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ARTICLE *in* ORGANOMETALLICS · FEBRUARY 2010

Impact Factor: 4.13 · DOI: 10.1021/om900807s

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Organometallics **2010,** *29,* 801–805 801
DOI: 10.1021/om900807s

Different Reactivities of Alkoxy- and Thiocarbene Complexes of Fischer-Type: Formation of (*N*-Enamino)ethoxycarbene Complexes and Quinolines, Respectively†

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Received September 15, 2009

Alkoxy- and thiocarbene complexes of chromium and tungsten afford different type of products on reaction with (*N*-aryl)imidoyl chlorides. The (*n*-butyl)ethoxycarbene complex $[(OC)_5W{=}C(OEt)n\text{-Bu}]$ and (*N*-aryl)imidoyl chlorides *t*-BuClC$=$N$C_6H_4R^4$ (R^4 = H, *O*Me) undergo a rearrangement to (*N*-enamino)ethoxycarbene complexes, whereas quinolines are obtained from the corresponding reaction of (alkyl)thiocarbene complexes $[(OC)_5M{=}C(SEt)CH_2R]$ (M = W, Cr; R = *n*-Pr, Me) with (*N*-aryl)imidoyl chlorides $R^1ClC{=}NC_6H_2R^2R^3R^4$ (R^1 = *t*-Bu, Ph; R^2, R^3 = H, HC$=$CH−CH$=$CH; R^4 = H, OMe, Me) by β-cyclization.

Introduction

Efficient ring construction has continued to be a challenge in organic synthesis. Although a variety of success has been achieved over the decades,[1] much effort is still contributed to the development of novel synthetic methodologies and new building blocks for this purpose. Organometallic compounds are usually considered as potential building blocks for rings that cannot be readily constructed by conventional methods.[2] Fischer carbene complexes have been found very useful building blocks in this context.[3] Cyclopropanation,[4] Dötz benzannulation,[5] and Hegedus reactions[6] of Fischer carbene complexes have been extensively investigated for the construction of both carbocyclic and *N*-heterocyclic compounds. Elaborate combinations of Fischer carbene complexes with N−H and/or C$=$N bond containing reagents lead to novel Fischer carbene complexes or *N*-heterocyclic compounds.[7] Quinoline rings are important members of the latter and attract, therefore, the interest of both synthetic and medicinal chemists.[8,9] They are synthetically useful building blocks in the preparation of several alkaloids and also find applications as pharmaceuticals and agrochemicals. The structural core of quinoline has generally been synthesized by various conventional named reactions such as Skraup,[10] Doebner von Miller,[11] Combes,[11] Friedländer,[12] Pfitzinger,[13] and Conrad−Limpach[14] syntheses, but due to its biological importance, new synthetic methods still remain an active area of research.[8,15]

Recently, we have reported[16a] on the very different reactivity behavior of (alkyl)ethoxycarbene complexes $[(OC)_5M{=}C(OEt)CH_2R]$ **1** (M = W; R = *n*-Pr, Me, *c*-C_7H_7) and (alkyl)thiocarbene complexes $[(OC)_5M{=}C(SEt)CH_2R]$ **2**

† Organic Synthesis via Transition Metal Complexes, Part 123. For Part 122 see ref 16a.

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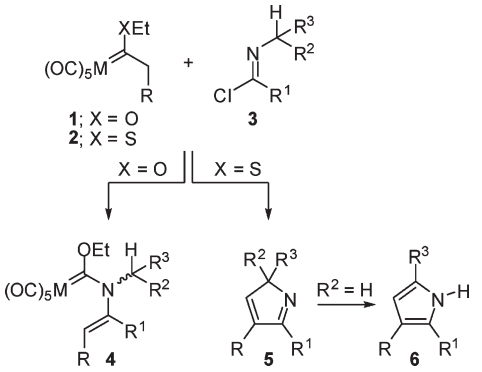
Published on Web 01/25/2010

Scheme 1. Influence of Heteroatom X on the Reaction of (Alkyl)ethoxycarbene Complexes and (Alkyl)thiocarbene Complexes with (*N*-Alkyl)imidoyl Chlorides 3 to Give (*N*-Enamino)ethoxycarbene Complexes 4 and Pyrroles 5 and 6, Respectively[16a]



(M = W, Cr; R = *n*-Pr, Me, *c*-C_7H_7, *c*-$C_6H_7Fe(CO)_3$) toward (*N*-alkyl)imidoyl chlorides $R^1ClC{=}NCHR^2R^3$ **3** (R^1 = *t*-Bu, Ph, 2-furyl; R^2 = H, Me; R^3 = Me, Et, Ph). (Alkyl)ethoxycarbene complexes **1** and imidoyl chlorides **3** give (*N*-enamino)ethoxycarbene complexes[16b] **4** by a metalla(di-π-methane) skeletal rearrangement,[16c] whereas 2*H*-pyrroles **5** and 1*H*-pyrroles **6** are obtained from the corresponding reaction of (alkyl)thiocarbene complexes by α-cyclization (Scheme 1). We now report on an extension of the cyclization to pyrroles to the formation of quinolines.

Results and Discussion

The (*n*-butyl)ethoxycarbene complex [$(OC)_5W{=}C(OEt)n$-Bu] (**1a**) reacts with (*N*-aryl)imidoyl chlorides *t*-$BuClC{=}NC_6H_4R^4$ (**7a**,**b**; R^4 = H, OMe) in the presence of triethylamine to afford (*N*-enamino)ethoxycarbene complexes **10a**,**b** (Scheme 2, path 1), whereas quinolines **11a**−**g** are obtained from the corresponding reaction of compounds $R^1ClC{=}NC_6H_2R^2R^3R^4$ (**7a**−**e**; R^1 = *t*-Bu, Ph; R^2, R^3 = H, HC=CH−CH=CH; R^4 = H, OMe, Me) with (alkyl)thiocarbene complexes [$(OC)_5M{=}C(SEt)CH_2R$] (**2a**−**c**; M = W, Cr; R = *n*-Pr, Me) (Scheme 2, path 2).

It is suggested that (β-imino)heterocarbene complexes **8a**,**b** (X = O) and **9a**−**h** (X = S) generated by addition of the imidoyl chlorides **7a**−**e** to (*n*-butyl)ethoxycarbene complex **1a** and (alkyl)thiocarbene complexes **2a**−**c** are precursors common to reaction paths (Scheme 2). Compounds **8a**,**b** afford (*N*-enamino)ethoxycarbene complexes **10a**,**b** by metalla(di-π-methane) skeletal rearrangement. The reaction involves formation of a new bond between the carbene carbon and the nitrogen atom of the β-imino group and breaking of the bond between the α-carbon and the carbene carbon atom.[16c] In our earlier experiments, the formation of *syn*- and *anti*-isomers was observed among four possible isomers. However, in the present case, only the *anti*-isomer is generated apparently due to stronger sterical interaction of the aryl substituent and the *tert*-butyl group in the *syn*-isomer as compared to the *anti*-isomer.

The (β-imino)heterocarbene complexes **8a**,**b** (X = O) and **9a**−**h** (X = S) are assumed to undergo different multistep processes.[16a] (*N*-Enamino)ethoxycarbene complexes **10** are generated as a result of an associative process by a nucleophilic addition of the β-imino nitrogen atom to the carbene carbon atom, while (β-imino)thiocarbene complexes **9a**−**h** undergo a dissociative process resulting in vinylidenes **13** (Scheme 3). Compounds **13** are transferred into quinolines **11** by β-cyclization. Ethanthiol, eliminated in this reaction, forms the corresponding thioesters $R^1(EtS)C{=}NC_6H_2R^2R^3R^4$ **12** with imidoyl chlorides **7a**−**e**.

The conversion of vinylidenes into quinolines resembles the Povarov reaction[17], which involves [4+2] cycloaddition of *N*-aryl imines (Schiff bases) to nucleophilic olefins catalyzed by a Lewis acid,[18] Brønsted acid[19], or lanthanide triflate[20] (Scheme 4). The Povarov reaction is a one-pot, but multicomponent reaction. Where the synthesis of substituted quinolines from (alkyl)thiocarbene complexes **2a**−**c** is concerned, fewer components and reaction steps are required; thus it can be considered as an alternative to the Povarov reaction. Moreover, substitutions at C-3 and C-4 positions of quinolines are less common and often suffer from harsh reaction conditions, expensive reagents, or both.[17,21] However, substituted quinolines at C-2 and C-3 positions could be conveniently synthesized by our method.

The isolated yields of quinolines **11a**−**g** (40−58%) are not as high as that of (*N*-enamino)ethoxycarbene complexes **10a**,**b** (75−80%) (Scheme 2). However, in our syntheses, quinolines are obtained under milder conditions than applied for the common Skraup synthesis performed in the presence of a concentrated acid and an oxidizing agent. The (alkyl)thiocarbene complexes **2a**−**c** are more reactive than (*n*-butyl)ethoxycarbene complex **1a** toward (*N*-aryl)imidoyl chlorides **7**. The latter compounds are consumed in several days at 20 °C. Therefore, the reaction is accelerated by using catalytic amounts of *N*,*N*-dimethylamino pyridine. The former compounds, on the other hand, are consumed within minutes at −40 °C.

Conclusion

We could show the influence of *N*-aryl substituents on the reaction of (alkyl)thiocarbene complexes [$(OC)_5M{=}C(SEt)CH_2R$] (**2a**−**c**; M = Cr, W; R = *n*-Pr, Me) with (*N*-aryl)imidoyl chlorides $R^1ClC{=}NC_6H_2R^2R^3R^4$ (**7a**−**e**; R^1 = *t*-Bu, Ph; R^2, R^3 = H, HC=CH−CH=CH; R^4 = H, OMe, Me) to give quinolines **11a**−**g** by β-cyclization of the vinylidenes **13**. On the other hand, the (*n*-butyl)ethoxycarbene complex [$(OC)_5W{=}C(OEt)(n$-Bu)] (**1a**) and *N*-aryl-substituted imidoyl chlorides *t*-$BuClC{=}NC_6H_4R^4$ (**7a**,**b**; R^4 = H, *O*Me) afforded (*N*-enamino)ethoxycarbene complexes **10a**,**b** by metalla(di-π-methane) skeletal rearrangement. Thus, the use of (*N*-aryl)imidoyl chlorides only affects the product formation when they are reacted with (alkyl)thiocarbene complexes.

Experimental Section

Reagents and solvents obtained from commercial suppliers were used without further purification unless otherwise noted.

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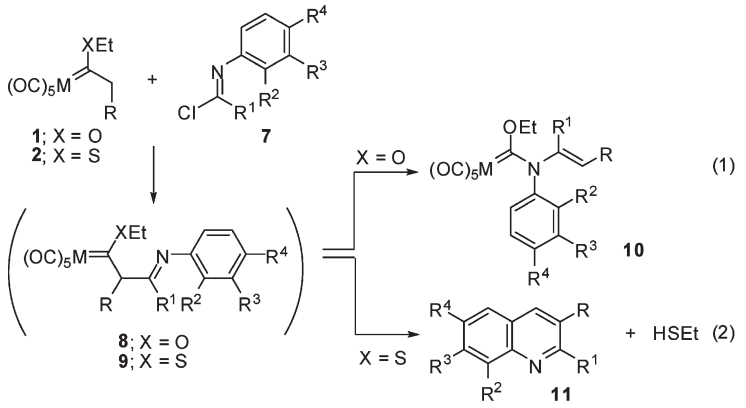
Scheme 2. (*N*-Enamino)ethoxycarbene Complexes 10 and Quinolines 11, Respectively, from (*n*-Butyl)ethoxycarbene Complex 1a and (Alkyl)thiocarbene Complexes 2a−c



1,2	M	R
a	W	*n*-Pr
b	W	Me
c	Cr	*n*-Pr

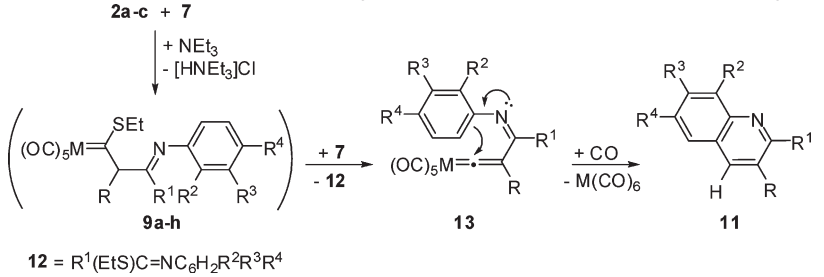
7	R^1	R^2	R^3	R^4
a	*t*-Bu	H	H	H
b	*t*-Bu	H	H	OMe
c	*t*-Bu	H	H	Me
d	Ph	H	H	H
e	*t*-Bu	⩘		H

8,10	M	X	R	R^1	R^2	R^3	R^4	10[a]
a	W	O	*n*-Pr	*t*-Bu	H	H	H	75
b	W	O	*n*-Pr	*t*-Bu	H	H	OMe	80

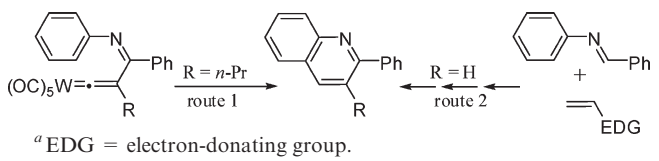
9,11,13	M	X	R	R^1	R^2	R^3	R^4	11[a]
a	W	S	*n*-Pr	*t*-Bu	H	H	H	48
b	W	S	*n*-Pr	*t*-Bu	H	H	OMe	51
c	W	S	*n*-Pr	*t*-Bu	H	H	Me	45
d	W	S	*n*-Pr	Ph	H	H	H	44
e	W	S	*n*-Pr	*t*-Bu	⩘		H	51
f	W	S	Me	*t*-Bu	H	H	Me	58
g	W	S	Me	*t*-Bu	H	H	H	53
h	Cr	S	*n*-Pr	*t*-Bu	H	H	Me	40

[a] Isolated chemical yields of compounds **10** and **11** in [%].

Scheme 3. Formation of Quinolines 11 from (β-Imino)thiocarbene Complexes 9a−h by β-Cyclization



Scheme 4. Representative Quinoline Synthesis via Our Method (route 1) and the Povarov Reaction (route 2)[a]



[a] EDG = electron-donating group.

All reactions were performed under a static pressure of argon. Analytical TLC plates, Merck TLC aluminum sheets with silica gel 60_{F240}, were viewed by UV light (254 nm). R_f values refer to TLC tests. Flash chromatographic purification was performed on Merck silica gel 60 under a pressure of argon. ^{1}H and ^{13}C NMR spectra were recorded on Bruker ARX 300, Bruker AMX 400, Inova 500, and Varian Unity Plus 600 instruments. Chemical shifts are reported in ppm against TMS (δ = 0) as the internal standard. AB signals in the ^{1}H NMR spectra are denoted by the symbol "◇". IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer. EI mass spectra were obtained on a double beam focusing Sektorfeld-MS MAT 8200 (Thermo-Finnigan-MAT) spectrometer, and HRMS spectra were obtained by electron spray ionization mass spectrometry (ESI-MS)

using a Bruker MicroTOF instrument. Elemental analyses were obtained using a Elementar Vario EL III instrument. **2a**−**c**[16a] were prepared according to literature methods, and the syntheses of (*N*-aryl)imidoyl chlorides **7a**−**e**[22] were achieved analogous to the synthesis of *N*-phenylbenzimidoyl chloride.

(4*E*)-[2-Ethoxy-3-phenylamino-4-*tert*-butyl]-3-aza-1-pentacarbonyltungstaocta-1,4-diene (*anti*-10a). To pentacarbonyl-[1-ethoxypentylidene]tungsten (**1a**) (219 mg, 0.50 mmol) in dichloromethane (1 mL) in a 5 mL screw-top vessel was first added a mixture of 2,2-dimethyl-*N*-phenylpropionimidoyl chloride (**7a**) (196 mg, 1.00 mmol) and *N,N*-dimethylamino pyridine (6 mg, 0.05 mmol) in dichloromethane (2 mL) at 20 °C. Triethylamine (51 mg, 0.50 mmol) in dichloromethane (0.5 mL) was dropwise added, and the reaction progress was controlled by TLC. After 1 day at 20 °C, the starting carbene complex **1a** was consumed completely. Diethyl ether (10−15 mL) was added, and the precipitate was discarded after centrifugation. The solvent was removed at reduced pressure. Chromatography at 25 °C on silica gel (column 20 × 2 cm, *n*-pentane/dichloromethane, 4:1) afforded compound **10a** (223 mg, 75%, R_f = 0.7 in *n*-pentane/dichloromethane, 4:1, pale yellow oil).

***anti*-10a.** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.42−7.31 (m, br, 5H; *o*-, *m*-, *p*-H Ph), 5.19 (t, ^3J = 8.1 Hz, 1H; C═CH), 4.73$^\diamond$ (q, ^3J = 7.1 Hz, 1H; OCH_A) 4.65$^\diamond$ (q, ^3J = 7.1 Hz, 1H; OCH_B), 2.27 and 2.12 (each m, each 1H; $CH_2CH_2CH_3$), 1.46 (t, ^3J = 7.1 Hz, 3H; OCH_2CH_3), 1.40 (m, 2H; CH_2CH_3), 1.19 [s, 9H; $C(CH_3)_3$], 0.89 (t, ^3J = 7.4 Hz, 3H; CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 234.4 (C_q, W═C), 200.8 and 198.0 [C_q, 1:4 C; *trans*- and *cis*-CO of $W(CO)_5$], 151.6 (C_q, *C*═CH), 146.3 (C_q, *i*-Ph), 130.7 (CH, C═*C*H) 129.1, 128.9, and 128.1 (each CH, br, *o*-, *m*-, and *p*-C Ph), 73.7 (OCH_2), 35.2 [C_q, $C(CH_3)_3$], 30.4 (CH_2, $CH_2CH_2CH_3$), 30.4 [$C(CH_3)_3$], 22.7 (CH_2, CH_2CH_3), 15.5 (OCH_2CH_3), 13.7 (CH_3, CH_2CH_3) ppm. IR (cyclohexane): $\tilde{\nu}$ 2064.1 (10), 1931.6 (100), 1922.5 (50) cm^{-1} (C≡O). MS (70 eV, EI): *m*/*z* (%) 597 (8) $[M]^+$, 569 (14) $[M - CO]^+$, 513 (100) $[M - 3CO]^+$, 397 (29). Anal. Calcd (%) for $C_{23}H_{27}O_6NW$ (597.3): C 46.25, H 4.56, N 2.34. Found: C 46.31, H 4.44, N 2.37.

(4*E*)-[2-Ethoxy-3-(4-methoxyphenyl)amino-4-*tert*-butyl]-3-aza-1-pentacarbonyltungstaocta-1,4-diene (*anti*-10b). Pentacarbonyl-[1-ethoxypentylidene]tungsten (**1a**) (219 mg, 0.50 mmol), *N*-(4-methoxyphenyl)-2,2-dimethylpropionimidoyl chloride (**7b**) (226 mg, 1.00 mmol), *N,N*-dimethylaminopyridine (6 mg, 0.05 mmol), and triethylamine (51 mg, 0.50 mmol) were reacted for 1 day as described above to give compound **10b** (250 mg, 80%, R_f = 0.5 in *n*-pentane/dichloromethane, 4:1, pale yellow oil).

***anti*-10b.** ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.28 (s, br, 2H; Ar-H), 6.90 (d, ^3J = 9.0 Hz, 2H; Ar-H), 5.16 (t, ^3J = 7.9 Hz, 1H; C═CH), 4.70$^\diamond$ (q, ^3J = 7.1 Hz, 1H; OCH_A) 4.63$^\diamond$ (q, ^3J = 7.1 Hz, 1H; OCH_B), 3.82 (s, 3H; OCH_3), 2.27 and 2.12 (each m, each 1H; $CH_2CH_2CH_3$), 1.46 (t, ^3J = 7.1 Hz, 3H; OCH_2CH_3), 1.41 (m, 2H; CH_2CH_3), 1.18 [s, 9H; $C(CH_3)_3$], 0.90 (t, ^3J = 7.4 Hz, 3H, CH_2CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 234.1 (C_q, W═C), 201.0 and 198.1 [C_q, 1:4 C; *trans*- and *cis*-CO of $W(CO)_5$], 159.1 (C_q, *C*-OCH_3), 151.7 (C_q, *C*═CH), 139.5 (C_q, C−N), 130.1 (CH, C═*C*H) 129.9 and 114.2 (each CH, br, Ar-C), 73.6 (OCH_2), 55.5 (OCH_3), 35.1 [C_q, $C(CH_3)_3$], 30.4 (CH_2, $CH_2CH_2CH_3$), 30.3 [$C(CH_3)_3$], 22.8 (CH_2, CH_2CH_3), 15.6 (OCH_2CH_3), 13.8 (CH_3, CH_2CH_3) ppm. IR (cyclohexane): $\tilde{\nu}$ 2063.3 (10), 1930.2 (100), 1920.5 (50) cm^{-1} (C≡O). MS (70 eV, EI): *m*/*z* (%) 627 (8) $[M]^+$, 599 $[M - CO]^+$, 543 (100) $[M - 3CO]^+$, 427 (27). Anal. Calcd (%) for $C_{24}H_{29}O_7NW$ (627.4): C 45.95, H 4.66, N 2.23. Found: C 46.00, H 4.51, N 2.12.

2-*tert*-Butyl-3-propylquinoline (11a) and 2,2-Dimethyl-*N*-phenylthiopropionimidic Acid Ethyl Ester (12a). To a mixture of pentacarbonyl[1-(ethylthio)pentylidene]tungsten (**2a**) (454 mg, 1.00 mmol) and 2,2-dimethyl-*N*-phenylpropionimidoyl chloride (**7a**) (391 mg, 2.00 mmol) in diethyl ether (3 mL) was added triethylamine (101 mg, 1.00 mmol) in diethyl ether (0.5 mL) with stirring at −40 °C. The reaction was continued for 10−15 min at this temperature. After the consumption of **2a** (controlled by TLC), diethyl ether (50 mL) was added and the reaction mixture was extracted with water (3 × 30 mL). Then the organic phase was extracted with HCl solution (1.0 M, 3 × 30 mL). After the extraction, the rest of the organic phase was dried over magnesium sulfate and the solvent was removed to give compound **12a**. Afterward, sodium hydroxide solution (1.0 M) was added to the aqueous phase until a turbid and basic solution was obtained. Finally, the aqueous phase was extracted with ether (3 × 50 mL) and the combined organic phases were dried over magnesium sulfate. The solvent was removed under reduced pressure to give compound **11a** (108 mg, 48%, R_f = 0.6 in *n*-pentane/dichloromethane, 4:1, yellowish oil).

11a. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.99 (dd, br, ^3J = 8.3 and ^4J = 0.6 Hz, 1H; 8-H), 7.85 (s, 1H; 4-H), 7.66 (dd, br, ^3J = 8.1 and ^4J = 1.2 Hz, 1H; 5-H), 7.56 and 7.40 (each m, each 1H; 6-H and 7-H), 2.94 (m, 2H; $CH_2CH_2CH_3$), 1.72 (m, 2H; CH_2CH_3), 1.54 [s, 9H; $C(CH_3)_3$], 1.07 (t, ^3J = 7.5 Hz, 3H; CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 166.3 (C_q, C2), 145.3 and 126.8 (each C_q, C4*a* and C8*a*), 136.9 (CH, C4), 134.6 (C_q, C3), 129.2 and 126.2 (each CH, C5 and C8), 128.0 and 125.6 (each CH, C6 and C7), 39.8 [C_q, $C(CH_3)_3$], 35.5 (CH_2, $CH_2CH_2CH_3$), 30.5 [$C(CH_3)_3$], 25.6 (CH_2, CH_2CH_3), 14.9 (CH_3, CH_2CH_3) ppm. MS (70 eV, EI): *m*/*z* (%) 227 (44) $[M]^+$, 212 (100), 182 (17), 170 (28), 143 (17). HRMS (ESI^+): *m*/*z* calcd for $C_{16}H_{21}NH$, 228.1747; found, 228.1741 $[M + H]^+$.

12a. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.24, 6.99, and 6.91 (each m, 2:1:2 H; *o*-, *m*-, *p*-H Ph), 2.10 (q, ^3J = 7.3 Hz, 2H; SCH_2), 1.30 [s, 9H; $C(CH_3)_3$], 0.95 (t, ^3J = 7.3 Hz, 3H; SCH_2CH_3).

2-*tert*-Butyl-6-methoxy-3-propylquinoline (11b) and *N*-(4-Methoxyphenyl)-2,2-dimethylthiopropionimidic Acid Ethyl Ester (12b). Pentacarbonyl[1-(ethylthio)pentylidene]tungsten (**2a**) (454 mg, 1.00 mmol), *N*-(4-methoxyphenyl)-2,2-dimethylpropionimidoyl chloride (**7b**) (451 mg, 2.00 mmol), and triethylamine (101 mg, 1.00 mmol) were reacted as described above to give compounds **11b** (132 mg, 51%, R_f = 0.4 in *n*-pentane/dichloromethane, 2:1, yellowish oil) and **12b**.

11b. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.88 (d, ^3J = 9.2 Hz, 1H; 8-H), 7.76 (s, 1H; 4-H), 6.94 (d, ^4J = 2.7 Hz, 1H; 5-H), 7.23 (dd, br, ^3J = 9.2 and ^4J = 2.7 Hz, 1H; 7-H), 3.85 (s, 3H; OCH_3), 2.91 (m, 2H; $CH_2CH_2CH_3$), 1.71 (m, 2H; CH_2CH_3), 1.52 [s, 9H; $C(CH_3)_3$], 1.06 (t, ^3J = 7.3 Hz, 3H; CH_2CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): 163.6 (C_q, C2), 157.2 (C_q, C6), 141.3 (C_q, C8*a*), 135.9 (CH, C4), 134.8 (C_q, C3), 130.6 (CH, C8), 127.5 (C_q, C4*a*), 120.6 (CH, C7), 103.8 (CH, C5), 55.3 (OCH_3), 39.4 [C_q, $C(CH_3)_3$], 35.4 (CH_2, $CH_2CH_2CH_3$), 35.4 [$C(CH_3)_3$], 25.6 (CH_2, CH_2CH_3), 14.4 (CH_3, CH_2CH_3) ppm. MS (70 eV, EI): *m*/*z* (%) 257 (41) $[M]^+$, 242 (100), 215 (16), 200 (24), 187 (28), 134 (40), 57 (20), HRMS (ESI^+): *m*/*z* calcd for $C_{17}H_{23}ONH$, 258.1852; found, 258.1837 $[M + H]^+$.

12b. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 6.89$^\diamond$ (d, ^3J = 9.0 Hz, 2H; Ar-H_A) 6.82$^\diamond$ (d, ^3J = 9.0 Hz, 2H; Ar-H_B), 3.77 (s, 3H; OCH_3), 2.09 (q, ^3J = 7.3 Hz, 2H; SCH_2), 1.29 [s, 9H; $C(CH_3)_3$], 0.95 (t, ^3J = 7.3 Hz, 3H; SCH_2CH_3).

2-*tert*-Butyl-6-methyl-3-propylquinoline (11c) and 2,2-Dimethyl-*N*-*p*-tolylthiopropionimidic Acid Ethyl Ester (12c) (from 2a). Pentacarbonyl[1-(ethylthio)pentylidene]tungsten (**2a**) (454 mg, 1.00 mmol), 2,2-dimethyl-*N*-*p*-tolylpropionimidoyl chloride (**7c**) (419 mg, 2.00 mmol), and triethylamine (101 mg, 1.00 mmol) were reacted as described above to give compounds **11c** (109 mg, 45%, R_f = 0.5 in *n*-pentane/dichloromethane, 4:1, yellowish oil) and **12c**.

11c. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.87 (d, ^3J = 8.5 Hz, 8-H), 7.77 (s, 1H; 4-H), 7.42 (s, 1H; 5-H), 7.39 (dd, br, ^3J = 8.5 and ^4J = 1.5 Hz, 1H; 7-H), 2.93 (m, 2H; $CH_2CH_2CH_3$), 2.48 (s, 3H; CH_3), 1.71 (m, 2H; CH_2CH_3), 1.52 [s, 9H; $C(CH_3)_3$], 1.06 (t, ^3J = 7.5 Hz, 3H; CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 165.3 (C_q, C2), 143.9 and 126.8 (each C_q, C4*a* and C8*a*), 136.3

(22) (a) Nerdel, F.; Weyerstahl, P.; Dahl, R. *Liebigs Ann. Chem.* **1968**, *716*, 127–134.

(CH, C4), 135.3 (C_q, C6), 134.5 (C_q, C3), 130.2 (CH, C7), 128.9 (CH, C8), 125.1 (CH, C5), 39.6 [C_q, $C(CH_3)_3$], 35.5 (CH_2, $CH_2CH_2CH_3$), 30.5 [$C(CH_3)_3$], 25.7 (CH_2, CH_2CH_3), 21.5 (CH_3), 14.4 (CH_3, CH_2CH_3) ppm. MS (70 eV, EI): m/z (%): 241 (41) $[M]^+$, 226 (100), 184 (28), 171 (32), 157 (15). HRMS (ESI^+): m/z calcd for $C_{17}H_{23}NH$, 242.1903; found, 242.1903 $[M + H]^+$.

12c. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.08$^\diamond$ (d, ^3J = 8.2 Hz, 2H; Ar-H_A), 6.81$^\diamond$ (d, ^3J = 8.2 Hz, 2H; Ar-H_B), 2.31 (s, 3H; CH_3), 2.13 (q, ^3J = 7.3 Hz, 2H; SCH_2), 1.32 [s, 9H; $C(CH_3)_3$], 0.97 (t, ^3J = 7.3 Hz, 3H; SCH_2CH_3).

2-Phenyl-3-propylquinoline (11d) and *N*-Phenylthiobenzimidic Acid Ethyl Ester (12d). Pentacarbonyl[1-(ethylthio)pentylidene]tungsten (**2a**) (454 mg, 1.00 mmol), *N*-phenylbenzimidoyl chloride (**7d**) (431 mg, 2.00 mmol), and triethylamine (101 mg, 1.00 mmol) were reacted as described above to give compounds **11d** (108 mg, 44%, R_f = 0.7 in *n*-pentane/ether, 1:1, yellowish oil) and **12d**.

11d. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.13 (d, ^3J = 8.3 Hz, 1H; 8-H), 8.0 (s, 1H; 4-H), 7.78 (d, ^3J = 8.0 Hz, 1H; 5-H), 7.64 (m, 1H; 7-H), 7.55−7.39 (m, 6H; 6-H and *o*-, *m*-, *p*-H Ph), 2.74 (m, 2H; $CH_2CH_2CH_3$), 1.56 (m, 2H; CH_2CH_3), 0.85 (t, ^3J = 7.3 Hz, 3H; CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 160.7 (C_q, C2), 146.4 (C_q, C8*a*), 141.0 (C_q, *i*-Ph), 135.6 (CH, C4), 133.7 (C_q, C3), 129.2 (CH, C8), 128.7 (CH, C7), 128.7, 128.2, and 127.9 (each CH, *o*-, *m*-, *p*-C Ph), 127.5 (C_q, C4*a*), 126.8 (CH, C5), 126.3 (CH, C6), 34.8 (CH_2, $CH_2CH_2CH_3$), 23.6 (CH_2, CH_2CH_3), 13.8 (CH_3, CH_2CH_3) ppm. MS (70 eV, EI): m/z (%): 247 (99) $[M]^+$, 232 (100), 127 (38) 57 (15). HRMS (ESI): m/z calcd for $C_{18}H_{17}NH$, 248.1434; found, 248.1442 $[M + H]^+$.

12d. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.56−7.14 (m, 10 H; *o*-, *m*-, *p*-H Ph), 1.95 (q, ^3J = 7.4 Hz, 2H; SCH_2), 0.74 (t, ^3J = 7.4 Hz, 3H; SCH_2CH_3).

2-*tert*-Butyl-3-propylbenzo[*h*]quinoline (11e). Pentacarbonyl[1-(ethylthio)pentylidene]tungsten (**2a**) (454 mg, 1.00 mmol), 2,2-dimethyl-*N*-naphthalen-1-ylpropionimidoyl chloride (**7e**) (491 mg, 2.00 mmol), and triethylamine (101 mg, 1.00 mmol) were reacted as described above. Chromatographic purification of the crude reaction mixture at 25 °C on silica gel (column 2 × 20 cm, *n*-pentane/dichloromethane, 4:1) afforded compound **11e** (140 mg, 51%, R_f = 0.9 in *n*-pentane/dichloromethane, 4:1, oil). Compound **12e** could not be obtained due to the hydrolysis on silica gel.

11e. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 9.30 (dd, br, ^3J = 8.0 and ^4J = 0.5 Hz, 1H; 10-H), 7.88 (s, 1H; 4-H), 7.83 (d, ^3J = 7.7, 1H; 7-H), 7.69$^\diamond$ (d, ^3J = 8.8 Hz, 1H; 5-H_A), 7.56$^\diamond$ (d, ^3J = 8.8 Hz, 1H; 6-H_B), 7.67 (m, 1H; 8-H), 7.60 (m, 1H; 9-H), 2.98 (m, 2H; $CH_2CH_2CH_3$), 1.75 (m, 2H; CH_2CH_3), 1.62 [s, 9H; $C(CH_3)_3$], 1.08 (t, ^3J = 7.3 Hz, 3H; CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 164.5 (C_q, C2), 142.5, 133.4, 132.1, and 124.5 (each C_q), 137.3 (CH, C4), 135.0 (C_q, C3), 127.6 (CH, C7), 127.3 (CH, C8), 126.8 (CH, C6), 126.6 (CH, C9), 124.6 (CH, C5), 124.4 (CH, C10), 40.2 [C_q, $C(CH_3)_3$], 35.4 (CH_2, $CH_2CH_2CH_3$), 30.7 [$C(CH_3)_3$], 25.7 (CH_2, CH_2CH_3), 14.5 (CH_3, CH_2CH_3) ppm. MS (70 eV, EI): m/z (%) 277 (53) $[M]^+$, 262 (100), 232 (18), 220 (29), 207 (35). HRMS (ESI^+): m/z calcd for $C_{20}H_{23}NH$, 278.1903; found, 278.1894 $[M + H]^+$.

2-*tert*-Butyl-3,6-dimethylquinoline (11f) and Ethyl 2,2-Dimethyl-*N*-*p*-tolylthiopropionimidic Acid Ethyl Ester (12c). Pentacarbonyl[1-(ethylthio)propylidene]tungsten (**2b**) (426 mg, 1.00 mmol), 2,2-dimethyl-*N*-*p*-tolylpropionimidoyl chloride (**7c**) (419 mg, 2.00 mmol), and triethylamine (101 mg, 1.00 mmol) were reacted as described above to give compounds **11f** (124 mg, 58%, R_f = 0.5 in *n*-pentane/dichloromethane, 4:1, yellowish oil) and **12c**.

11f. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.88 (d, ^3J = 8.0 Hz, 8-H), 7.65 (s, 1H; 4-H), 7.38 (dd, br, ^3J = 8.0 and ^4J = 2.0 Hz, 1H; 7-H), 7.37 (s, 1H; 5-H), 2.62 (s, 3H; CH_3), 2.46 (s, 3H; CH_3), 1.52 [s, 9H; $C(CH_3)_3$]. ^{13}C NMR (100 MHz, $CDCl_3$): 165.7 (C_q, C2), 144.1 and 126.9 (each C_q, C4*a* and C8*a*), 137.5 (CH, C4), 135.3 (C_q, C6), 130.2 (CH, C7), 129.3 (C_q, C3), 128.9 (CH, C8), 125.0 (CH, C5), 39.6 [C_q, $C(CH_3)_3$], 29.8 [$C(CH_3)_3$], 22.4 and 21.5 (each CH_3) ppm. HRMS (ESI^+): m/z calcd for $C_{15}H_{19}NH$, 214.1590; found, 214.1591 $[M + H]^+$. Anal. Calcd (%) for $C_{15}H_{19}N$ (213.3): C 84.46, H 8.98, N 6.57. Found: C 84.40, H 8.92, N 6.60.

12c. See the above synthesis of **11c** for spectroscopic data.

2-*tert*-Butyl-3-methylquinoline (11g) and 2,2-Dimethyl-*N*-phenylthiopropionimidic Acid Ethyl Ester (12a). Pentacarbonyl[1-(ethylthio)propylidene]tungsten (**2b**) (213 mg, 0.50 mmol), 2,2-dimethyl-*N*-phenylpropionimidoyl chloride (**7a**) (196 mg, 1.00 mmol), and triethylamine (51 mg, 0.50 mmol) were reacted as described above to give compounds **11g** (53 mg, 53%, R_f = 0.5 in *n*-pentane/dichloromethane, 4:1, yellowish oil) and **12a**.

11g. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.99 (d, br, ^3J = 8.3 Hz, 1H; 8-H), 7.77 (s, 1H; 4-H), 7.65 (d, br, ^3J = 8.1 Hz, 1H; 5-H), 7.57 (m, 1H; 6-H), 7.41 (m, 1H; 7-H), 1.53 [s, 9H; $C(CH_3)_3$], 1.07 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 166.7 (C_q, C2), 145.4 and 126.8 (each C_q, C4*a* and C8*a*), 138.1 (CH, C4), 129.4 (C_q, C3), 129.1 and 126.1 (each CH, C5 and C8), 128.0 and 125.7 (each CH, C6 and C7), 39.7 [C_q, $C(CH_3)_3$], 29.7 [$C(CH_3)_3$], 22.5 (CH_3) ppm. HRMS (ESI^+): m/z calcd for $C_{14}H_{17}NH$, 200.1434; found, 200.1436 $[M + H]^+$. Anal. Calcd (%) for $C_{14}H_{17}N$ (199.3): C 84.37, H 8.60, N 7.03. Found: C 84.27, H 8.42, N 6.91.

12a. See the above synthesis of **11a** for spectroscopic data.

2-*tert*-Butyl-6-methyl-3-propylquinoline (11c) and 2,2-Dimethyl-*N*-*p*-tolylthiopropionimidic Acid Ethyl Ester (12c) (from 2c). Pentacarbonyl[1-(ethylthio)pentylidene]chromium (**2c**) (322 mg, 1.00 mmol), 2,2-dimethyl-*N*-*p*-tolylpropionimidoyl chloride (**7c**) (419 mg, 2.00 mmol), and triethylamine (101 mg, 1.00 mmol) were reacted as described above to give compounds **11c** (96 mg, 40%) and **12c**.

11c and 12c. See the above synthesis of **11c** for spectroscopic data.

Acknowledgment. The authors thank Organish-Chemisches Institut der Universität Münster for financial support.