% ethyl acetate in hexane as the eluant resulted in 6 mg of biphenyl, 7 mg of a contaminant, and 156 mg of the product.

1-Phenyl-4-(1-methyl-1-cyanoethyl)cyclohexa-1,3-diene. ^1H NMR (CDCl_3) δ 7.40 (d, 2 H, $J = 7.20$ Hz), 7.30 (t, 2 H, $J = 7.54$ Hz), 7.20 (t, 1 H, $J = 7.21$ Hz), 6.32 (d, 1 H, $J = 5.86$ Hz) 6.16 (d, 1 H, $J = 5.76$ Hz), 2.65 (t, 2 H), 2.37 (t, 2 H), 1.50 (s, 6 H); ^{13}C NMR (CDCl_3) δ 140.24, 136.82, 136.61, 128.34, 127.22, 124.93, 123.24, 120.13, 120.05, 41.86, 25.85; IR (neat) 3060, 2990,

2950, 2885, 2830, 2230, 1650, 1600, 1500, 1470, 1450, 750, 690, cm^{-1} ; mass spectrum, calcd for $\text{C}_{16}\text{H}_{17}\text{N}$ 223.1361, found 223.1359.

Attempted Metalation of $(\eta^6\text{-}\eta^6\text{-Biphenyl})[\text{Cr}(\text{CO})_3]_2$ with *n*-Butyllithium. To a solution of $(\eta^6\text{-}\eta^6\text{-Biphenyl})[\text{Cr}(\text{CO})_3]_2$ (0.426 g, 1.0 mmol) in THF (10 mL) at -78°C under argon was added 0.4 mL of *n*-BuLi (1.0 mmol, 1.0 equiv of 2.5 M solution in hexane). A dark red solution was immediately observed which gradually deepened as stirring was continued at -78°C for 25 min. Acetaldehyde (0.08 g, 1.0 mmol) was then injected into the red solution, and stirring was continued at -78°C for 15 min and then at 0°C for 30 min. The reaction flask was once again cooled to -78°C and then quenched with a solution of iodine (1.778 g, 7 mmol) in THF (15 mL). Stirring was continued overnight, during which time it gradually warmed up to room temperature. The reaction mixture was then partitioned between ether (30 mL) and saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution (50 mL). The organic layer was washed twice with saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution, twice with water, and once with saturated NaCl solution and dried over MgSO_4 . Filtration followed by evaporation of the solvent gave 0.51723 g of a dark black compound. GC analysis of a small aliquot indicated the presence of several components, which were not easily separated when eluted on a column of silica gel with 5% ethyl acetate in hexane as the solvent. Preparative GC analysis of the fractions was carried out to obtain and characterize the two butylated biphenyls.

2-Butylbiphenyl. ^1H NMR (acetone- d_6) δ 7.12–7.48 (m, 9 H), 2.58 (t, 2 H), 1.43 (m, 2 H), 1.18 (m, 2 H), 0.76 (t, 3 H); ^{13}C NMR (CDCl_3) δ 141.92, 141.71, 140.21, 129.89, 129.15 (2X), 129.10, 127.85 (2X), 127.18, 126.58, 125.39, 33.63, 32.74, 22.58, 13.92; IR (neat) 3070, 3030, 2970, 2940, 2870, 1600, 1480, 1380, 1010, 750, 690 cm^{-1} ; mass spectrum, calcd for $\text{C}_{16}\text{H}_{18}$ 210.1408, found 210.1409.

4-Butylbiphenyl: ^1H NMR (acetone- d_6) δ 7.63 (d, 2 H, $J = 7.56$ Hz), 7.51 (d, 2 H, $J = 7.92$ Hz), 7.44 (t, 2 H), 7.28–7.37 (m, 3 H), 2.66 (t, 2 H), 1.63 (m, 2 H), 1.39 (m, 2 H), 0.94 (t, 3 H); ^{13}C NMR (CDCl_3) δ 141.94, 141.08, 138.42, 128.72, 128.58, 126.88 (2X), 126.83, 35.36, 33.71, 22.50, 14.08; IR (neat) 3070, 3040, 2970, 2940, 2870, 1605, 1490, 1410, 1380, 1010, 835, 760, 695 cm^{-1} ; mass spectrum, calcd for $\text{C}_{16}\text{H}_{18}$ 210.1408, found 210.1402.

Reaction of $(\eta^6\text{-}\eta^6\text{-Biphenyl})[\text{Cr}(\text{CO})_3]_2$ with the Anion of Acetonitrile: NMR Experiment To Determine the Structure of the Intermediate. The preparation of the anion and the reaction of the anion of acetonitrile was performed in the drybox. In a vial was dissolved the solid lithium diisopropylamide (17.6 mg, 0.16 mmol) in THF- d_8 (0.1 mL). Acetonitrile (33 μL , 0.15 mmol) was then syringed in. In another vial $(\eta^6\text{-}\eta^6\text{-biphenyl})[\text{Cr}(\text{CO})_3]_2$ (64 mg, 0.15 mmol) was dissolved in THF- d_8 (0.20 mL). The orange bis complex solution was then pipetted into the pale yellow anion solution; the color changed to dark brown. The dark brown solution was transferred to a NMR tube, which was sealed by a J. Young valve. The NMR tube was brought out of the drybox and the ^{13}C NMR of the brown reaction mixture determined on the Varian VXR-200-MHz NMR spectrometer.

Acknowledgment. We thank the National Science Foundation for support of this research (Grant CHE-8318335).