ORGANOMETALLICS
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New Approach to the Synthesis of Azinylcymantrenes

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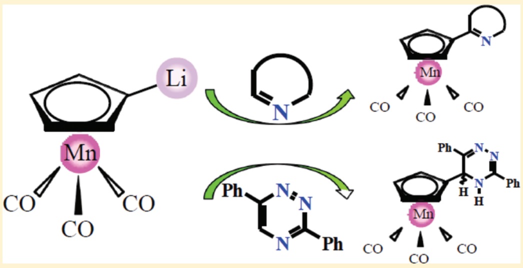
Supporting Information

ABSTRACT: A versatile synthetic protocol was proposed for direct C−C coupling of a cymantrene fragment with various azaheterocycles on the basis of nucleophilic substitution of hydrogen in the absence of metal catalysts.



INTRODUCTION

Nowadays, different synthetic approaches are used to modify hetaryl-containing metallocenes.[1] The majority of experimental studies deal with derivatives of ferrocene. Thus, hetarylferrocenes can be constructed either by building up the heterocyclic subunits based on functional groups attached to the ferrocene fragment or by coupling reactions in order to incorporate heterocyclic fragments into the core structure of ferrocenes. However, the first method has a number of inherent limitations: the range of the available ferrocene blocks is rather limited or cannot be obtained in principle. Therefore in modern synthetic studies, transition metal catalyzed cross-coupling reactions leading to the formation of various C−C and C−X (X is a heteroatom) bonds have found increasing use. Previously, we have shown that the synthetic strategy of the oxidative nucleophilic substitution of hydrogen ($S_N{}^H$(AO)) without transition metal catalysts can be successfully applied to the synthesis of molecular assemblies of ferrocene with azines,[2] including planar chiral compounds[3] as well as hetaryl-substituted nitronyl nitroxides.[4]

Cyclopentadienyltricarbonylmanganese (cymantrene) is an interesting analogue of ferrocene half-sandwich transition metal complexes.[5] Cymantrene derivatives are used as base compounds to obtain metallic nanostructured materials,[6] metal complex−peptide bioconjugates with cytotoxic activity,[7] sensors,[8] and ligands for metallocomplexes.[9] The possibility of the use of cymantrene derivatives in bioorganic chemistry as redox labels for proteins is extensively examined at the present time.[10] High catalytic activity in asymmetric reactions is peculiar to the cymantrene derivatives bearing the azomethine bond.[11] Certain hetarylcymantrenes under UV irradiation proved to eliminate one of the carbonyl ligands following the formation of chelate complexes with a manganese−azine nitrogen bond. These compounds have been shown to be applicable for the design of photochromic systems.[12]

To our knowledge there are no available data concerning the synthesis of hetarylcymantrenes. α-Pyridylcymantrenes and γ-pyridylcymantrenes were synthesized by the recyclization of pyrylium salts with ammonium acetate in 9% yield.[13] The (quinolin-8-yl)cymantrene was synthesized by the Negishi cross-coupling of a zinc derivative of cymantrene with 8-bromoquinoline catalyzed by $Pd(PPh_3)_2$ with prolonged storage of the reaction mixture.[14]

In this paper we describe the nucleophilic substitution of hydrogen in π-deficient azines using a lithiocymantrene as the nucleophilic reagent. This strategy first was used as a synthetic approach to the C−C coupling of cymantrene with heterocyclic derivatives. It has been shown that this versatile approach can be applied to various azines, such as mono-, di-, and triazines bearing heteroatoms in different positions in the ring, to substituted and unsubstituted azines, and to benzannelated systems.

The obtained hetarylcymantrenes bear complexing groups and can be used as ligands for the synthesis of complexes with metals and charged or neutral molecules.

RESULTS AND DISCUSSION

According to the current conception of the $S_N{}^H$ reactions mechanism,[15] the first step is known to be the addition of lithiocymantrene to azine to form σ^H-adducts **A** (Scheme 1). The addition step runs without the commonly used activation of hetarenes. Lithium derivatives are supposed to undergo hydrolysis in the presence of water to dihydro compounds **3**. The second step is the aromatization of dihydroazines **3**. Oxidation of σ^H-adducts of mono- and diazines runs spontaneously due to the contact of **3a**−**i** with air, analogous to the synthesis of azinylferrocenes.[2] The yields of the reaction products are increased

Received: February 19, 2011
Published: May 16, 2011

Scheme 1. S_N^H Reaction of the Lithiocymantrene with Mono- and Diazines

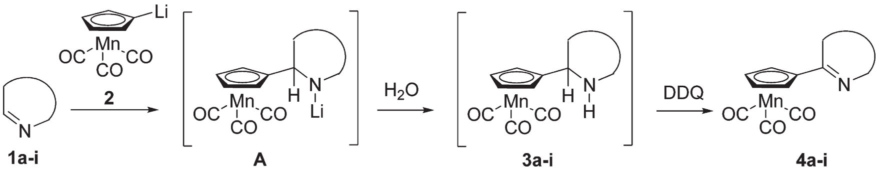
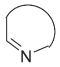
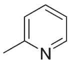
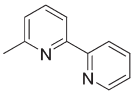
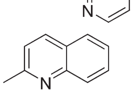
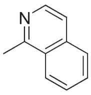
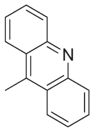
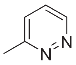
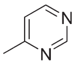
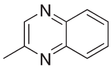
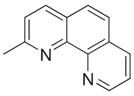
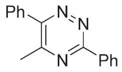


Table 1. Yields of Compounds 4a−j

Compound	Azinyl residue		Yield, %	M.p., °C
4a	Pyridyl-2		40	20
4b	2,2′-Bipyridyl-6		45	96
4c	Quinolin-2-yl		56	90
4d	Isoquinolin-1-yl		50	52
4e	Acridin-9-yl		54	156
4f	Pyridazine-3-yl		50	109
4g	Pyrimidin-4-yl		51	93
4h	Quinoxalin-2-yl		60	139
4i	[1,10]-Phenanthrolin-3-yl		45	164
4j	3,6-Diphenyl-1,2,4-triazin-5-yl		80	165

about 20% if a mild oxidizing agent such as DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) is used instead of atmospheric oxygen.

Lithiocymantrene **2** has been synthesized by the metalation of cymantrene with *n*-BuLi for 0.5 h in dry THF under an atmosphere of argon.[16] Lithiocymantrene **2** readily reacts with azines **1a**−**i** in a molar ratio of ca. 1:1 (Scheme 1). After addition of the solution of electrophilic reagents **1a**−**i** in dry THF to colorless lithium derivatives of cymantrene at −78 °C the solution immediately becomes dark. The reaction mixture was kept at this temperature for 1.5 h and then was gradually warmed to room temperature. Then DDQ in THF was added, and the color of the solution changed from dark brown to dark green. All hetarylcymantrenes are light brown, stable, solid compounds with melting points varying from 20 to 170 °C (Table 1).

The yields of the reaction products vary from 50% to 80%. The low yields of compounds **4a**,**b**,**i**, 20−30%, are due to the side reaction of butylation of azines **1a**,**b**,**i** with using *n*-BuLi as reagent. The butylation products were observed (about 5%), but they were easily separated from the target products **4** by column chromatography. *t*-BuLi as a lithiated agent for cymantrene was used to prevent the formation of the products of butylation of heterocycles **1a**,**b**,**i**.

The structures of the cymantrenes (**4**) bearing azines were proved by NMR and IR spectroscopy, mass spectrometry, and elemental analysis. In the ^{1}H NMR spectra the characteristic signals of protons of monosubstituted cymantrene are observed as two multiplets with the two-proton intensity at δ 4.9−6.2 ppm and the signals of heterocyclic protons at δ 7.2−9.2 ppm. All the mass spectra have a peak of molecular ions. In the IR spectra the characteristic absorption bands (ν = 1900−2020 cm^{-1}) corresponding to CO stretching vibrations of cymantrene are observed. The molecular and crystal structures of the products were obtained by X-ray analysis. The crystal of quinoxalinylcymantrene

(Figure 1) was obtained by recrystallization from a diethyl ether/methanol mixture.

It is well known that increasing the substrate electrophility by an introduction of electron-withdrawing exocyclic groups or heteroatoms leads to an increase of the stability of σ^H-adducts in S_N^H transformations. The use of 1,2,4-triazine derivatives as more electrophilic reagents has allowed us to isolate and to characterize the intermediates, contrary to the unstable σ^H-adducts of mono- and diazines with lithiocymantrene. Thus, lithium derivatives of cymantrene readily react with azine **1j**, forming the corresponding stable adduct **3j**. Compound **3j** is transformed into aromatic product triazinylcymantrene **4j** in the presence of DDQ in THF at room temperature with nearly quantitative yield (Scheme 2).

In the IR spectrum of compound **3j** the NH stretching vibrations at 3300−3500 cm^{-1} are observed. In the ^{1}H NMR spectrum of compound **3j** the characteristic signals of dihydroazines are observed: a singlet at δ 5.77 ppm assigned to the proton at the sp^3-hybridized C atom and a signal of the NH group at δ 11.38 ppm. In the ^{13}C NMR spectrum of derivative **3j** the signal of the sp^3-hybridized C(5) at δ 49.79 ppm is observed.[17] In the ^{1}H NMR spectra of aromatic compound **4j** the signals of the protons at C(5) and N(4) are absent. The signals of the protons of the Cp fragment of **4j** (4.8−5.4 ppm) are shifted from those of adduct **3j** (4.4−5.0 ppm downfild in comparison with **4j**). In the ^{13}C NMR spectra the characteristic signal of the sp^3-hybridized carbon atom is absent. It was impossible to ascertain the position of the proton at the N atom in **3j** based on 2D heteronuclear ^{1}H−^{13}C HSQC and ^{1}H−^{13}C HMBC experiments. Due to the prototropic tautomerism, this proton can be bound to either N(2) (structure **A3j**) or to N(4) (structure **B3j**) (Scheme 3). In the 2D HMBC spectra of **3j** only the cross-peaks between this proton and the signals of C(3) and C(6) are observed. The singlet structure of the signals of H(5) and of NH in the ^{1}H NMR spectra (in $CDCl_3$ and C_3D_6O at room temperature) of compound **3j**, in turn, makes it clear that the hydrogen atom is bound to N(2).

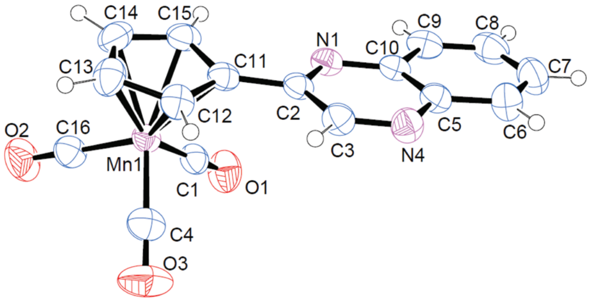


Figure 1. ORTEP structure of **4h** with 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg): C(2)−C(11), 1.470(2); C(15)−C(11)−C(2), 125.33(16); N(1)−C(2)−C(11), 117.56(15); C(3)−C(2)−C(11), 120.98(15); C(12)−C(11)−C(2), 127.50(16).

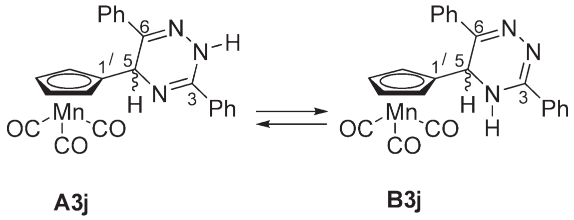
The NMR spectrum is not essentially changed upon a temperature decrease to −40 and −75 °C. The signal of the proton of the NH group in $(CD_3)_2CO$ is shifted downfield upon the temperature decrease from 25 °C to −75 °C with the spectra recorded every 10 degrees.

The ethylated **3j** derivative was synthesized because no single crystal of σ^H-adduct could be obtained. However, the alkylation of derivative **3j** runs on N(4). Thus derivative **5** was synthesized by the reaction of **3j** with iodoethane. The reaction took place at room temperature in dry THF under basic conditions in the presence of sodium hydride (Scheme 4).

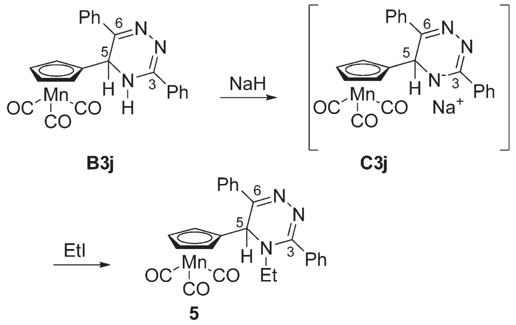
The position of the ethyl group at N(4) of the 1,2,4-triazine part in compound **5** is evident from the observed cross-peak between C(5) and protons of the NCH_2 group in the HMBC spectrum. When alkylation of **3j** proceeds, the upfield shifts of signals of sp^3-hybridized C(5) (Δδ 4.1 ppm) and C(3) (Δδ 1.4 ppm) are observed in the ^{13}C NMR spectra of compounds **5**. The structure of compound **5** has been proved by X-ray analysis (Figure 3). The crystal of **5** was obtained by crystallization from a mixture of dichloromethane and heptane.

According to the X-ray analysis, derivative **4h** crystallizes in the space group $P2_1/c$ (monoclinic crystal system). The bond lengths and bond angles are within the normal range. The quinoxaline ring is planar; the deviations of the atoms from the mean square plane are <0.027 Å. The angle between the

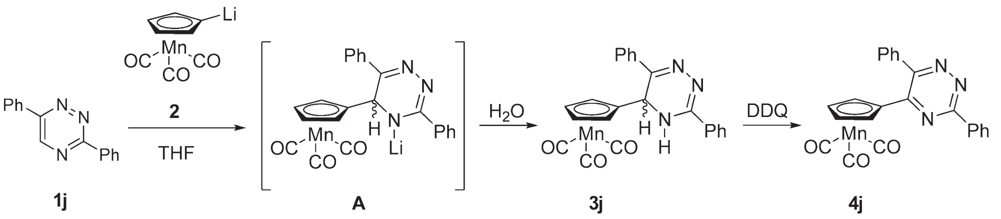
Scheme 3. Tautomeric Transformation of 3j



Scheme 4. Reaction of Ethylation of the σ^H-Adduct



Scheme 2. Reaction of Lithiocymantrene with 3,6-Diphenyl-1,2,4-triazine



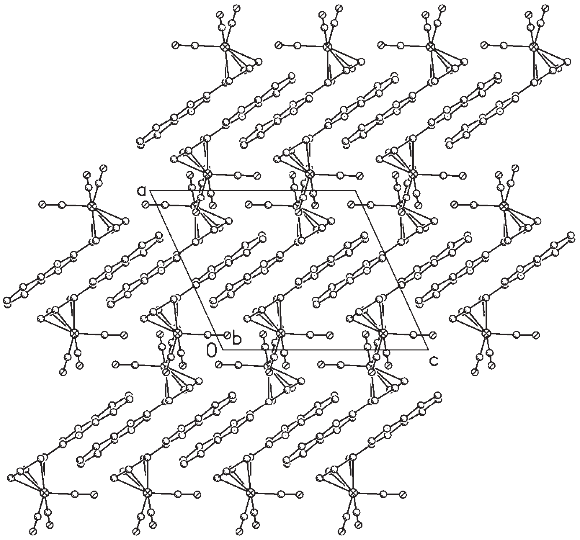


Figure 2. Fragment of the molecular packing of quinoxalin-2-ylcymantrene **4h**.

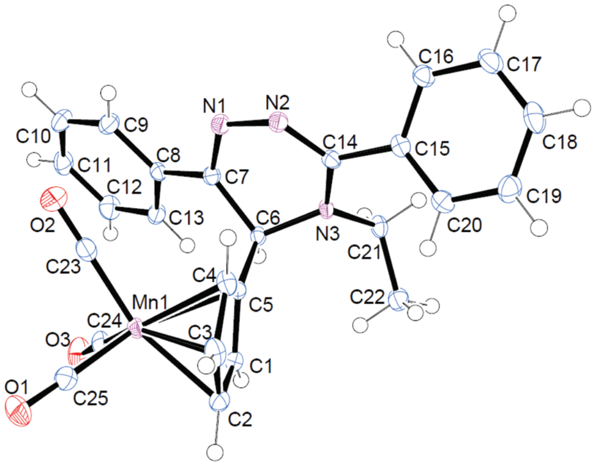


Figure 3. ORTEP drawing of **5** with 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg): C(6)–C(5), 1.5073(19); N(3)–C(6), 1.4729(16); N(3)–C(14), 1.3577(17); N(2)–C(14), 1.3077(18); N(2)–N(1), 1.4014(16); C(6)–C(7), 1.5186(19); C(7)–N(1), 1.2868(17); C(5)–C(6)–C(7), 113.73(11); C(4)–C(5)–C(6), 127.79(12); N(1)–C(7)–C(6), 120.24(12); N(3)–C(6)–C(7), 105.68(10); C(14)–N(3)–C(6), 115.72(11); N(2)–C(14)–N(3), 123.29(12); C(14)–N(2)–N(1), 116.51(11); C(7)–N(1)–N(2), 120.15(12); N(3)–C(6)–C(5), 111.17(11); C(1)–C(5)–C(6), 125.17(13).

cyclopentadienyl and quinoxaline planes is 9.67(5)°. The distance from the Mn atom to the centroid of the cyclopentadienyl ring is 1.772(2) Å. Compound **4h** has a laminate molecular packing characterized by the alternation of the layers of cymantrene and quinoxaline fragments (Figure 2) oriented in the plane *b*0*c*. There are the following short contacts within the layers: the short contact between the carbonyl oxygen atoms (O1···O1 [2−*x*, −*y*, −*z*], 3.039(2) Å), the short π–π contact between the quinoxaline fragments (C2···C8 [*x*, 0.5−*y*, 0.5+*z*], 3.397(2) Å), and the short π–π contact between the quinoxaline and cymantrene fragments (C10···C12 [*x*, 0.5−*y*, 0.5+*z*], 3.335(2) Å). The distance between the Mn atoms in the molecular packing is >6.5 Å.

According to the X-ray analysis, derivative **5** crystallizes in the centrosymmetric space group $P2_1/c$ (monoclinic crystal system). The triazine ring is nonaromatic, no equalization of the bond lengths in the conjugated double bond system of dihydrotriazine being observed. The triazine cycle is bent along the C6···N2 line. The angle between the mean square C6C7N1N2 and C6N3C14N2 planes is 34.45(5)°. The deviations of the corresponding atoms from the C6C7N1N2 plane are smaller than 0.02 Å, whereas the deviation from the C6N3C14N2 plane is 0.09 Å due to steric distortions caused by the sp^3-hybridized atom C6. The distance between the Mn atom and the centroid of the cyclopentadienyl ring is 1.770(2) Å. The distance between the Mn atoms in the molecular packing is more than 6.0 Å. The molecular packing is formed by chains of the molecules running along the 0*c* axis.

It has been shown that lithiocymantrene is less stable than the ferrocene analogue. Lithioferrocene was obtained at room temperature or under heating. Lithiocymantrene is stable only at negative temperatures. The rise in temperature results in a drastic decrease of the yields of the products or even in the absence of them. Lithiocymantrene is prone to have less reactivity in reactions with azines in comparison with lithioferrocene.[2] The yields of azinylcymantrenes are lower than those for azinylferrocenes, 10% on average. This might be connected with the sudden change of the temperature at the moment of the heterocycle addition to **1**, leading to lithiocymantrene destruction. In some organic solvents (hexane, benzene) hetarylcymantrenes are not stable in light; the solutions become disturbed owing to the precipitation.

■ CONCLUSION

An efficient, versatile, noncatalytic method of C–C coupling for the synthesis of monosubstituted heterocyclic cymantrene derivatives has been proposed. This method provides a common approach to the synthesis of cymantrene ensembles with various azaheterocycles.

■ EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under argon using standard Schlenk techniques. The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) and 2D ^{13}C and ^1H NMR spectra were recorded on a Bruker AVANCE II (400 MHz) instrument. Chemical shifts are given in δ values (ppm) using TMS as the internal standard and $CDCl_3$ as the solvent. The mass spectra were measured on a Bruker Daltonics micrOTOF-Q II mass spectrometer equipped with an orthogonal electrospray ionization (ESI) source, a six-port divert valve, and syringe pump kd Scientific with a flow rate of 180 μL/h. The IR spectra were recorded using a Perkin-Elmer Spectrum One B Fourier-transform infrared spectrometer equipped with a diffuse reflection attachment. The elemental analysis was carried out on an automated Perkin-Elmer PE 2400 series II CHNS/O analyzer. The course of the reactions was monitored by TCL on 0.25 mm silica gel plates (Merck 60F 254). Column chromatography was performed on Alfa Aesar silica gel (Avocado Research Chemical Ltd., silica gel 60, 0.035–0.070 mm (220–440 mesh)). Cymantrene and starting heterocycles were purchased from Aldrich.

3,6-Diphenyl-1,2,4-triazine was prepared according to the published procedure.[19]

Crystallographic Data for 4h and 5. Crystals of **4h** and **5** were obtained by crystallization from diethyl ether as yellow single crystals. X-ray diffraction analysis was performed on an Xcalibur S X-ray diffractometer equipped with CDD detector (Mo Kα graphite-

Table 2. R_f, IR, Elemental Analysis, and ESI-MS Data for 4a−j

	R_f (eluent)	IR (cm^{-1})	elemental analysis	ESI-MS
4a	0.5 (benzene/EtOAc, 9.5:0.5)	ν(CO) 2010, 1917	Found: C, 55.27; H, 3.31; N, 4.66 Calc for $C_{13}H_8MnNO_3$: C, 55.52; H, 2.85; N, 4.98	282
4b	0.2 (hexane/EtOAc, 8:2)	ν(CO) 2001, 1922, 1908	Found: C, 59.65; H, 3.11; N, 7.51 Calc for $C_{18}H_{11}MnN_2O_3$: C, 60.34; H, 3.07; N, 7.82	359
4c	0.5 (CH_2Cl_2)	ν(CO) 2011, 1940, 1911	Found: C, 61.35; H, 3.18; N, 4.12 Calc for $C_{17}H_{10}MnNO_3$: C, 61.63; H, 3.02; N, 4.23	332
4d	0.4 (CH_2Cl_2)	ν(CO) 2011, 1910	Found: C, 61.60; H, 2.88; N, 4.17 Calc for $C_{17}H_{10}MnNO_3$: C, 61.63; H, 3.02; N, 4.23	332
4e	0.3 (benzene/EtOAc, 9.5:0.5)	ν(CO) 2021, 2012, 1923	Found: C, 66.12; H, 3.09; N, 3.59 Calc for $C_{21}H_{12}MnNO_3$: C, 66.14; H, 3.15; N, 3.67	382
4f	0.3 (EtOAc)	ν(CO) 2021, 2012, 1929, 1915	Found: C, 50.95; H, 2.63; N, 9.55 Calc for $C_{12}H_7MnN_2O_3$: C, 51.06; H, 2.48; N, 9.93	283
4g	0.6 (EtOAc)	ν(CO) 2014, 1913	Found: C, 51.03; H, 2.27; N, 9.93 Calc for $C_{12}H_7MnN_2O_3$: C, 51.06; H, 2.48; N, 9.93	283
4h	0.4 (CH_2Cl_2)	ν(CO) 2016, 1947, 1917	Found: C, 56.34; H, 3.31; N, 8.57 Calc for $C_{16}H_9MnN_2O_3$: C, 57.83; H, 2.71; N, 8.43	333
4i	0.4 (hexane/EtOAc, 1:1)	ν(CO) 2012, 1910	Found: C, 62.74; H, 2.95; N, 7.13 Calc for $C_{20}H_{11}MnN_2O_3$: C, 62.83; H, 2.88; N, 7.33	383
4j	0.5 (benzene/EtOAc, 9.5:0.5)	ν(CO) 2016, 1914	Found: C, 63.49; H, 3.54; N, 9.66 Calc for $C_{23}H_{14}MnN_3O_3$: C, 63.45; H, 3.22; N, 9.66	436

monochromated radiation, λ = 0.71073 Å, ω-scanning technique, the scanning step was 1° and the exposure time per frame was 10 s at 295(2) K for **4h** and 120(2) K for **5**. The low temperature was maintained with a Cryojet (Oxford Instruments) open-flow N_2 gas cryostat. Analytical absorption correction was used in the reflection intensity integration.[20] The structure was solved by the direct method and refined applying full matrix least-squares against F^2_{hkl} with anisotropic displacement parameters for all non-hydrogen atoms using the SHELX97 program package.[21] All hydrogen atoms were located in different electron density maps and refined using a riding model with fixed thermal parameters.

General Procedure for the Synthesis of 4a,b,i. A 1.7 M solution of *t*-BuLi in pentane (0.71 mL, 1.2 mmol) was added to a solution of cymantrene (1 mmol) in anhydrous THF (5 mL) under an atmosphere of argon at −78 °C. After 40 min stirring of the reaction mixture the solution of corresponding heterocycles **2a,b,i** (1.0 mmol) in anhydrous THF (7 mL) was added. After stirring the reaction mixture at −78 °C for 1.5 h and then for an hour at room temperature, water (2 mmol) and a solution of DDQ (3.8 mmol) in THF (10 mL) were added. Finally, the reaction mixture was filtrated off through neutral alumina and was purified on silica gel (using appropriate solvent as the eluent). The eluate was concentrated to dryness in vacuo.

General Procedure for the Synthesis of 4c−h. The synthetic approach is similar to the procedure described above: 1.6 M solution of *n*-BuLi in hexane (0.76 mL, 1.2 mmol), cymantrene (1 mmol) in dry THF (5 mL), heterocycles **1c**−**h** (1.0 mmol) in anhydrous THF, water (2 mmol), and DDQ (3.8 mmol) in THF (10 mL).

Experimental data for **4a**−**j** are summarized in Tables 2 and 3.

Synthesis of (*R*,*S*)-[(3,6-Diphenyl-2,5-dihydro-2(*H*)-1,2,4-triazin-5-yl)]cymantrene, 3j. A 1.6 M solution *n*-BuLi in hexane (0.76 mL, 1.2 mmol) was added to a solution of cymantrene (204 mg, 1 mmol) in anhydrous THF (5 mL) under an atmosphere of argon at −78 °C. After 30 min of stirring of the reaction mixture a solution of 3,6-diphenyl-1,2,4-triazine (**1j**) (233 mg, 1 mmol) in anhydrous THF (7 mL) was added. The reaction mixture was stirred for 1.5 h at −78 °C and then for 1 h at room temperature. Finally, the reaction mixture was purified on silica gel (using benzene as the eluent). The eluate was concentrated to dryness in vacuo.

Yield: 350 mg (80%). Mp: 165 °C. R_f = 0.2 (eluent benzene). ^{1}H NMR (400 MHz, $CDCl_3$): δ −4.47 (s, 1H, C_5H_4), 4.54 (s, 1H, C_5H_4), 4.82 (s, 1H, C_5H_4), 4.89 (s, 1H, C_5H_4), 5.77 (s, 1H, 5-H), 7.49 (m, 6H, Ph), 7.82 (m, 4H, Ph), 8.98 (s, 1H, NH) ppm. ^{1}H NMR (400 MHz, $(CD_3)_2CO$, 25 °C): δ −4.74 (m, 2H, C_5H_4), 4.92 (s, 1H, C_5H_4), 5.10 (s, 1H, C_5H_4), 5.76 (s, 1H, 5-H), 7.49 (m, 6H, Ph), 7.97 (t, 2H, ^3J = 6.5 Hz, Ph), 8.10 (t, 2H, ^3J = 6.5 Hz, Ph), 10.69 (s, 1H, NH) ppm. ^{1}H NMR (400 MHz, $(CD_3)_2CO$, −75 °C): δ −4.80 (s, 1H, C_5H_4), 4.91 (s, 1H, C_5H_4), 4.96 (s, 1H, C_5H_4), 5.29 (s, 1H, C_5H_4), 5.81 (s, 1H, 5-H), 7.51 (m, 6H, Ph), 8.11 (m, 4H, Ph), 11.29 (s, 1H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ −49.79 (C5); 79.51, 81.18, 84.41, 85.03 (CH-Cp); 100.85 (C-Cp); 126.24, 126.56, 128.87, 128.94, 129.90, 131.30 (CH-Ph); 132.20, 134.04 (C-Ph); 143.56 (C6); 153.12 (C3). IR (cm^{-1}): ν(NH) 2954, 2923, 2853, ν(CO) 2012, 1915. ESI-MS: 438. Anal. Found: C, 63.63; H, 3.38; N, 9.34. Calc for $C_{23}H_{16}MnN_3O_3$: C, 63.16; H, 3.66; N, 9.61.

Synthesis of (3,6-Diphenyl-1,2,4-triazin-5-yl)cymantrene, 4j. A solution of DDQ (227 mg, 1 mmol) in THF (5 mL) was added to a solution of (3,6-diphenyl-2,5-dihydro-2(*H*)-1,2,4-triazin-5-yl)cymantrene (**3j**) (437 mg, 1 mmol) in anhydrous THF (7 mL) at room temperature. The suspension was immediately filtrated off through the neutral alumina layer, the alumina layer was repeatedly washed with THF, and the solvent was evaporated. The residue was purified on silica gel. The eluate was concentrated to dryness in vacuo.

Synthesis of (*R*,*S*)-[(4-Ethyl-3,6-diphenyl-5(*H*)-1,2,4-triazin-5-yl)]cymantrene, 5. Sodium hydride (24 mg, 1 mmol) was added to a solution of ligand **3j** (437 mg,1 mmol) in dry THF (10 mL) under argon at room temperature, and the reaction mixture was stirred until complete dissolution. Then EtI (0.9 mL, 4 mmol) was added, and the mixture was stirred at room temperature for 5 h. The solution was concentrated in vacuo and purified on silica gel. Yield: 279 mg (60%). Mp: 167 °C. R_f = 0.2 (eluent benzene/EtOAc, 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −1.03 (t, 3H, ^3J = 6.7 Hz, N-CH_2-$\underline{Me}$), 3.51 (m, 2H, N-$\underline{CH_2}$-Me), 4.61 (d, 1H, ^3J = 1.5 Hz, C_5H_4), 4.75 (m, 2H, C_5H_4), 5.24 (t, 1H, ^3J = 1.5 Hz, C_5H_4), 5.60 (s, 1H, 5-H),7.48 (m, 6H, Ph), 7.80 (t, 2H, ^3J = 6.2 Hz, Ph), 8.17 (t, 2H, ^3J = 1.5 Hz, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ −15.18 (N-CH_2-$\underline{Me}$); 45.63 (N-$\underline{CH_2}$-Me);

Table 3. ^{1}H and ^{13}C NMR Data for 4a−j

compound	^{1}H NMR data	^{13}C NMR data
4a	4.99 (m, 2H, C_5H_4), 5.76 (m, 2H, C_5H_4), 7.20 (s, 1H, 5′-H), 7.66 (m, 2H, 3′-H, 4′-H), 8.48 (s, 1H, 2′-H)	82.38, 82.61 (CH-Cp); 100.24 (C-Cp); 119.67 (C3); 122.57 (C5); 136.52 (C4); 149.48 (C6); 152.16 (C2)
4b	4.85 (m, 2H, C_5H_4), 5.63 (m, 2H, C_5H_4), 7.31 (m, 1H, 5′-H), 7.35 (d, 1H, ^3J = 7.8 Hz, 5-H), 7.77 (t, 1H, ^3J = 7.8 Hz, 4-H), 7.83 (t, 1H, ^3J = 7.8 Hz, 4′-H), 8.29 (d, 1H, ^3J = 7.5 Hz, 3-H), 8.49 (d, 1H, ^3J = 8.0 Hz, 3′-H), 8.66 (d, 1H, ^3J = 4.3 Hz, 6′-H)	82.43, 83.13 (CH-Cp); 100.24 (C-Cp); 119.52 (C5); 119.83 (C3); 121.32 (C3′); 123.89 (C5′); 136.93 (C4′); 137.57 (C4); 149.07 (C6′); 151.55 (C6); 155.82 (C2′); 155.88 (C2)
4c	4.92 (m, 2H, C_5H_4), 5.73 (m, 2H, C_5H_4), 7.46 (d, 1H, ^3J = 8.5 Hz, 4-H), 7.54 (m, 1H, 7-H), 7.73 (m, 1H, 6-H), 7.80 (d, 1H, ^3J = 8.3 Hz, 5-H), 8.06 (d, 1H, ^3J = 8.6 Hz, 8-H), 8.15 (d, 1H, ^3J = 8.5 Hz, 3-H)	82.85, 83.44 (CH-Cp); 100.12 (C-Cp); 118.06 (C4); 126.53 (C7); 127.36 (C8a); 127.57 (C5); 129.39 (C8); 129.91 (C6); 136.66 (C3); 147.99 (C4a); 152.27 (C2)
4d	4.93 (m, 2H, C_5H_4), 5.30 (m, 2H, C_5H_4), 7.59 (d, 1H, ^3J = 5.6 Hz, 5-H), 7.79 (m, 1H, 6-H), 8.25 (m, 1H, 7-H), 7.86 (d, 1H, ^3J = 8.4 Hz, 8-H), 8.38 (d, 1H, ^3J = 8.6 Hz, 4-H), 8.51 (d, 1H, ^3J = 5.6 Hz, 3-H)	82.36, 85.58 (CH-Cp); 103.05 (C-Cp); 120.69 (C5); 125.60 (C4); 126.25 (C8a); 127.49 (C6); 127.62 (C8); 130.00 (C7); 136.75 (C4a); 141.98 (C3); 152.29 (C1)
4e	5.09 (m, 2H, C_5H_4), 5.50 (m, 2H, C_5H_4), 7.61 (m, 2H, 2-H, 7-H), 7.80 (m, 2H, 3-H, 6-H), 8.16 (d, 2H, ^3J = 7.0 Hz, 1-H, 8-H), 8.59 (d, 2H, ^3J = 8.04 Hz, 4-H, 5-H)	82.46, 87.66 (CH-Cp); 99.72 (C-Cp); 125.05 (C8a, C10a); 125.72 (C4, C5); 126.09 (C2, C7); 129.93 (C3, C6); 130.59 (C1, C8); 136.26 (C4a, C9a); 148.76 (C9)
4f	4.98 (m, 2H, C_5H_4), 5.43 (m, 2H, C_5H_4), 7.42 (s, 1H, 4-H), 9.17 (s, 1H, 6-H), 9.24 (s, 1H, 5-H)	82.80, 83.52 (CH-Cp); 92.79 (C-Cp); 121.72 (C4); 133.05 (C3); 148.46 (C5); 151.27 (C6)
4g	4.92 (m, 2H, C_5H_4), 5.66 (m, 2H, C_5H_4), 7.30 (s, 1H, 5-H), 8.71 (d, 1H, ^3J = 2.5 Hz, 6-H), 9.15 (s, 1H, 2-H)	83.26, 84.20 (CH-Cp); 94.80 (C-Cp); 116.19 (C5); 157.35 (C6); 159.18 (C2); 160.67 (C4)
4h	5.15 (m, 2H, C_5H_4), 6.13 (m, 2H, C_5H_4), 7.77 (m, 2H, 6-H, 7-H), 8.00 (m, 2H, 5-H, 8-H), 9.20 (s, 1H, 3-H)	83.30, 83.92 (CH-Cp); 96.07 (C-Cp); 129.35 (C8); 129.41 (C5); 129.86 (C6); 130.71 (C7); 141.80 (C4a); 142.22 (C8a); 142.28 (C3); 147.97 (C2)
4i	4.93 (m, 2H, C_5H_4), 5.83 (m, 2H, C_5H_4), 7.62 (m, 1H, 8-H), 7.68 (d, 1H, ^3J = 8.6 Hz, 3-H), 7.77 (m, 2H, 5-H, 6-H), 8.23 (t, 2H, ^3J = 8.2 Hz, 7-H, 4-H), 9.21 (d, 1H, ^3J = 3.2 Hz, 9-H)	82.19, 83.65 (CH-Cp); 101.50 (C-Cp); 120.54 (C3); 123.16 (C8); 126.46 (C6); 126.77 (C5); 127.99 (C4a); 129.30 (C6a); 136.25 (C7); 136.86 (C4); 145.95 (C1a); 146.12 (C10a); 150.57 (C9); 152.84 (C2)
4j	4.82 (m, 2H, C_5H_4), 5.30 (m, 2H, C_5H_4), 7.61 (m, 6H, Ph), 7.67 (m, 2H, Ph), 8.65 (m, 2H, Ph)	82.88, 88.05 (CH-Cp); 91.98 (C-Cp); 128.37, 128.86, 129.05, 129.13, 129.95, 131.72 (CH-Ph); 134.51, 135.35 (C-Ph); 151.18 (C6); 154.40 (C5); 161.41 (C3)

45.68 (C5); 80.21, 81.13, 84.87, 85.16 (CH-Cp); 97.46 (C-Cp); 126.35, 127.80, 128.09, 128.79, 129.29, 130.17 (CH-Ph); 132.81, 133.41 (C-Ph); 148.06 (C6); 151.69 (C3). IR (cm^{-1}): ν(CO) 2015, 1948, 1921. ESI-MS: 466. Anal. Found: C, 64.24; H, 4.56; N, 8.60. Calc for $C_{25}H_{20}MnN_3O_3$: C, 64.52; H, 4.30; N, 9.03.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Crystallographic data in CIF format, experimental details, and characterization for other hetarylcymantrenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This study was financially supported by the Council on Grants of the President of the Russian Federation (Program for State Support of Leading Scientific Schools of the Russian Federation, Grant NSh-65261.2010.3, Grant MK-1901.2011.3) and the Russian Foundation for Basic Research (Project No. 10-03-00756-a).

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